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Université Libre de Bruxelles Faculté des Sciences Service de Chimie des Polymères

Discotic liquid crystals as organic semiconductors for photovoltaic device applications

Julien Tant

Directeur de thèse : Prof. Yves Geerts Travail présenté en vue de l'obtention du grade de Docteur es Sciences Chimiques

2004



| Abbreviation | Meaning | | |
|-----------------------|---------------------------------|--|--|
| LIDC PLC | hexa-dodecyl hexa-phenyl | | |
| HBC-PhC ₁₂ | hexabenzocoronene | | |
| HOMO(a) | highest occupied molecular | | |
| HOMO(S) | orbital(s) | | |
| UDLC | high performance liquid | | |
| nrte | chromatography | | |
| I-V | current-voltage | | |
| I | isotropic phase | | |
| IP | ionisation potential | | |
| IPA | isopropanol | | |
| Isc | short-circuit current | | |
| ITO | indium-tin-oxide | | |
| K | crystalline phase | | |
| L | lamellar mesophase | | |
| LC(s) | liquid crystal(s) | | |
| L _e | exciton diffusion length | | |
| LUMO(a) | lowest unoccupied molecular | | |
| LOMO(S) | orbital | | |
| MD | metal phthalocyanine (M = | | |
| MPC | corresponding metal) | | |
| MS | mass spectrometry | | |
| OLED(s) | organic light-emitting diode(s) | | |
| Pc(s) | phthalocyanine(s) | | |
| Pn(s) | phthalonitrile(s) | | |
| DD TDMC | pulse radiolysis time-resolved | | |
| FR-TRMC | microwave conductivity | | |
| PTCDI | perylene | | |
| FICDI | tertracarboxdiimide | | |
| PVC(s) | photovoltaic cell(s) | | |
| RF | retention factor | | |
| PT | room temperature (between 20 | | |
| KI | and 27°C) | | |
| SAXS | small-angle X-ray scattering | | |
| SC | short-circuited | | |
| SCE | saturated calomel electrode | | |
| TOF | thin layer chromatography | | |
| UV | ultra-violet | | |
| Voc | open-circuit voltage | | |
| WAXS | wide-angle X-ray scattering | | |
| | | | |

| Abbreviation | Meaning | | |
|-------------------|--------------------------------|--|--|
| LIC NRAP | carbon 13 nuclear magnetic | | |
| CNMK | resonance | | |
| ILLAND | proton nuclear magnetic | | |
| HNMK | resonance | | |
| AFM | atomic force microscopy | | |
| C60 | fullerene | | |
| | ordered (o) and disordered (d) | | |
| Colho-d | hexagonal columnar | | |
| | mesophase | | |
| Colob | oblique columnar mesophase | | |
| Cal | disordered rectangular | | |
| Col _{rd} | columnar mesophase | | |
| СРМ | cross polarising microscopy | | |
| СТ | charge transfer | | |
| DBU | 1,8-diazabicyclo[5.4.0]undec- | | |
| DBU | 7-ene | | |
| DLC(s) | discotic liquid crystal(s) | | |
| DMF | N,N-dimethylformamide | | |
| DMSO | methyl sulfoxide | | |
| DSC | differential scanning | | |
| DSC | calorimetry | | |
| e | electron | | |
| EA | electron affinity | | |
| EI | electron impact | | |
| EQE | external quantum efficiency | | |
| ET | electron transfer | | |
| FD | field desorption | | |
| FET(s) | field effect transistor(s) | | |
| FF | fill factor | | |
| h ⁺ | hole | | |
| H ₂ Pc | metal-free phthalocyanine | | |
| HAT | hexaazatriphenylene | | |
| HATNA | hexaazatrinaphthylene | | |
| HATMA OR | hexaalkoxy- | | |
| HAINA-OR | hexaazatrinaphthylene | | |
| HATNA OD | hexaalkylthio- | | |
| HAINA-SK | hexaazatrinaphthylene | | |
| HBC(s) | hexabenzocoronene(s) | | |
| - | | | |
| | | | |

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La chimie, comme les mathématiques ou la physique, est souvent mal considérée par le grand-public. Les scientifiques sont encore vus, de nos jours, comme des savants fous ou des pollueurs en puissance. Comment expliquer alors que quelqu'un puisse avoir envie de faire de telles études?

Pour ma part, l'amour des sciences, et de la chimie en particulier, m'a été donné par deux professeurs (Claire et Jacques) qui, durant mes années de secondaire, ont su me transmettre leur passion.

Si les études universitaires sont une étape essentielle, une thèse en est une beaucoup plus exaltante. Quatre années durant, on apprend à gérer son temps, à accepter et à apprendre de ses échecs ou de ses erreurs, à prendre toute réussite comme une victoire. Chaque jour réserve son nouveau lot de questions et de réponses, de nouveaux défis à relever, de rencontres aussi intéressantes qu'inattendues.

On dit que les voyages forment la jeunesse ... Ils sont source de rencontres et d'échanges uniques. Voyager, c'est s'ouvrir à d'autres façons d'aborder les problèmes, à d'autres visions de la Science. Ce sont aussi des périodes d'enrichissement personnel, où l'on découvre ses limites et comment les repousser, où l'on tisse des liens d'amitié très solides avec des gens venus des quatre coins du monde.

Cette thèse est l'aboutissement d'un travail d'équipe. Même s'ils n'en ont pas toujours conscience, de nombreuses personnes ont directement ou indirectement contribué à sa réalisation. Un soutien, une oreille attentive, une contradiction parfois difficile à entendre mais si indispensable, ne sont que quelques exemples de leur participation.

Ces parents et amis ont eu une importance prépondérante dans ce travail, et dans tout le reste. Ces pages leurs sont entièrement dédiées

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C'est en faisant confiance aux gens qu'on les fait grandir.

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Heureusement, un laboratoire, ce n'est pas uniquement un chef. Dans la vie de tous les jours, ce sont les collègues (et amis) qui créent la convivialité indispensable à un tel travail. Durant ces quelques années, ils ont supporté mes humeurs, parfois (très) mauvaises, parfois (trop) enthousiastes. Par leur présence de chaque instant, par leurs réponses aux questions que l'on se pose devant le goutte-à-goutte d'une colonne chromato ou devant une solution rouge alors qu'on l'attendait verte, ils m'ont tous apporté une écoute, une attention et un soutien sans faille. Adrienne, Anton, Gaël (les 2), Géraldine (les 2), Hafid, Isabelle, Jérémy, Julie, Matthias, Olivier, Rafaël, Véronique, Vinciane et Zoubir ont tous, de très près ou d'un peu plus loin, contribués à ce travail. Merci infiniment.

Outre les membre du laboratoire de chimie des polymères, de nombreux chercheurs ou employés de l'ULB ont participé activement à cette recherche. De nombreuses mesures de diffraction des rayons X ont été faites et traitées par Raluca Gearba. L'analyse chimique des produits synthétisés a été faite en collaboration avec le Prof Michel Luhmer et Rita D'Orazio (pour la RMN), et avec Claude Moulard (pour la masse). Les analyses électrochimiques ont été effectuées en collaboration avec le Prof Claudine Buess-Herman.

This work does not only result from a single laboratory research. I have had the chance to start my PhD when the European project DISCEL was at its beginning. Including chemists, physicists, and materials scientists, this project has been the origin of many fruitful contacts all around Europe. Moreover, I have had the unique opportunity to stay sometime in three of these institutions, following my samples in Germany, in Denmark, and in the United-Kingdom. More particularly, I would like to thank:

From the University of Mons Hainaut (B): Dr Jérôme Cornil and Vincent Lemaur for their so important theoretical calculations,

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Beside science, there are all the people you meet every mornings, evenings and week-ends in the kitchen and in the corridor. All these people that create a nice atmosphere in your everyday life. Darryl, Julie, Ganzalo, Francesca, ..., you are all part of this work.

And all the other DISCEL partners. This PhD would have been totally different without you.

Finally, I would like to express my gratitude towards all the foundations and public organisations that have financially supported this work: Le Fond pour la Recherche pour l'Industrie et l'Agriculture (FRIA), la Fondation Philippe Wiener - Maurice Anspach, le Fond National pour la Recherche Scientifique (FNRS), la Bourse de Voyage de BrouckèreSolvay, la Bourse EURESCO, la Commission Européenne.

The only way to progress in Science is to collaborate and exchange knowledge with people. During this PhD thesis, I have had the exceptional opportunity to travel all around Europe, and to work with a lot of highly interesting scientists. Their kindness and their patience have made the last four years one of the most enriching period of my life.

Thanks to all of you ...

Go confidently in the direction of your dreams. Live the life you have imagined. Henry David Thoreau (1817 – 1862)

Materials chemistry: Definition

The important thing in science is not so much to obtain new facts as to discover new ways of thinking about them.

Sir William Bragg (1862 - 1942)

This PhD thesis has been performed in a particular domain of chemical sciences, called materials chemistry. The philosophy of this recently developed field of research is sometime misunderstood. A definition of its aims and position toward the other science research topics is then necessary (Figure 1).



Figure 1: Principle and aims of materials chemistry.

Materials chemistry has for aim to obtain molecules that exhibit specific properties, chosen according to the desired application(s). It uses organic chemistry and physical chemistry as tools for the synthesis and the physical properties characterisation of the materials.

The development of materials chemistry is illustrated by the large number of (new) journals devoted to this specific topic. Their impact factors are generally higher than for older journals of the American Chemical Society, devoted to organic or physical chemistry.

| Journal | First publication | Impact factor in 2002 |
|--|-------------------|-----------------------|
| Nature Materials | 2002 | |
| Advanced Functional Materials | 2001 | 4.656 |
| Journal of Materials Chemistry | 1991 | 3.967 |
| Advanced Materials | 1990 | 6.801 |
| Chemistry of Materials | 1989 | 3.967 |
| Macromolecules | 1968 | 3.751 |
| Angewandte Chemie International Edition | 1962 | 7.671 |
| Journal of Organic Chemistry | 1936 | 3.217 |
| Journal of Physical Chemistry A and B | 1896 | 2.765 and 3.611 |
| Journal of the American Chemical Society | 1879 | 6.201 |

The most important ones are summarised in the following table.

Table 1: Comparison between the principal material chemistry journals and some important organic and physical chemistry journals from the American Chemical Society.

Summary of the Thesis

In the industrialised countries, the demands in energy are getting higher and higher. The actual energy sources are based on the combustion of non-renewable fossil materials (oil, coal, gas) or on the use of highly controversial radioactive materials (uranium, plutonium). Alternative energy sources exist but still require expensive investments.

The photovoltaic devices have for purpose to transform light energy into electricity. The actual solar cells, based on silicon, require very high purity materials and high temperature processing, making them unable to compete with the actual energy sources.

An alternative might come from organic semiconductors. Indeed, solution-based processing could permit manufacturing cheap flexible devices. Promising results have already been obtained with conjugated polymers and low molecular weight organic compounds. Discotic liquid crystals DLCs form a particularly interesting family of materials.

DLCs have the capacity to self-organise into one-dimensional semiconducting columns of molecules. Their interesting semiconducting properties, combined with an ease of device manufacturing by solution-based processes, make them good candidates for future commercial applications. The actual problem in the use of DLCs for the manufacturing of solar cells, is the lack of tailor-made materials.

In this work, two complementary families of discotic materials have been developed, forming a pair of n- and p-type semiconductors. Their chemical structures were designed in order to obtain materials that show a specific set of properties, chosen to optimise the different key parameters of the charge photo-generation process. These properties are the following: a strong light absorption in the visible, a strong n- or p-type character, a noncrystalline phase at RT, a columnar LC phase, an isotropic phase present below 200 °C. Moreover, the materials have to be accessible with a high degree of purity, in a minimum number of efficient synthetic steps. They also have to be highly soluble in common organic solvents.

This work encompasses, for both families of materials, the design of their molecular structure, their synthesis, and their physical properties characterisation (thermotropic, optoelectronic, electrochemical).

As potentially p-type semiconductors, five tetra-alkoxy-substituted metal-free phthalocyanine derivatives have been synthesised, giving one material that fits all the requirements defined above. As potentially n-type semiconductors, six hexa-alkoxy-substituted hexaazatrinaphthylene derivatives have been studied. One of them behave as required.

Finally, the optoelectronic and photovoltaic properties of bends of the two most promising materials, together and with other disk-like materials, have been studied. Solar cells with a maximum efficiency of 1 % at one wavelength have been obtained with two different device compositions.

These efficiencies, however lower than the ones reported by other groups (today, up to 34 %), reveal the important potential of organic materials, and more particularly of discotic liquid crystals, for future electronic devices applications.

Résumé de la Thèse

Dans les pays industrialisés, la demande en énergie augmente continuellement. Les sources d'énergie actuelles sont basées sur la combustion de matériaux fossiles non-renouvelables (pétrole, charbon, gaz), ou sur l'utilisation très controversée de matières radioactives (uranium, plutonium). Des sources d'énergie alternatives existent, mais requièrent des investissements coûteux.

Les cellules photovoltaïques ont pour objet la transformation de la lumière en électricité. Les cellules solaires actuelles, basées sur le silicium, requièrent des matériaux d'une très grande pureté et des hautes températures de mise en œuvre, les empêchant de concurrencer les principales sources d'énergie actuelles.

Une alternative pourrait provenir des matériaux semi-conducteurs organiques. En effet, l'utilisation de méthodes de mise en œuvre à partir de solutions pourrait permettre la fabrication de dispositifs flexibles et bon marchés. Des résultats encourageants ont été obtenus avec des polymères conjugués et de petites molécules organiques. Les cristaux liquides discotiques CLDs forment une catégorie particulièrement intéressante de matériaux.

Les CLDs ont la capacité de s'organiser spontanément en colonnes de molécules, formant des semi-conducteurs à une dimension. Leurs propriétés intéressantes en tant que semi-conducteurs, combinées à une mise en œuvre facile, en font de bons candidats pour de futures applications commerciales.

Le problème actuel de l'utilisation de CLDs dans la fabrication de cellules solaire vient du manque de matériaux aux propriétés "sur mesure". Dans ce travail, deux familles complémentaires de matériaux discotiques ont été développées, formant une paire de semiconducteurs de type n et p. Leurs structures chimiques ont été étudiées de manière à obtenir des matériaux possédant un ensemble de propriétés choisies afin d'optimiser les paramètres clefs du processus de photo-génération de charges. Ces propriétés sont les suivantes: une forte absorption de la lumière dans le visible, un fort caractère semiconducteur de type n ou p, pas de phase cristalline à température ambiante, une phase cristal liquide colonne, une phase isotrope en-dessous de 200 °C. De plus, les matériaux doivent être accessibles en un nombre minimum d'étapes d'un synthèse efficace, et ce avec un haut niveau de pureté. Ils doivent également être fortement soluble dans les solvants organiques usuels. Cette étude comporte, pour chacune des deux familles de matériaux, le design de leur structure chimique, leur synthèse et la caractérisation de leurs propriétés physiques (thermotropes, optoélectroniques, électrochimiques).

Comme possible semi-conducteur de type p, cinq dérivés tétrasubstitués de la phthalocyanine non-métallée ont été synthétisés, donnant un matériau possédant l'ensemble des propriétés recherchées. Comme possible semi-conducteur de type n, six dérivés hexasubstitués de l'hexaazatrinaphthylène ont été étudiés. L'un d'eux possède les propriétés requises.

Finalement, les propriétés optoélectroniques et photovoltaïques de mélanges des deux matériaux les plus prometteurs, ensemble ou avec d'autres matériaux, ont été étudiées. Des cellules solaires de rendement maximum de 1 % ont été obtenues pour deux dispositifs de composition différentes.

Ces rendements, bien qu'inférieurs à ceux obtenus précédemment par d'autres groupes (jusqu'à 34 % à ce jour), sont néanmoins révélateurs des potentialités des matériaux organiques, et plus particulièrement des cristaux liquides discotiques, pour de futures applications dans le domaine des dispositifs électroniques.

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| Abbreviation | Meaning | Abbreviation | Meaning |
|---|--------------------------------------|-----------------------|--|
| ¹³ C NMR carbon 13 nuclear magnetic resonance | | HBC-PhC ₁₂ | hexa-dodecyl hexa-phenyl hexabenzocoronene |
| ¹ H NMR | proton nuclear magnetic resonance | HOMO(s) | highest occupied molecular orbital(s) |
| AFM | atomic force microscopy | LIDI C | high performance liquid |
| C60 | fullerene | HPLC | chromatography |
| | ordered (o) and disordered (d) | I-V | current-voltage |
| Col _{ho-d} | hexagonal columnar | I | isotropic phase |
| | mesophase | IP | ionisation potential |
| Col _{ob} | oblique columnar mesophase | IPA | isopropanol |
| C 1 | disordered rectangular | Isc | short-circuit current |
| Col _{rd} | columnar mesophase | ITO | indium-tin-oxide |
| CPM | cross polarising microscopy | К | crystalline phase |
| CT | charge transfer | L | lamellar mesophase |
| | 1,8-diazabicyclo[5.4.0]undec- | LC(s) | liquid crystal(s) |
| DBU | 7-ene | Le | exciton diffusion length |
| DLC(s) | discotic liquid crystal(s) | LINIO | lowest unoccupied molecular |
| DMF | N,N-dimethylformamide | LUMO(s) | orbital |
| DMSO | methyl sulfoxide | MB | metal phthalocyanine (M = |
| DCC | differential scanning | MPc | corresponding metal) |
| DSC | calorimetry | MS | mass spectrometry |
| e | electron | OLED(s) | organic light-emitting diode(s) |
| EA | electron affinity | Pc(s) | phthalocyanine(s) |
| EI | electron impact | Pn(s) | phthalonitrile(s) |
| EQE | external quantum efficiency | DD TDMC | pulse radiolysis time-resolved microwave conductivity |
| ET | electron transfer | PK-IKMC | |
| FD | field desorption | PEODI | perylene |
| FET(s) | field effect transistor(s) | PICDI | tertracarboxdiimide |
| FF | fill factor | PVC(s) | photovoltaic cell(s) |
| h ⁺ | hole | RF | retention factor |
| H ₂ Pc | metal-free phthalocyanine | DT | room temperature (between 20 |
| HAT | hexaazatriphenylene | KI | and 27°C) |
| HATNA | hexaazatrinaphthylene | SAXS | small-angle X-ray scattering |
| HATSIA OB | hexaalkoxy- | SC | short-circuited |
| HAINA-OR | hexaazatrinaphthylene | SCE | saturated calomel electrode |
| TIATALA OD | hexaalkylthio- | TOF | thin layer chromatography |
| HAINA-SR | hexaazatrinaphthylene | UV | ultra-violet |
| HBC(s) | hexabenzocoronene(s) | Voc | open-circuit voltage |
| | | WAXS | wide-angle X-ray scattering |



Chapter 1

Introduction

1.1 A world based on energy

Our world in getting more and more industrialised. Since the beginning of the XXs century, the economic development of industrialised countries has had for consequence to dramatically increase the demands in energy. Indeed, people can not live without electricity, central heating, hot water, or cars anymore.



Figure 1.1: Evolution of the energy consumption in France since 1973. tep = ton equivalent petroleum.[1]

The predictions for the future are not optimistic. Regarding to the actual evolution of energy consumption, the production has to follow. At the present time, three main energy sources are exploited: fossil (crude oil, coal, natural gas), nuclear (uranium, plutonium), and renewable (aeolian, hydroelectric, from biomass, solar, ...) energies.



Figure 1.2: Part of the different energy sources in electricity consumption in France. Primary electricity = nuclear .[1]

Fossil energy represented in 2002 more than 53 % of energy consumption in France. It is based on the combustion of hydrocarbons by the oxygen present in the atmosphere, and subsequently produces energy, water H₂O, and carbon dioxide CO₂ (Equation 1.1 corresponds to the total combustion of an alkane such as propane, with n = 3).

$$2 C_n H_{2n+2} + (3n+1) O_2 \longrightarrow (2n+2) H_2 O + 2n CO_2 + Energy$$
 (1.1)

The emission of CO_2 in high quantity has dramatic effects of the Earth, and more particularly on our atmosphere. By increasing the Earth greenhouse effect, this energy production is partially responsible for the Earth global warming. Another aspect of fossil energy sources is their non-renewability, meaning that the raw material cannot be produced in the same timescale than its consumption. The stocks are limited and, even if extraction methods are getting more and more sophisticated, specialists foresee an exhaustion before 2050.[2] Since the oil crisis of the 1970s, crude oil has become a political and military concern. The apprehension against a new economic blackout has already been behind many deaths.

The use of nuclear power, which corresponded, in 2002, to 41 % of the electricity consumed in France, avoids production of CO_2 and, even if nuclear is not a renewable energy

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source, the quantity of raw material (mainly the pechblende, a rock rich in uranium oxide UO_2) available can cover electrical demands over a very long period of time. The plutonium ²³⁹Pu is mainly obtained as a product of the bombardment of ²³⁸U with neutrons. The nuclear energy is based on nuclear fission processes (Equation 1.2).

When a fissile atom is bombarded with neutrons, the splitting of the atomic nucleus into parts comes with the production of other nuclea, of neutrons, and of energy. The neutrons liberated during the nuclear reaction eventually produce other fission, creating an autosustained chain reaction.

The actual problem of nuclear energy is the subsequent production of radioactive fission products of high radiation intensity and/or long lifetime. Many governmental institutes have been created in order to solve this environmental problem, but no definitive solution has been found yet. Today, the nuclear waste is treated and the different atoms composing it are separated according to their dangerousness.[3] They are stored and not destroyed, giving rise to potential future contaminations. Some dramatic events such as the highly mediatised Tchernobyl disaster in 1986, and the confusion between nuclear energy and nuclear weapons, have created an apprehension of the people against this energy.

The "cleaner" nuclear fusion energy, obtained by coalescence of two small nuclea (e.g. hydrogen) into one heavier (e.g. helium) (Equation 1.3), will become an alternative when the process will be fully controlled. It is not yet used as domestic energy source.

$$4 {}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 2 {}^{0}_{1}e$$

$$(1.3)$$

All the scientists agree with the fact that the production of CO_2 , gas proven to contribute to the Earth greenhouse effect, is going to be responsible for a global warming of our planet. In September 16th 1987 was ratified the Montreal protocol on the substances that impoverish to ozone shield. In 1998, 39 countries signed the Kyoto protocol on the progressive reduction or stabilisation of the production of greenhouse effect gases (carbon dioxide, methane, nitrogen oxide, hydrofluorocarbons, perfluorinated hydrocarbons, and sulfur hexafluoride). In this agreement, the states commit themselves to push for the renewable energy sources, which are seen as a potential alternative to the "traditional" energy sources.

Renewable energy sources are based on the exploitation of phenomena that naturally take place in the Earth, without consuming any material or any material that can not be produced in the exploitation timescale. The main alternative energy sources are based on the use of natural motions like wind (aeolian energy), waterfalls (hydroelectricity), waves (tidal energy), ..., on solar radiations (photovoltaic energy) and Earth geological activities (geothermic energy), or on the combustion of plants that can grow up rapidly (energy from biomass).

Unfortunately, ecology has a prize. These "green" energies still require expensive investments that most of the particulars are not ready to do. The high majority of the renewable energy is produced by big electricity companies, with governmental financial supports. The type of energy sources exploited mainly depends on their production capacity in the country: aeolian in Denmark, hydroelectrical in Switzerland or France, geothermic in Iceland, Nevertheless, certain energy sources are underexploited. Photovoltaic energy production, based on the direct conversion of sunshine into electricity, is still negligible. The potential power of the sunshine is huge. Specialists estimate the sun radiation power to about 1 kW/m^2 in average, mainly concentrated in the Third World countries (Africa, South America, ...).



Figure 1.3: Average balance of the solar hearth irradiation.

Today, photovoltaic energy is too expensive to compete with the classical sources. The future of this technology is endangered by its incapacity to be accessible to the consumers.

1.2 Photovoltaic devices

1.2.1 History

The ability of a material to produce an electric current, also termed "photocurrent", under illumination is called the photovoltaic effect. [4] It is based on the conversion of solar photon energy into a motion of charges. The photovoltaic cells PVCs efficiency is defined as the number of charges produced per photon absorbed over the entire solar spectrum. [5] The photo-electric effect was discovered by Becquerel in 1839, [6] by observing the production of electricity when light was shined on an electrode in an electrolyte solution.



Figure 1.4: Schematic representation of the two main cell configurations used in inorganic solar cells: (a) Schottky type devices and (b) n/p junction devices.[7]

In 1877, Adams and Day reported the first fully solid solar cell, based on selenium material. This result is the origin of the development of selenium based modules, widely used in photographic luxmeters. One had to wait until 1941 to reach about 1 % efficiency in directly converting sunshine into electricity with a thallium sulfide Tl₂S device. Up to then all the devices consisted in one layer of active material sandwiched between two electrodes. This cells configuration is called Schottky type devices (Figure 1.4). It had been wildly studied because of its ease of manufacturing. But the use of only one semiconducting layer has for consequence to decrease the energy conversion efficiency by reducing the domain of light absorption and by changing the device internal electric field.

At that time, PVCs were seen as an attraction and not as something that can be used

in everyday life. The revolution occured in 1941, when the first silicon Si-based bilayer solar cell, also called p/n junction cell, was made. The rapid evolution in performances that followed this discovery resulted, in 1954, in the work of Chapin *et al.*, from Bell Telephone Laboratories, who reported a 6 % efficiency device,[8] suitable for small low consumption apparatus applications such as pocket calculators. Only four years later, 16 % efficiency devices were achieved, making solar cells really practical electricity sources.

In the mid-1980s a revolutionary increase in cells efficiency was obtained by improving materials purification and manufacturing technics.[9] Today, different types of PVCs are commercially available. They are complementary: when single-crystal silicon devices are expensive, because of difficult manufacturing processes, but highly efficient (up to 24.4 % efficiency), multi-crystalline and amorphous silicon PVCs are cheaper but do not give efficiencies higher than 19.8 and 13 %, respectively. As a result, the prize of the photoelectricity produced is almost the same for all the Si-based PVCs (7 to 21 Euro/Wp [Wp = watt peak][10]).

The high manufacturing cost of inorganic solar cells makes them unable to compete with the "classical" energy sources. Almost the half of the prize of inorganic PVCs comes from the very high purity materials needed for efficient devices manufacturing. An alternative to that might come from organic materials.

In 1977, when Shirakawa, MacDiarmid and Heeger discovered that certain organic molecules can act as electrical conductors, [11] electronic device applications became accessible to organic materials. This revolution led the Nobel committee to award them with the Nobel Prize in Chemistry in 2000. Since then, a lot of effort has been gone into the development of organic electronic device technology. The possible applications are varied and in an expanding domain. The potential of organic materials in devices such as organic light emitting diodes OLEDs, [12, 13] field effect transistors FETs, [14] sensors, [15] or photovoltaic cells [16, 17] has already been demonstrated. A wide range of organic materials has been used for their capacity to conduct charges, going from polymers to small molecules, soluble or not.

In order to improve organic PVCs efficiency, tailor-made materials are needed. The definition of the key properties requires a good understanding of the phenomena involved in the light energy conversion process.

1.2.2 How do organic solar cells work?

The conversion of light energy into electricity encompasses a succession of complex phenomena. A description of the major steps of photovoltaic energy conversion is given in this section.



Figure 1.5: Schematic representation of the different phenomena involved in charge photogeneration in a bilayer organic photovoltaic device. **1**. Light absorption and creation of an exciton. **2**. Exciton diffusion through the materials. **3**. Exciton dissociation at the interface between the two semiconducting layers. **4**. Charges migration trough the materials and their collection at the electrodes.

An organic photovoltaic cell can be schematised by Figure 1.5. Four main processes are involved in light conversion:

- 1. Absorption of a photon by the materials, and subsequent formation of an exciton,
- 2. diffusion of the exciton through the semiconducting materials,
- splitting of the exciton into a pair of free charges, at the interface between the two semiconductors,
- 4. migration of the charges through the materials and their collection at the electrodes.

Light absorption and formation of an exciton

The absorption of light by a molecule corresponds to a transition between two of its energetic states. In organic materials, it usually goes with the transfer of an electron from the Highest (in energy) Occupied Molecular Orbital HOMO to the Lowest Unoccupied Molecular Orbital LUMO. This transition is only possible if the photon energy is equal or superior to the band gap (i.e. the difference in energy between the initial fundamental state (HOMO) and the final excited state (LUMO)).



Figure 1.6: Conjugation effect in butadiene 2 in comparison to ethylene 1. In ethylene 1, the π -electrons, forming the double bond, are fixed between two carbon atoms. In butadiene 2, the resonance structures 2a and 2b can be drawn, showing that π electrons are not fixed between two carbon atoms, but are delocalised over the molecular backbone.

In a molecule where all the electrons are sheared by only two atoms (e.g. 1 in Figure 1.6), the band gap is large and no light absorption in the visible range of the electromagnetic radiation is possible. In conjugated materials, π -electrons are not fixed between two atoms. They are delocalised over the entire molecule, or a part of it. This delocalisation effect has for consequence to reduce the difference in energy between the fundamental and the first excited state.

Electron delocalisation is responsible for the ability of a material to absorb light in the visible region of the electromagnetic radiation (wavelength λ from 400 to 700 nm).[18] The conjugated part of a molecule is called "chromophore" if it allows light absorbtion in this photochemical region. The absorption spectrum of a molecule depends on the size

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and structure of its conjugated system, on the presence and nature of heteroatoms such as oxygen O, nitrogen N, sulfur S, ..., and/or of chemical functions (ester, ether, amide, nitro, nitrile, ...) in and around the chromophore. As illustrated in Figure 1.7 with the oligo[n]acenes, an increase in the size of the conjugated moieties gives rise to lower energy light absorption, i.e. at higher radiation wavelength (according to $E = h\nu = hc/\lambda$, with E the energy, h Planck's constant, ν the frequency, c the speed of light, and λ the wavelength).



Figure 1.7: Influence of the size of the conjugated system on its absorption spectrum. Absorption spectra of oligo[n]acenes (naphthalene 3, anthracene 4, tetracene 5) in solution in hexane.

When a photon is absorbed by a molecule in its condensed state, a pair of charges is formed: an electron e⁻ in the LUMO and a hole h⁺ (corresponding to the absence of an electron in a molecular orbital) in the HOMO, linked together by Coulombic interactions (Figure 1.8). The neutral exited state formed is commonly called "exciton".[19] In inorganic materials, where the HOMO corresponds to the valence band and the LUMO to the conduction band, the exciton stabilisation energy ΔE is weak (≈ 0.005 eV for gallium arsenide GaAs) and charge separation takes place spontaneously. In organic materials, ΔE is usually estimated to 0.35 eV,[20] depending on the material and on the intermolecular interactions present in the system. With such a stabilisation energy, organic excitons can not spontaneously split into two free charges. Consequently, organic excitons have a lifetime of about 1 ns [21] during which they can diffuse through the material, as discussed in the next section.



Figure 1.8: Exciton formation in an inorganic (a) and an organic (b) material. In both cases, absorption of a photon $h\nu$ gives rise to the formation of an exciton composed by a electron (1) - hole (\bigcirc) pair, linked together with a Coulombic stabilisation energy ΔE .

Exciton diffusion

In the case of conjugated organic semiconductors, the excitons are not fixed on molecules. They can travel through the material by successive energy transfer reactions. Two main energy transfer mechanisms are in competition. They are depicted in Figure 1.9.[18]

In the Dexter or electron exchange mechanism, the electron in the LUMO of the excited molecule \mathbf{A}^* , is transferred to the LUMO of the target molecule \mathbf{B} , together with the backward transfer of one electron of the HOMO of \mathbf{B} to the HOMO of \mathbf{A}^* . Consequently, both electron and hole are transferred from \mathbf{A}^* to \mathbf{B} , resulting in an energy transfer. The Dexter mechanism requires a molecular orbitals overlap between the donor \mathbf{A}^* and the acceptor \mathbf{B} . As electron densities usually fall off exponentially as the distance between the electron and the nucleus is increased, the energy transfer rate by electron exchange is expected to fall off exponentially too. Dexter showed that: [22]

$$k_{ET}(exchange) = K Jexp^{\frac{-2R_{AB}}{L}}$$
(1.4)

where K is related to specific orbital interactions, J is the integrated overlap of the normalised acceptor absorption and the donor emission curves, and R_{AB} is the donor-acceptor



Figure 1.9: Schematic views of the two mechanisms of energy transfer: (a) Dexter and (b) Förster. The arrows show the movements of the electrons.

separation relative to their van der Waals radii, L. Dexter energy transfer mechanism is only efficient when the donor and the acceptor are close (< 5-10 Å), and operates for both singlet and triplet excited states.

The Förster mechanism, also called dipole-dipole mechanism or Coulombic energy transfer, consists in the simultaneous electronic desexcitation of the donor \mathbf{A}^* together with the excitation of the acceptor \mathbf{B} . Förster showed that the rate of energy transfer by dipole-dipole mechanism k_{ET} can be related to experimental quantities as follows:[23]

$$k_{ET}(Coulombic) = k \frac{\kappa^2 k_A^o}{R_{AB}^6} J(\varepsilon_B)$$
(1.5)

The term k is a constant determined by experimental conditions. κ^2 is a geometrical factor that takes into account the fact that the interactions differ according to the relative molecular orientation in space. k_A° is the pure radiative rate of **A**, corresponding to its ability of being desexcited in a radiative way. The term $J(\varepsilon_B)$ is similar to the spectral overlap integral of Equation 1.2.2 except that the absorption (or extinction) coefficient ε_B of the acceptor **B** is included in the integration. Finally, R_{AB} is the distance between **A** and **B**.

In other words, Förster energy transfer is only efficient for singlet excited states since direct desexcitation of a triplet state is not allowed by quantum mechanics, reducing k_A°



Figure 1.10: Influence of the distance R_{DA} ($\equiv R_{AB}$) between the donor \mathbf{A}^* and the acceptor \mathbf{B} on the electron transfer rate ratio for the Dexter (exchange) and the Förster (dipole-dipole) energy transfer mechanisms. k_0 is the maximum rate constant for energy transfer which occurs when \mathbf{A}^* and \mathbf{B} are in the state of a "classical" collision.[18]

dramatically. The dipole-dipole energy transfer rate is proportional to the inverse sixth power of the separation between the donor and the acceptor. For large distances between the donor and the acceptor, this mechanism is predominant (Figure 1.10).

Energy transfer can not proceed indefinitely. After a certain time, corresponding to a certain distance of energy diffusion, the exciton has a high probability of being deactivated by radiative (fluorescence, phosphorescence) or non-radiative (transfer of the excitation energy to vibrational levels of surrounding molecules) processes. This maximum distance is called exciton diffusion length L_e . This parameter is of high importance for organic photovoltaic device applications because, since excitons can not be split into free charges spontaneously, they have to reach a "splitting site" before their deactivation. Otherwise the photonic energy absorbed will be lost by photon emission or transformation into heat. The influence of the chemical structure on L_e will be discussed in more details in Section 1.3.4.

Exciton splitting at the interface

Exciton self-dissociation is not efficient in organic semiconductors. Charge separation can only take place at the interface between two materials of different orbital energies (i.e. of different redox potentials):

- An organic p-type semiconductor is defined as a material that can easily be oxidised. Oxidation reaction consisting in removing an electron from the HOMO, i.e. introducing a hole on the molecule.
- An organic **n-type semiconductor** is characterised by its ease of being reduced. Reduction reaction consisting in introducing an electron in the LUMO.



Figure 1.11: Summary of the different phenomena that can be encountered when an exciton reaches the interface between two organic semiconductors. In this example, the p-type semiconductor has been excited. n-type excitation gives rise to the same possibilities.

When an exciton reaches the interface between a n-type and a p-type semiconductor, three phenomena can take place:

 Nothing might happen, the characteristics of the n-type and the p-type materials do not allow the exciton to react;

- Energy transfer ET might occur, both electron and hole, forming the exciton, are transferred from the excited material to the other;
- Charge transfer CT might take place between the two materials, giving rise to a pair of charges with the hole in the p-type semiconductor and the electron in the n-type material.

The three cases are illustrated in Figure 1.11.

It is possible to theoretically estimate which of these three phenomena will dominate for a specific n-type – p-type pair of materials.[20, 24]

We define Δ_{HOMO} and Δ_{LUMO} as

$$\Delta_{HOMO} = HOMO(p) - HOMO(n) \tag{1.6}$$

and

$$\Delta_{LUMO} = LUMO(p) - LUMO(n) \tag{1.7}$$

 Δ_{HOMO} and Δ_{LUMO} being both positive.

The energy of an exciton in the p-type in given by

$$E_{p-type} = LUMO(p) - HOMO(p) \qquad (1.8)$$

For the n-type material, the exciton energy is

$$E_{n-type} = LUMO(n) - HOMO(n)$$

$$= LUMO(p) - \Delta_{LUMO} - (HOMO(p) - \Delta_{HOMO})$$

$$= LUMO(p) - HOMO(p) + (\Delta_{HOMO} - \Delta_{LUMO})$$

$$= E_{p-type} + (\Delta_{HOMO} - \Delta_{LUMO})$$
(1.9)

If CT takes place, the exciton stabilisation energy has to be broken. The energy of the charge transfer state E_{CT} is given by

$$E_{CT} = (LUMO(p) - HOMO(p)) - \Delta_{LUMO} + E_{exciton}$$

$$= E_{p-type} - \Delta_{LUMO} + E_{exciton}$$
(1.10)
The exciton dissociation energy $E_{exciton}$ is usually estimated to be around 0.3 - 0.35 eV. As the dominant process will be the less energy consuming one, charge transfer will only take place if and only if the energy of the charge transferred state is the lowest (case 1 in Figure 1.12). We can then write the following inequalities:

$$E_{p-type} - \Delta_{LUMO} + E_{exciton} < E_{p-type} - \Delta_{LUMO} + \Delta_{HOMO}$$
and
$$E_{p-type} - \Delta_{LUMO} + E_{exciton} < E_{p-type}$$
(1.11)

which become:

$$\Delta_{HOMO}$$
 and $\Delta_{LUMO} > E_{exciton}$ (1.12)

If both, Δ_{HOMO} and Δ_{LUMO} are higher than the exciton stabilisation energy, ET will dominate at the interface.

If the exciton is initially on the p-type material, as shown in Figure 1.11, ET to the n-type material will occur if $\Delta_{HOMO} < \Delta_{LUMO}$ (case 2 in Figure 1.12), with Δ_{LUMO} and/or $\Delta_{HOMO} < E_{exciton}$. Finally, if $\Delta_{LUMO} < \Delta_{HOMO}$ (case 3 in Figure 1.12), with Δ_{HOMO} and/or $\Delta_{LUMO} < E_{exciton}$, nothing will happen, the initial state being the lowest energy configuration. In the other hand, if the exciton is initially on the n-type material, the conclusions of cases 2 and 3 have to be inverted.

As we have seen, CT can occur indiscriminately if the p-type material is photo-excited as well as if the exciton is in the n-type semiconductor, even if the reaction kinetic might be completely different. The exciton dissociation energy plays an important role in the choice of the process that dominates at the interface. The difference in energy between the HOMOs and the LUMOs of the two molecules is the driving force of the CT reaction.

In conclusion, the nature of the phenomenon that will dominate when an exciton reaches an interface not only depends on the n- or p- character of the two materials, but also on their respective orbital energies. To obtain a high efficiency electronic device, a careful choice of a pair of materials is required. If they do not match each other, no high efficiency can be expected.



Figure 1.12: Illustration of the three situations that can be encountered when an exciton reaches the interface between a n-type and a p-type semiconductor. In the calculations, $E_{exciton} = 0.3 \text{ eV}.$

Charge migration and collection at the electrodes

When the exciton has split into an electron e⁻ in the n-type material and a hole h⁺ in the p-type, free charges can travel separately through the materials and eventually reach their respective electrodes.

The conductivity σ of a material is defined as the sum of the product of the charge densities N_{h^+} and N_{e^-} and their mobilities μ_{h^+} and μ_{e^-} (Equation 1.13).

$$\sigma = e(N_{h+}\mu_{h+} + N_{e^-}\mu_{e^-}) \tag{1.13}$$

where e is the charge of the electron.

In the case of PVCs, charge density N is an extrinsic parameter: it does not only depend on the materials themselves, but also and mainly on the efficiency of all the previous phenomena (light absorption, exciton diffusion and charge separation). Indeed, the intrinsic charge density of an organic material is very low ($\approx 10^{14}$ charges.m⁻³), making it insulator. The appearance of photo-induced charges leads to a dramatic increase of N(to $\approx 10^{21}$ charges.m⁻³ [25]).

Nevertheless, no charge conduction is possible if they are fixed or trapped in the matter. The charge mobility of a material is an intrinsic parameter: it only depends on the nature of the material and on its molecular organisation (distances, orientation of the molecules in space, position of the molecular orbitals in the conjugated moiety, \dots).

The mechanism of charge migration is best described by successive charge "jumps" from one molecule to the other.[26] This hopping mechanism can be seen as a sequence of electron transfer reactions. As all charge transfer reactions, it is governed by the Marcus's theory, awarded by the Nobel Prize in Chemistry in 1992.[27] The simplified Marcus's equation (Equation 1.14) expresses the charge transfer rate k_{ct} in terms of two essential parameters: the intermolecular transfer integral t and the reorganisation energy λ .

$$k_{ct} = \frac{4\pi^2}{h} t^2 \frac{1}{\sqrt{4\pi\lambda RT}} exp^{\frac{-\lambda}{4RT}}$$
(1.14)

The intermolecular transfer integral t describes the interactions between the donor and the acceptor. It is a measurement of the strength of interactions between the molecular orbitals. The transfer integral highly depends on the molecular organisation (distance and relative orientation of the donor and the acceptor) and, by the way, on the temperature. High values of t mean that a good orbital overlap is present in the system, making charge transfer more favourable.

The reorganisation energy λ is a measurement of the energy needed to transfer the charge from the donor to the acceptor. It is composed of two terms: one internal λ_i , describing the amplitude of the changes induced by introduction of a charge in the molecule, and one external λ_e , which depends on the surrounding medium. This last takes into account the changes in interactions between the newly charged molecule and its surroundings (solvent, other molecules, ...).

Quantum chemical calculations can give a relative estimation of the reorganisation energy parameter, which is directly proportional to the material intrinsic charge mobility.[28] In theory, electron mobility (μ_{-}) can be higher hole mobility (μ_{+}). In practice, the measured μ_{-} is usually lower than the theoretical value. This fact is explained by the ease of electron trapping. Indeed, the presence of impurities easy to reduce, such as oxygen O_2 and water H_2O , is difficult to avoid. The following reactions are commonly encountered in negatively charged n-type materials:[29]

$$2 Ar^{-} \rightleftharpoons 2 Ar + 2 e^{-}$$

$$2 H_2O + 2 e^{-} \rightleftharpoons H_2 + 2 OH^{-}$$

$$2 Ar^{-} + 2 H_2O \rightleftharpoons 2 Ar + H_2 + 2 OH^{-}$$

$$(1.15)$$

When an electron reacts with oxygen or water, it becomes unable to reach the electrode. It is lost regarding to electrical conduction.

In photovoltaic cells, the direction of charge migration is given by the electric field created by the difference in potential between the materials composing the two electrodes. A further discussion on the importance of the electrodes will be given in Section 4.1.2.

An electric current is obtained when both charges, electron and hole, have reached their respective electrodes, creating a current flow that can be used has energy source. The light absorbed at the beginning of the process has finally been transformed into electricity.

1.2.3 Organic photovoltaics

The external quantum efficiency EQE is often used to characterise organic solar cells. It is defined as the number of charges collected at the electrode divided by the number of incident photons of specific wavelength:

$$EQE = \frac{number \ of \ collected \ charges}{number \ of \ incident \ photon} \tag{1.16}$$

Table 1.1 summarises the best results obtained for different categories of organic materials, and different cell configurations.

The first attempt to prepare photovoltaic elements only with organic semiconducting materials was rather discouraging.[17] A revolutionary development came in the mid-1990s, with the introduction of dispersed heterojunction, in which an electron accepting and an electron donating material are blended together. The improvement in molecular design and in the material purity allowed the fabrication of polymer PVCs with external quantum efficiency EQE of 6 % at optimum wavelength.[30] In parallel to the development of purely polymer based devices, extensive work has been devoted to the study of fullerene-based PVCs. The high electron affinity of fullerene C60 allows charge transfer to be very efficient (close to 100 %).[31] Evaporated under vacuum on the top of a polymer film, or blended together with it, C60 has already shown its aptitude in photovoltaic applications. Indeed, maximum EQE of 23 and 29 % (at optimum wavelength) have been reported respectively for the bilayer and the blend of C60 and polymers.[32, 33]

| combination | device structure | EQE^{a} (%) | year | reference | |
|--------------------------|------------------|---------------|------|-----------|--|
| Polymer – Polymer | bilayer | ≈ 3 | 1997 | [34] | |
| | blend | 6 | 1995 | [30] | |
| Polymer – C60 | bilayer | 23 | 1998 | [32] | |
| | blend | 29 | 1995 | [33] | |
| Polymer – Pigment | bilayer | 6 | 1996 | [35] | |
| | blend | 11 | 2000 | [36] | |
| Pigment – Pigment | bilayer | ≈ 30 | 1985 | [37] | |
| | blend | 28 | 2003 | [38] | |
| Liquid crystal – Pigment | bilayer | 0.5 | 1999 | [39] | |
| | blend | 34 | 2001 | [40] | |

^a EQE value at the most efficient wavelength.

Table 1.1: Summary of significative organic photovoltaic device efficiencies for various organic semiconducting materials blended together of deposited on the top of each other (bilayer structures).

By replacing C60 by small crystalline organic semiconducting materials (commonly called "molecular crystals"), maximum EQE of 6 and 11 % have been achieved for bilayer and blend devices, respectively.[35, 36] This result was quite disappointing since molecular crystals had shown their capacity to conduct charges and excitons by giving device efficiencies up to 30 % for a bilayer PVC made by successive vacuum evaporation of two low molecular weight crystalline materials.[37] The developments in the comprehension of the importance of phase separation in bulk heterojunction devices have recently given 29 % efficiency solar cells based on crystalline organic materials.[38]

Recently, a new family of organic semiconducting materials has been used in the manufacturing of PVCs. The introduction of discotic liquid crystals in PVCs has been first reported by Petritsch *et al.* in 1999.[39, 41] A bilayer device made by vacuum vapour deposition of a perylene dye on the top of a spin-coated layer of a room temperature liquid crystalline phthalocyanine derivative was described, with a quantum efficiency approaching 0.5 % at one specific wavelength of monochromatic illumination. Two years later, Schmidt-Mende *et al.*, also from the group of Professor Friend in Cambridge (UK), reported the achievement of a 34 % efficiency device made by spin-coating a blend of a crystalline perylene dye and a room temperature liquid crystalline hexabenzocoronene derivative.[40, 42]

This promising result has confirmed the outstanding photovoltaic potentialities of discotic liquid crystals.

A explanation of the values obtained for the different device compositions and structures will be attempted in Section 1.3.4.

In the next section, liquid crystals will be introduced. Their semiconducting character will be discussed in the view of their use in solar cells.

1.3 Liquid crystals: definitions, characterisation and properties

1.3.1 Definitions

The matter, this thing that surrounds us, that we consist in; the air, the water, the steel, ..., are in a certain physical state. We usually distinguish three different states of the matter: solid, liquid, and gaseous.



Figure 1.13: Schematic representation of the three main states of the matter.

- Solid state: ≪ of, concerned with, or being a substance in a physical state in which it resists changes in size and shape. ≫ [43] In the solid state the molecules constituting the matter are close to each other and have got not enough energy to move freely. In a crystalline phase, molecules (or atoms) form a three-dimensional assembly, in which their relative position and orientation are fixed. A glassy phase is characterised by an absence of long-range order and of large amplitude molecular motion, making the material hard to put out of shape.
- Liquid state: ≪ a substance in a physical state in which it does not resist change of shape but does resist change of size. ≫ [43] In a liquid phase, no long-range order exists any more. The properties of a liquid do not depend on the direction or on its orientation. It is isotropic. The molecules (or atoms) can rotate and move, but the presence of surrounding molecules still create a short-range stabilising order.
- Gas state: « a substance in a physical state in which it does not resist change of shape and will expand indefinitely to fill any container. » [43] In a gas phase, the molecules do not interact with each other any more. They can move freely.

This limitation to three states of the matter is a simplification of the reality. Indeed, certain materials exhibit states that have intermediate characteristics to the crystal (solid)



Figure 1.14: Schematic drawing of the different states of the condensed matter.

and to the liquid phase. In these states, called mesophases, the materials combine a certain deformability and a long-distance order.

A first distinction can be made between the different mesophases. This classification identifies the phases according to their degree of molecular order (Figure 1.15). A material possesses an **orientational order** if the molecules that compose it have a preferred orientational direction. This direction is commonly called "director" and is represented by a vector \vec{n} . The **positional order** is achieved when the centre of gravity of the molecules that compose the material lays in a crystal lattice.



(a) Liquid crystal Partial or full long range orientational order



(b) Liquid crystal Partial or full long range orientational order and partial long range positional order



(c) Plastic crystal Long range positional order

Figure 1.15: Distinction of the mesophases according to their degree of molecular order. (a) and (b) represent different types of liquid crystal phases. In (c), the molecules are in a plastic crystal phase.

Two main families of mesophases are encountered: the **plastic crystal phases** are characterised by a positional order, combined with a certain orientational disorder (e.g. in the C60 at room temperature, the molecules display a three dimensional order, but are free to spin on their axis [44]); and the **liquid crystal LC phases**, where the molecules are oriented in a preferential direction and/or positioned in a partially regular manner.

The large majority of the compounds that exhibit thermotropic liquid crystalline properties (i.e. where the mesophases appear in a certain range of temperature) are characterised by at least one anisotropy:[45]

• An anisotropy of shape: The molecules that show a liquid crystalline behaviour usually have one of their molecular axis very different than the two others (Figure 1.16). They are anisometric. On one hand, if one molecular axis (z) is much longer than the other two (x,y), the resulting rod-shaped molecule is called **calamitic** liquid crystal. On the other hand, disk-like molecules, obtained when one molecular axis (z) is much shorter than the other two (x,y), are called **discotic** liquid crystals.



Figure 1.16: schematic illustration of the anisotropy of shape in thermotropic liquid crystals LCs. Representation and typical chemical structures of the two main families of thermotropic LCs: (a) the calamitics and (b) the discotics. R stands for an alkyl chain.

• An anisotropy of rigidity: The chemical structure of both calamitic and discotic LCs can usually be divided in three parts (Figure 1.17): a rigid, most of the time aromatic and planar centre; a flexible periphery, usually composed by aliphatic or oligoether side-chains; and between the two, an intermediate zone consisting in a linking chemical function such as an heteroatom (oxygen, sulfur, nitrogen), a carbon atom, an ester, or an amide. The nature and the size of these three parts are responsible for the mesogenic behaviour of the resulting material.



Figure 1.17: Illustration of the anisotropy of rigidity in discotic liquid crystals DLCs, with the hexa-hexylthio-triphenylene HHTT 7a.

• An anisotropy of interactions: The general feature of the high majority of the mesogenic materials is amphiphilicity, i.e. these materials are built up of at least two different molecular parts that are incompatible with each other. In such molecules, the flexible and rigid parts, the hydrophilic and hydrophobic parts, the perfluorinated and hydrocarbonated parts, tend to segregate into distinct subspaces, separated by interfaces of minimum interfacial energy and well-defined shape. The term "microsegregation" is usually used to describe this pattern formation.[46, 47]

Figure 1.18 represents three molecules that tend to self-organise into LC phases by micro-segregation. The unexpected liquid crystallinity of **8** has been explained by the authors by the presence of a "hard" aromatic structure surrounded by "soft" polarizable chlorine atoms. The segregation between the "hard" and the "soft" parts of the molecule leads to the observed liquid crystal behaviour.[48] For compound **9**, micro-segregation occurs between the highly hydrophilic polyhydroxy chains and the long hydrophobic alkyl chains (polar – apolar segregation).[49] In the case of **10**, very slight differences in the nature of the different molecular parts are sufficient for mesophase formation.[50]

Depending on the molecular structure and the temperature, different LC phases can be obtained (Figure 1.19). The **nematic** phases of calamitic and discotic LCs are the most simple ordered structures. In these phases, the molecules maintain a preferred orientation



Figure 1.18: Illustration of the anisotropy of interaction and the effect of micro-segregation in the formation of liquid crystal phases. These three molecules 8-10 tend to organise themselves into columnar LC phases by micro-segregation. $R = n - C_{10}H_{21}$.



Figure 1.19: Schematic drawing of the different liquid crystalline mesophases accessible for the calamitic and the discotic LCs. \vec{n} represents the preferential orientation direction.

 \vec{n} as they diffuse throughout the sample. No positional order is observed in the nematic phases. In addition to the orientational order of the nematic phases, the **smectic** phases are characterised by a molecular positional order, since the centre of mass of the molecules are arranged in layers.

In addition to the rarely observed discotic nematic arrangement, disc-like molecules have the tendency to arrange themselves into columns, forming the discotic **columnar** mesophases.

1.3.2 Discotic liquid crystals

The first discotic liquid crystals DLCs were discovered by Chandrasekhar *et al.* in 1977.[51, 52] Their existence had been theoretically predicted since 1970. During the last 27 years, considerable efforts have been devoted to the synthesis and the physical properties characterisation of the mesophases formed by discotic molecules.



Figure 1.20: Schematic drawing of a columnar mesophase. The discotic molecules (a) stack together to form columns (b) which arrange themselves into a two-dimensional lattice (c) (here, hexagonal).

Discotic molecules usually consist in an aromatic central core, surrounded by flexible side-chains. The micro-segregation of the rigid and the flexible parts of the molecule leads to spontaneous columnar stacks formation (Figure 1.20b). The average distance between two discotic molecules in a columnar stack, also called intracolumnar distance, is usually of 3.4 - 3.6 Å. Depending on the strength of the interactions between the π -systems, the mesophases produced can be ordered, i.e. a long-range positional order is present along the columnar axis, or disordered, i.e. only a short-range positional order is achieved (Figure 1.21).

In addition to the formation of columns, the columnar mesophases are characterised by their ability to order the columns into a two-dimensional lattice. The hexagonal geometry (Col_h) is the most usual, but rectangular (Col_r) and oblique (Col_{ob}) phases are also common (Figure 1.21). The lattice parameter(s) are called intercolumnar distance(s).

Today, no reliable prediction of the thermotropic properties of a material can be made from its chemical structure. Several factors and variables influence the thermotropic behaviour of discotic mesogens. Nevertheless, strong tendencies can be pointed out. In the next sections, the different factors that influence the thermotropic behaviour of discotic



Figure 1.21: Schematic drawing of the most commonly encountered columnar mesophases. The ordered and disordered columnar hexagonal phases (Col_{ho} and Col_{hd}), the columnar rectangular phase (Col_r), and the columnar oblique phase (Col_{ob}).

mesogens are discussed. They have to be taken as illustrations of the complexity of this field, and not as general conclusions.

Influence of the nature and the size of the aromatic centre



Figure 1.22: Chemical structures and thermotropic behaviour of hexaalkoxy-triphenylene 11 and of *peri*-hexabenzoconene HBC 12, substituted by six n-alkyl side-chains R.

The influence of the size of the aromatic centre into the mesogenic properties of DLCs is difficult to establish practically since rare are the systems where only this parameter is modified. Most of the time, the number and the length of the side-chains, their relative position around the centre, the geometry of the molecule, and the nature of the link between the rigid and the flexible parts of the structure are not identical. No direct comparison is then possible. Nevertheless, strong tendencies can be found. The increase in size comes together with an increase in the proclivity to micro-segregation, enhancing the attraction of neighbouring rigid cores and stabilising the columnar packing. This observation is illustrated by the fact that six short n-alkyl side-chains (of 6 carbon atoms each) give to triphenylene 11¹ a clearing temperature (transition temperature between the columnar mesophase and the isotropic liquid phase) of 97 °C, when even with six n-alkyl chains of 14 carbon atoms each, hexabenzocoronene HBC 12 does not show any clearing up to decomposition around 400 °C (Figure 1.22).[53] Micro-segregation takes place only if a good balance is found between the rigid and the flexible moieties. The length and the nature of the side-chains have to be adapted to the size and the nature of the core.



Figure 1.23: Chemical structures and thermotropic behaviour of HHTT **7a** [54] and of hexa(hexylthio)-hexaaza-triphenylene HAT **13a**. [55] H stands for an columnar helicoidal mesophase.

Even if the size of the aromatic part of a discotic molecule is of crucial importance, its nature (presence of heteroatoms, of dipole moment, its geometry, ...) is also essential. To illustrate that, Figure 1.23 shows the chemical structures and the thermotropic behaviour of two discotic molecules that differ only by the presence of six nitrogen atoms in the aromatic centre. The nitrogens change the electronic distribution in the molecules, changing the interactions between the cores. The consequence of that is a complete destruction of the columnar stacks, no mesophases being observed in the nitrogen containing compound **13a**.

¹How to read thermotropic behaviours: for example, 11 shows a melting of a crystal phase K into a columnar hexagonal mesophase Col_h at 68 °C, which remains until the clearing into an isotropic phase, at 97 °C.

Influence of the nature of the linking group

An other crucial variable in the chemical structure of discotic mesogens is the atom or the chemical functional group that links the rigid and the flexible parts of the molecule. The atomic diameter (in correlation with its polarisability), the bond length and angle, and the presence of specific interactions such as H-bonding, are some of the main parameters that have an influence on the thermotropic behaviour of the resulting material. Table 1.2 summarises the thermotropic behaviour of different metal-free ($M = H_2$) phthalocyanine Pc derivatives 14, that differ only by the nature of the link between the aromatic Pc core and the height n-dodecyl side-chains.



Figure 1.24: Chemical structure of height-fold substituted phthalocyanine 14.

| Side-chains R | phase | $T/^{\rm o}{\rm C}$ | phase | $T/^{\rm o}{\rm C}$ | phase | $T/^{\rm o}{\rm C}$ | phase | Ref |
|--|-------|---------------------|------------------------|---------------------|---------------------------|---------------------|-------|------|
| $-\mathbf{R_1}$ | Kª | 120 | | | Col_{hd} | 252 | Ι | [56] |
| $- OR_1$ | К | 83 | | | Colho | 309 | I | [57] |
| $- \mathrm{CH}_2\mathrm{OR}_1$ | к | 79 | Col_x | 185 | Col_{hd} | 260 | I | [58] |
| $-\operatorname{CO}_2\operatorname{R}_1$ | К | 12 | | | Col_{ho} | | ь | [59] |

^a K: crystal phase. Col_x: columnar mesophase of unidentified geometry. Col_{ho}, Col_{ho}; ordered and disordered hexagonal columnar mesophase. I: isotropic phase.

^b no clearing point observed below decomposition temperature.

Table 1.2: Thermotropic behaviour of different octa-n-dodecyl substituted metal-free phthalocyanine derivatives 14 (M = H₂, R₁ = n-C₁₂H₂₅), differing from one another by the nature of the linking group.

- The atom or the group of atoms that link the aromatic core and the flexible sidechains can be seen as a partially flexible joint. If the joint is more flexible, for example in the presence of a – OR₁ bond, the side-chains have more freedom to move and less thermic energy will be needed to overcome the crystal network energy. The transition temperature between the crystal and the liquid crystal phase (melting point) is usually decreased by introduction of an heteroatom such as oxygen and sulfur between the rigid and the flexible moieties.
- The presence of a methylene group between the oxygen and the aromatic centre
 (- CH₂OR₁) increases the number of degrees of freedom accessible to the chains
 in comparison to the OR₁ substituted molecules. The increase of the potential
 disorder of the flexible chains leads to a decrease in the transition temperature
 between the liquid crystalline and the isotropic phase (clearing point).
- Direct interactions between highly polarizable atoms (i.e. capable to deform themselves by interacting with their surroundings) such as oxygen, for example with ester (- CO₂R₁) groups, and their capacity to prevent disks rotation by steric hindrance, tends to stabilise the columnar packing, increasing the transition temperatures.
- In the presence of specific interactions such as H-bonding between the disks, for example in presence of amine (- NHR₁) or amide (- CONHR₁) functional groups, attractive interactions between the discotic molecules in a column are enhanced. They can be seen as non-covalent "clamps".[60, 61] The high stabilisation of the columnar packing makes the molecules to be thermally decomposed prior having enough thermal energy to break the columnar arrangement. No isotropisation is usually observed.

Influence of the nature and the length of the flexible side-chains

An other aspect that influence the thermotropic behaviour of DLCs is the length and the nature of the peripheral flexible side-chains.

In the LC phases, the chains participate to the partial molecular disordering. When the length of the chains is increased (Figure 1.25), the transition temperatures usually decrease. When the aromatic centre is small, a minimum in phase transition temperatures is usually observed for a certain length of the side-chains. The increase in transition



Figure 1.25: Influence of the length of the side-chains for a family of height-fold substituted phthalocyanine 14, wherein $M = H_2$ and $R = -OC_nH_{2n+1}$.[57, 62]

temperatures observed with longer flexible moieties is explained by the capacity of long alkyl chains to crystallise.[63]

| Side-chains R | phase | $T/^{\rm o}{\rm C}$ | phase | $T/^{\rm o}{\rm C}$ | phase | Ref |
|---|-------|---------------------|---------------------------|---------------------|-------|------|
| $- OC_{10}H_{21}$ | К | 94 | Col_{ho} | 345 | Ι | [57] |
| $- \mathrm{O}(\mathrm{CH}_2\mathrm{CH}_2\mathrm{O})_3\mathrm{CH}_3$ | K | 19 | Colho | 293 | I | [64] |
| $- \operatorname{OC_7H_{15}[3,7-(CH_3)_2]}$ | К | 70 | Colhd | 295 | Ι | [65] |

Table 1.3: Thermotropic behaviour of different phthalocyanine derivatives 14 (M = H₂), differing from one another by the nature of the height flexible side-chains.

The introduction of heteroatoms in the paraffinic chains, as in the case of oligoether moieties, makes them more flexible and less outstretched. The outcome is that the transition temperatures are significantly decreased (Table 1.3). Unfortunately, oligoether chains containing molecules are usually difficult to purify.

When a racemic mixture of optically active branched chains is used, the material obtained consists in a mixture of diastereoisomers that have, by definition, slightly different physical properties. The formation of a mixture makes regular columnar packing often less favourable, reducing the material clearing temperature (Table 1.3).

Conclusion

As we have seen in the above sections, in spite of the absence of reliable structure – properties relationship for discotic mesogens, the impact of each part of the molecule on the material thermotropic behaviour can be roughly predicted. The different parameters have to be carefully chosen in order to obtain the desired properties.

1.3.3 Characterisation of columnar mesophases

As said previously, a liquid crystal phase is characterised by a certain material fluidity combined with a long-distance one- or two-dimensional order. To determine the thermotropic behaviour of a material, three techniques have to be associated:

- The hot plate equipped cross polarising microscopy CPM provides information about the transition temperatures, and the nature of each phase (solid, liquid crystalline, liquid).
- The differential scanning calorimetry DSC is the choice technique for fine transition temperature determination. It is also useful to probe transitions that do not appear by CPM.
- Finally, X-ray diffraction is a powerful technique for the characterisation of lattice symmetry and parameters in crystal and LC phases.

The characteristics and the usefulness of each technique are depicted hereafter.



Cross polarising microscopy

Figure 1.26: Schematic representation of the principle of cross polarising microscopy in the study of birefringent materials. The white light is polarised by the polariser. The resulting light beam is split up into two components by the birefringent matter. A certain part of the resulting light run trough the analyser, crossed *versus* the former polariser.[66]

Cross polarising microscopy CPM is one of the essential tools for the characterisation of newly synthesised potentially mesogenic materials. This technique is based on a particular property of the vast amount of ordered or partially ordered materials, called birefringence. When light enters a material, its wavelength λ and velocity v decrease by a factor called the index of refraction n.

$$n = \frac{c}{v} \qquad n = \frac{\lambda_0}{\lambda} \tag{1.17}$$

where c and λ_0 are the speed and the wavelength of light in the vacuum, respectively.

An isotropic material, i.e. in which no privileged orientation and no long distance order is present, is characterised by a single index of refraction n. In such a material, light polarised in any direction travels at the same velocity through the material. Ordered materials are usually anisotropic. They display two different indexes of refraction.[67] A polarised light will interact differently with the two indexes of refraction and will be split up into a faster and a slower component (Figure 1.26). The difference in phase upon recombination of the two components allows a certain part of the light to run through a second polariser, called the "analyser", which is placed perpendicular (crossed) to the former. The relative retardation of one ray with respect to the other is indicated by an equation (thickness multiplied by refractive index difference) that relates the variation in speed between the two different rays, refracted by the anisotropic matter.

Crystalline and liquid crystalline materials behave as a chiral compound in their capacity to turn the polarisation plane of a polarised light beam that goes through it. The birefringence of calamitic mesogens has been extensively used commercially in passive matrix liquid crystal displays.[45]

If a film of material, sandwiched between two glass plates, is placed between two crossed polarisers in a microscope (Figure 1.26), a pattern will appear in the case of a crystal phase or a mesophase. The pattern is an image of the equilibrium position reached by the micro-domains of identical alignment. It is commonly called "texture".[63] As a liquid phase does not have the capacity to turn the light polarisation plane, it will appear dark under these conditions. A LC phase is also characterised by a certain fluidity of the matter that composes it. The distinction between a crystal and a liquid crystal phase is usually done by applying a pressure on the sample or by shearing it between the plates. In the case of a LC phase, the shape of the micro-domains will change according to the material viscosity; a plastic crystal phase will appear as a deformable highly viscus paste; finally, a crystal phase will appear as a network of sharp needles or as a frozen, breakable but not deformable, solid. If the microscope is equipped with a programmable heating plate, a scan in temperature can be achieved, allowing to establish a phase diagram by looking at the changes in textures.

Theoretical investigations on calamitic mesogens have demonstrated that textures originate from the defects in molecular organisation. As many defects are peculiar to one molecular packing, each phase possesses a few particular textures.[68] A texture is called "specific" if it is characteristic for a certain molecular organisation (Figure 1.27). Sometime, no direct phase identification is possible. The texture is then called "non-specific".



Figure 1.27: Examples of textures observed by CPM. a) Dendritic growth of a columnar mesophase (bright) from the isotropic melt (dark). b) Pseudo focal conic fan-shaped texture, specific for Col_h mesophases.[67]

A classical heating program consists in heating the film to a temperature where the material is isotropic, in order to erase its thermal history (accession to a particular state by the material preparation or purification procedure, or by environment modification (thermal, solvent, or gas annealing, ...) since the last sample isotropisation). The film is then cooled down slowly to the highest temperature LC phase. The LC phase appears as bright spots or areas in the dark liquid (Figure 1.27a). The mesophase growth is sometime specific for a particular molecular organisation. The film is then cooled down at $10 \,^{\circ}\text{C.min}^{-1}$ to room temperature, and the potential changes in textures are observed. A new heating – cooling scan is applied afterward to confirm the first observations.

In addition to the information on the transition temperatures and the nature of the



Figure 1.28: Homeotropic alignment in discotic columnar liquid crystals. a) CPM picture of an homeotropically aligned sample.[69] b) Schematic illustration of the linear defects in homeotropically aligned DLCs.[57]

phases, CPM gives sometime indications on the orientation of the columns versus the substrates. If the columnar axis (\vec{n} in Figure 1.16) is orthogonal to the substrates, as illustrated in Figure 1.28b, no birefringence is observed. Indeed, as the axis of observation corresponds to the columnar axis, the material will not be able to turn the light polarisation plane. In the oriented domains, no light can run through the analyser, giving rise to dark areas. When a default in the orientation is present, e.g. resulting from the presence of dusts, it propagates itself linearly, forming birefringent (bright) lines commonly called "linear defects" (Figure 1.28a). This situation, also called homeotropic alignment or face-on orientation, is usually produced by a slow cooling from the isotropic melt. The capacity of a material to be oriented in a specific direction highly depends on the nature of the substrates and their interactions with the mesogen.[70]

Due to the equipment simplicity, CPM has been widely used in material science laboratories. Unfortunately, many phase transitions do not lead to a change in material texture or happen in a temperature where the material viscosity is to high to allow molecules to move freely. Under these conditions, no transition is observed by this technique. In addition, even if some LC phases can be tentatively identified by the texture observed, no certitude is permitted.

Differential scanning calorimetry

Another method used to determine the thermotropic properties of a material involves the use of calorimetric analysis equipment.

Differential scanning calorimetry DSC reveals the presence of phase transitions in a material by detecting the associated changes in enthalpy. DSC does not give precise phase identification, but the enthalpy change involved at a particular phase transition does provide some indications on the nature of the phases involved. When a material melts, a change of state occurs from a more ordered to a less ordered state. This melting process requires energy (endothermic transition, $\Delta H > 0 \text{ J.mol}^{-1}$) from the surroundings. Similarly, crystallisation of a less ordered state is a exothermic process ($\Delta H < 0 \text{ J.mol}^{-1}$) and releases energy to the surroundings. The DSC instrument measures the energy absorbed or released by a sample as it is heated or cooled.[71]



Figure 1.29: Schematic representation of a typical DSC trace of a discotic mesogen. K: crystal phase; LC: liquid crystal phase; I: isotropic phase.

DSC employs two small furnaces, one for the sample under investigation and the other for an inert reference (an empty aluminium pan). The two furnaces are heated, following a heating – cooling program. The difference in energy supplied to the sample and to the reference is detected. A carefully calibrated instrument with a sample of known transition temperature and enthalpy enables precise measurement of these parameters for the sample under investigation. When the two furnaces reach a transition temperature, depending on its endo- or exo-thermic character, heat is required or released by the sample to remain at the same temperature than the reference. The difference in power supplied to the sample and the reference in order to compensate this variation in energy needs constitutes the DSC trace. A schematic DSC trace of a mesogen is given in Figure 1.29. The transition enthalpy is directly proportional to the area under the transition peak (hatched areas). The absolute energy value in given by comparison with the calibration trace.

Typically, a melting from a crystalline solid to a LC phase (K \longrightarrow LC) or to an isotropic liquid phase (K \longrightarrow I) generates an enthalpy change of about 30 to 50 kJ.mol⁻¹. The structural differences between LC phases and the liquid phase are smaller. Enthalpy changes associated with clearing transitions (LC \longrightarrow I) are typically less than 6 kJ.mol⁻¹. Mesomorphism transitions (LC \longrightarrow LC) usually involve very tiny structural modifications in comparison to the other phase changes, and the change in enthalpy is fairly small (< 1 kJ.mol⁻¹).[45]

Differential scanning calorimetry is the choice method for the determination of the transition temperatures and the enthalpy changes associated with them. DSC and CPM are complementary. Sometime, a transition that is not visible by CPM is detected by DSC. The contrary also appends when the enthalpy changes are under the limit of detection of the DSC instrument. Nevertheless, none of these two experiments gives reliable determination of the molecular conformation, the packing mode, and the lattice parameters of each phase. A third technique is then necessary.

Powder X-ray diffraction

X-ray diffraction is a powerful technique for the study of the molecular ordering. The short wavelength of the X radiation (1.54060 Å for the copper K α_1 line) used in X-ray experiments permits to investigate the ordering at a molecular and atomic level.

It has been known since the time of Christian Huygens (1629 – 1695) that the oscillating electric field of a light wave can interact with the electrons present in the matter to cause coherent scattering. If at least two interference centres are present, interactions between their scattered waves will produce constructive interferences at certain diffraction angles and destructive interferences at other angles, depending on the distance between the scatterers and the wavelength of the radiation. In 1913, William Henry Bragg and his son William Lawrence Bragg showed that the angle θ at which a constructive interference takes place, can be easily related to the distance d_{hkl} between two identical diffraction planes and the X radiation wavelength (λ) by the Bragg's law:[72]



Figure 1.30: a) Schematic representation of a θ : θ diffractometre and b) of a typical X-ray diffractogram (arbitrary intensity vs 2θ) of a discotic mesogen. Three main regions can be distinguished: the inter-columnar diffractions (in green), the amorphous halo (in blue) and the intra-columnar diffraction (in red). c) Illustration of the 2-dimensional X-ray diffraction experiment on oriented sample.

In the one-dimensional X-ray diffraction experiment, the sample is exposed to a X-ray source of radiation (Figure 1.30a) located at an angle θ to the sample plane. If the angle θ is characteristic for a repeated length of the sample, constructive interferences will occur at an angle θ in the reflected X beam, where the detector is placed. A scanning in angle is then performed, giving a diffractogram as a plot of the signal intensity (the number of photon X detected) versus the angle 2θ . A schematic diffractogram for a columnar LC phase is given in Figure 1.30b.

An other useful X-ray diffraction analysis, called 2-dimensional 2D X-ray diffraction, consists in exposing a mechanically oriented sample, obtained by extrusion, to X-ray. The refraction is recorded on a photosensitive paper or on a 2-dimensional detector (Figure 1.30c). As the sample is aligned in a preferential direction, this method allows separated observation of the different orientation planes.

In the case of a crystal phase, a set of sharp reflections corresponding to a correlation over long distances is obtained. The diffractogram recorded for a columnar LC phase can be divided in three main regions (Figure 1.30b): at small-angles (in green), the reflections give information about the geometry adopted by the columns, making a distinction between Col_h , Col_r , The amorphous halo (in blue) relates to broad diffractions of the liquid like flexible side-chains. Finally, in the case of an ordered columnar mesophase, a peak appears in the wide-angles region (in red), giving an estimation of the distance between the disks in a column (intra-columnar distance). In the 2D experiment, the diffractions corresponding to inter-columnar distances are observed in the horizontal axis, when intra-columnar diffractions are located in the vertical axis. The angle θ is determined by the distance between the sample and the detector, and by the distance between the signal and the centre of the diffractogram. Moreover, 2D X-ray experiments permit to probe possible tilting of the aromatic cores according to the columnar axis, which would be seen as a splitting of the intra-columnar signal.

To solve the molecular packing configuration, the diffraction pattern is compared with calculated values obtained by taking one or two of the peaks as references and deducting the position of the other peaks for different phase geometries. For example, in an hexagonal lattice, characterised by only one lattice parameter **a**, the X-ray pattern contains a set of sharp reflections at small angles with reciprocal spacings in the ratio $1 : \sqrt{3} : \sqrt{4} : \sqrt{7}$ (Equation 1.19), corresponding to the Miller indices (1,0) : (1,1) : (2,0) : (2,1) respectively. In the case of a rectangular centred lattice, two lattice parameters **a** and **b** are searched. Such a columnar arrangement is described by Equation 1.20.

$$\frac{1}{d^2} = \frac{4}{3} \frac{1}{a^2} (h^2 + k^2 + hk) \tag{1.19}$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} \tag{1.20}$$

where d is the distance between the layers of the lattice, h and k are the Miller indices and a and b the different unit cell parameters.

Different other important parameters such as the lattice characteristics (distances, angles, density) and the correlation distances can be deduced from the solved pattern.

The solving of a structure by X-ray is a speciality by itself. It requires expertise and experience. In this work, most of the phase geometry determination has been done by or in collaboration with Dr Matthias Lehmann (in our group) and Raluca I. Gearba (Polymer Physics group, ULB, Brussels).

1.3.4 Discotic liquid crystals as organic semiconductors

In organic compounds, three distinct families of semiconductors can be distinguished: the conjugated polymers, the molecular crystals, and the discotic liquid crystals. Different aspects of the three families are compared in Table 1.4, where only typically reported values are given.

| Properties | Conjugated polymers | Molecular crystals | DLCs | |
|-----------------------------|------------------------------------|--------------------|------------------------------------|--|
| Solubility | depends on the system | ** | * * * | |
| Device | spin-coating | vapour deposition | spin-coating | |
| manufacturing | | or spin-coating | | |
| Purity | * | *** | * * (*) | |
| L _e (in nm) | 10 | 100 - 1000 | 100 - 1000 | |
| μ (method) | $10^{-3} - 10^{-4}$ | 1 - 5 (TOF)[73] | K ^a 1.1 - 0.3 (PR-TRMC) | |
| $(in \ cm^2.V^{-1}.s^{-1})$ | $10^{-2} - 10^{-3}$ (PR-TRMC) [74] | | Col 0.4 - 0.002 (PR-TRMC | |
| | | | Col 0.01 - 0.0001 (TOF)[75 | |

^a K : measurement done in the crystal state. Col : measurement done in the columnar mesophase.

Table 1.4: Comparison of the different families of semiconducting organic materials.

When two conjugated molecules are close enough, energy and charge transfer might occur. It has been shown theoretically that the transfer rate is enhanced by a close and regular molecular packing.[76]

In conjugated polymers, structural and chemical defects are inherent to the synthetic procedures and to the methods of manufacturing. Extensive structural studies of polymers have shown the development of inhomogeneous disorder leaving regions within polymer films where the chains are relatively well packed, nearly crystalline, and nearly amorphous regions where interchain correlations are very short range. Moreover, the synthesis of high purity conjugated polymers is not trivial. Only a small amount of breaks in the conjugated segments might dramatically change the material properties.

Contrary to conjugated polymers, low molecular weight materials such as molecular crystals can be obtained with a very high degree of chemical purity by successive sublimation under carefully controlled conditions. Molecular crystals present also the advantage of allowing the formation of highly ordered single crystals. Nevertheless, large scale single crystalline films production is difficult to envisage. The processes used for thin film manufacturing (sublimation under vacuum or spin-coating) usually lead to the formation of poly-crystalline structures. The presence of grain-boundaries between highly ordered domains is detrimental to transport processes since they act as traps for charges and excitons.

DLCs can be obtained with a relatively high degree of chemical purity (> 99 %). Further purification can be achieved in certain cases by dry (sublimation, zone-refining) or wet (preparative high performance liquid chromatography HPLC) purification methods. Moreover, the molecular motions characteristic to the LC states permit the material to self-heal its defects. Indeed, if a disk comes out of the columnar axis, it will enter into an attractive potential that will put it back in its initial place.



Figure 1.31: (a) Schematic representation of a discotic molecule .(b) One-dimensional character of the conductivity of columnar DLCs.

In the columnar arrangement of DLCs, the neighbouring aromatic cores are commonly separated by 3.4 to 3.6 Å. The extended π -system created by overlap of the π -orbitals of neighbouring aromatic moieties creates a one-dimensional pathway for charges and excitons. The flexible non-conjugated chains present all around the aromatic cores act as an insulating coating. The one-dimensional character of the columnar phase conductivity has been proven by Boden *et al.*,[77] by aligning the columns in a specific direction by cooling down slowly the material from its isotropic phase in presence of a strong magnetic field. Charge conductivity has then been measured in the direction parallel to the columnar axis and perpendicular to it. Charge mobility has been found to be about $10^3 - 10^4$ times larger along the columns.

The capacity of DLCs to conduct charges and excitons in a specific direction highly depends on the columns orientation. Depending on the application and the device geometry, different alignment will be preferred. For example, in the case of bilayer photovoltaic cells (Figure 1.5), an homeotropic alignment is preferred in order to create high conductivity channels between the interface and the electrodes.

The conversion of light into electricity operates identically for all the organic semiconductors, but each organic semiconductor has got its particularities. They can be established by looking at two important parameters that govern the semiconducting ability of each material.

Exciton diffusion length

As we have shown previously, the distance that an excited state can cover before its radiative or non-radiative desexcitation, commonly called exciton diffusion length L_e , is of high importance for electronic device applications. Depending on the properties of the excited material (excited state multiplicity and energy, fluorescence quantum yield, separation and relative orientation of the neighbouring molecule, ...), the Dexter and Förster energy transfer mechanisms will operate or not. In most of the systems, a competition exists between the two mechanisms.[73]

Two independent methods for the estimation of L_e are used:

- By irradiating with monochromatic light a device of known thickness, made with the product under investigation and by measuring the photocurrent produced in function of the layer thickness. L_e is found as the thickness at which the maximum photocurrent runs through the semiconducting layer.[78, 21]
- By introducing a known quantity of luminescence quencher. By measuring the luminescence intensity of the mixture in function of the concentration in quencher, and assuming a random distribution of the impurities, one can observe a decrease in light emission corresponding to a certain average distance between two quenchers. This distance corresponds to L_e.[79]

The low molecular order present in conjugated polymer films gives rise to short L_e (about 10 Å).[30]

Different techniques have already been used for the study of energy diffusion in molecular crystals. Values of a few nm up to a few μ m have been reported for several materials.[19] The best value has been obtained by using the former method explained above, on polycrystalline films of a perylene derivative, with a L_e of 2.5 μ m.[21]

Experimental data are still rare for discotic semiconductors and focused on only a few families of compounds. Nevertheless, some indications can be given. In the crystal phase of a discotic mesogen, the former method has given L_e of about 700 Å for the hexa-hexyloxytriphenylene **11a**,[80] value corresponding approximately to the size of the micro-domains present in the sample. The later method has been used on an octa-substituted metal-free phthalocyanine derivative **14** (M = H₂, R = CH₂-O-C₁₂H₂₅) in function of temperature, using the corresponding copper Pc as quencher (M = Cu).[79] L_e of 100 - 200 Å has been obtained in the room temperature crystal phase. In the columnar mesophase, the increase in molecular disorder leads to a decrease of L_e of about one order of magnitude.[81]

Exciton diffusion is one of the key processes involved in the conversion of light into electricity. A long exciton diffusion length is essential to enable the absorbed photon energy to reach the "splitting site" before being trapped or lost by radiative or nonradiative processes. Conjugated polymers show very low values of L_e . For the molecular crystals and the crystalline state of DLCs, similar values have been reported. The rare data available for columnar mesophases, report diffusion length of about one order of magnitude lower than in the mesogens crystalline state.

When the exciton has reached the interface between two semiconductors of different electron affinity, it might split up into two free charges, an electron (in the n-type) and a hole (in the p-type). In order to create a electric current, both charges have to migrate separately to reach their respective electrodes (cathode for the electron and anode for the hole). Even if a long exciton diffusion length is essential in the production of a photocurrent, a good charge mobility is also required.

Charge carrier mobility

Two parameters have to be taken into account in the expression of the conductivity σ (Equation 1.13, page 16): the number (or the density) of charge carriers N_{h^+} and N_{e^-} and their respective mobility μ_{h^+} and μ_{e^-} . In organic materials, the intrinsic number of charge carriers is low, making them insulators in absence of doping. The doping can be chemical (e.g. by exposure to iodine vapour), electro-chemical (by introducing charges into the material), or induced by a radiation (by the creation of electronically excited states

that might split up into free charges). The conductivity measurements include always a step of "doping", where charge carriers are produced in the material, locally or not. A lot of techniques have been developed to estimate the charge carrier mobility of organic materials. The two most commonly encountered methods are depicted hereafter:[82]

- For Pulse Radiolysis Time-Resolved Microwave Conductivity PR-TRMC measurements, the sample is placed in a chamber which is irradiated by a pulsed beam of high-energy electrons (3 MeV). A nearly uniform concentration of charge carriers is created in the entire bulk sample. If these charge carriers are mobile, a change in the microwave conductivity will result as monitored as a change in the microwave power reflected by the cell. The method measures the charge carrier mobility on a nanometre length scale, minimising the disturbance due to the material electrode interface, to the presence of an electric field, and to structural defects in the material (grain-boundaries between micro-domains, impurities, ...). The values obtained by this method can be seen as the maximum mobilities obtainable in a device, with a defect-free semiconducting layer. No distinction between electron and hole mobility is done, both being measured indistinctly. [83, 75]
- For Time-Of-Flight TOF measurements, a glass or quartz cell coated with transparent electrodes is filled with the compound of interest and a constant voltage is applied to the electrodes. A pulsed laser (10 ns) irradiates the sample through one of the electrodes, generating charge carriers which travel along the electric field to the opposite electrode where the drift-time of charge carriers is recorded as a current response. The distinction between electrons and holes is obtained by inverting the direction of the electric field. The two electrodes are separated by about 30 μm of material. The charge carriers have to travel over a long distance before being collected at the opposite electrode. Since the rate of transport very much depends on the quality of the supramolecular structure of the entire layer, the charge carrier mobility obtained can be qualified as "macroscopic".[84]

Despite the experimental differences, the charge carrier mobility values obtained by TOF and PR-TRMC techniques can be very similar, although the TOF values are slightly lower since the technique is very sensitive to imperfections in the sample. For example, values of hole mobility for the discotic liquid crystalline hexa-hexyloxy-triphenylene **11a**, were found to be $0.44 \ge 10^{-3} \text{ cm}^2 \text{.V}^{-1} \text{.s}^{-1}$ by TOF and $0.2 \ge 10^{-2} \text{ cm}^2 \text{.V}^{-1} \text{.s}^{-1}$ by PR-TRMC.[83] However, quantitative comparison is rather complex, both methods including approximations in the mobility value calculation (e.g. the number and location of the produced charge carriers).

As for the exciton diffusion length, the low values of charge carrier mobility obtained with conjugated polymers can be attributed to the presence of chemical and conformational defects in the polymer structure.

The charge carrier mobility of numerous molecular crystals has already been studied. Electron and hole mobilities above 1 and 3 cm².V⁻¹.s⁻¹, respectively, have been reported at room temperature, for single crystals of aromatic molecules. The same order of magnitude has been found for the majority of the investigated materials.[73] It has to be noticed that such TOF mobility values are accessible only for single crystals. The mobilities recorded with poly-crystalline samples are two or three orders of magnitude lower.[75] Very recently, a mobility of 35 cm².V⁻¹.s⁻¹ at room temperature, has been reported for carefully purified single-crystals of pentacene. This result shows that the purity is one of the main issues in molecular electronics.[85] By avoiding the presence of structural or chemical traps for charges, their mobilities can be enhanced by (at least) one order of magnitude.

For the columnar mesophases of discotic compounds, typical charge carrier mobility values are in the range 0.4 - 0.002 cm².V⁻¹.s⁻¹. Their crystalline and liquid phases display "microscopic" (by PR-TRMC) values of about 1.1 - 0.3 and 10^{-4} - 10^{-5} cm².V⁻¹.s⁻¹, respectively. As the maximum charge carrier mobility value achievable with cofacially aggregated disk-shaped molecules has been found to increase linearly with the number of electron in the extended π -system,[86] the upper limit value achievable with discotic mesogens is estimated to be about 3 cm².V⁻¹.s⁻¹, which corresponds to the charge carrier mobility between the aromatic sheets of graphite.[87] The one-dimensional character of the charge mobility in DLCs, makes it difficult to study by TOF since the result dramatically depends of the orientation of the columns *versus* the electrodes. For PR-TRMC

The best photovoltaic device efficiency reported up to now (see Table 1.1) are in relatively good agreement with the values of exciton diffusion length and charge carrier mobility. In purely polymer PVCs, L_e is one order of magnitude lower than the film thickness, leading to a sizeable loss of excited states during their migration. The addition of low values of μ makes bilayer polymer-based PVCs efficiency relatively low. By blending two materials together, the interface is dispersed over the all film thickness. High exciton diffusion length and charge mobility are less necessary.

By applying the same reasoning to the CLDs - pigments system, the low efficiency obtained for the bilayer device can be explained by the poly-crystalline nature of the crystalline perylene derivative used.[39] The resulting low "macroscopic" charge mobility has a negative impact on the device efficiency. The exceptionally high efficiency obtained with the blend [40] has been explained by the spontaneous development of a multilayer structure with a large interface. The high exciton diffusion lengths and charge carrier mobilities are then combined with extended interface as "splitting site".

1.4 Scope of this thesis

1.4.1 Objectives

The main goal of this Thesis is to obtain discotic mesogens specifically developed for photovoltaic device applications.

As we have seen previously, an efficient solar cell consists in two materials of different electron affinity. In this work, two families of molecules, one potentially p-type and one potentially n-type semiconductors, have been investigated. To maximise their photovoltaic abilities, a set of required properties has been proposed. Resulting in tailor-made materials.

Physical requirements

- Strong light absorption in the visible: Light absorption is the first pre-requirement for a good photovoltaic ability. Only absorbed photons can lead to exciton formation. Both materials have to efficiently absorb light in the visible. In addition, the two materials will preferably absorb light in complementary colour ranges, minimising the part of not exploited light.
- A columnar mesophase: In order to form the one-dimensional semiconducting pathways for excitons and charges, a columnar liquid crystalline phase is required for both materials.
- Strong p- or n-type character: As we have seen previously, an interface between two semiconductors of different electron affinity is required for an efficient exciton splitting. In the two materials investigated, one must have a low ionisation potential (corresponding to a high hole affinity, p-type character); the second being characterised by a high electron affinity (n-type character).
- No crystal phase at room temperature: It has been shown that microscopic charge mobility is higher in the crystal phase than in the mesophases. Nevertheless, such a high crystal-state mobility can be obtained in macroscopic devices only if a mono-crystal is formed between the two electrodes. This condition is highly hypothetical and difficult to achieve experimentally. Indeed, crystallisation generally leads to the formation of a network composed by several micro-domains, to the detriment of macroscopic charge mobility. In mesophases, large domains can be obtained

with certain experimental precautions. The macroscopic charge mobility can then be enhanced in the mesophase in comparison to the crystal state if high conductivity channels are created between the electrodes.[88]

A mesophase (liquid crystal or plastic crystal) at room temperature would then be highly preferred.

• Clearing point below 200 °C: In the case of photovoltaic devices, a high conductivity is needed between the two electrodes located on the top and the bottom substrates (see Figure 1.5, page 7). The best molecular orientation to create channels for charges and excitons in this direction is the homeotropic arrangement. It has been shown that homeotropic orientation of the columns is only accessible by a slow cooling of the materials isotropic melt. The possibility to reach an isotropic phase at reasonable temperature is a *sine qua non* condition to obtain such a supramolecular assembly. In this work, homeotropic orientation of the columns is preferred, but is not essential. The limit of 200 °C has been taken for two reasons: to minimise thermal decomposition during the device manufacturing process, most of the aromatic materials being chemically stable below 200 °C; and to allow the use of flexible polymer substrates. Indeed, the absence of crystalline matter in the final device permits to envisage the use of flexible substrates. During the flexible device manufacturing, the polymer substrates must remains below its glass transition. Otherwise the substrates would melt and the device would be destroyed.

Chemical requirements

In addition to these physical properties restrictions, some chemical requirement have to be satisfied. As we are interested not only on the synthesis of new materials, but also on the characterisation of their physico-chemical properties (thermotropic, optoelectronics, semiconducting, photovoltaic, ...), they have to be accessible with a minimum number of efficient synthetic steps in order to permit their production in the g-scale. In order to minimise the losses, yields of at least 50 % are required for each steps of their synthesis.

Purity is also an essential issue. Since conduction properties dramatically depend on the nature and the level of impurity, a special attention has to be paid to the purification of the different products. At each steps of the synthesis, a minimum purity of 99 %, corresponding to the detection limit of an ¹H NMR spectrum, is required.
In the g-scale production point of view, the different reagents used in this work have been also chosen for their commercially availability and for their relative cheapness.

Finally, in order to allow the use of solution-based electronic device processing, such as spin-coating, the materials have to be highly soluble in common organic solvents (chloroform, toluene, hexane, ...).

1.4.2 Strategy

Materials chemistry is located at the frontier between chemistry and physics. This Thesis has been performed in this multidisciplinary spirit, using organic chemistry as a tool to obtain materials with specific properties, and physical chemistry as a tool for the determination and the comprehension of these properties.

For each family of materials studied in this work, a preliminary thought on the design of the molecules has been needed. To answer the question "Which molecules would possess all the wanted properties?", thorough literature research has been done, leading to molecular structures that could fit our criteria.

The second step has consisted in the synthesis of the different materials with a high degree of purity (> 99 %), and in sufficient quantities (0.2 to several g) for all the physical properties investigations. Depending on the thermotropic properties of the synthesised materials, the chemical structures have been adjusted in order to obtain the best system accessible.

The materials that fit our criteria the best have been further investigated. The solution and solid-state light absorption and emission of the pure products and of their blends, have been studied.

Finally, photovoltaic devices based on the best candidates obtained in this work, together or separately, have been manufactured.

1.4.3 Materials studied in this work

In practical, two families of DLCs have been studied in this work. The tetra-substituted metal-free phthalocyanine derivatives **15a-e** have been chosen as potentially p-type semiconductors (hole-accepting materials). As potentially n-type semiconducting materials, we have chosen to investigate the hexa-alkoxy-substituted hexaazatrinaphthylene derivatives **16a-f**.



Figure 1.32: Chemical structure of the two families of discotic semiconductors studied in this work.

1.4.4 Outline

In addition to this introductory chapter (Chapter 1), the Thesis includes four chapters. Chapter 2, is devoted to the development and the study of a new series of phthalocyanine derivatives as hole conducting materials (p-type semiconductors).

Chapter 3 deals with the development and the study of a new series of alkoxy-substituted hexaazatrinaphthylene materials, chosen for their potential high electron affinity (n-type semiconductors). In both cases, the design, the synthesis, the thermotropic behaviour, and the optoelectronic properties in solution and in the solid-state are developed.

In Chapter 4, the thin film physical properties of different blends of discotic materials are displayed. In addition to the optoelectronic and photovoltaic properties of blends of the discotic mesogens synthesised in this work, solar cells made with each of those, blended with other discotic materials known for their photovoltaic abilities, have been investigated. The data given in this chapter result from two stays spent abroad: six weeks in the Nano-Science Center of the University of Copenhagen (Denmark), under the supervision of Professor Thomas Bjørnholm; and six months in the Optoelectronics Group of the Cavendish Laboratory of Physics of the University of Cambridge (United-Kingdom), under the supervision of Professor Sir Richard Friend.

Finally, the dissertation is concluded with a chapter where all of the key results obtained in this work are summarised.



Chapter 2

Phthalocyanine derivatives as p-type semiconductors

2.1 Introduction



Figure 2.1: Most widely studied p-type semiconducting discotic materials. R = alkyl chain.

The p-type character of a semiconductor comes from its ability of being oxidised. The experimental parameter that expresses the ease of removing an electron from (or of introducing a hole in) the HOMO band of a material is its ionisation potential IP. It is defined as the energy needed to remove an electron of the HOMO or as the difference in energy between the HOMO and the vacuum level, where the electron does not interact with its molecule. Nevertheless, even if a low IP is essential, it is not a sufficient condition to have a good p-type material. Indeed, a good overlap of the HOMO levels of neighbouring molecules is crucial to have a high holes conductivity.

Many materials are known for their ability to accept holes. Three families have been more extensively studied: the triphenylenes 7 and 11, the hexabenzocoronenes HBCs 12, and the phthalocyanines Pcs 14. They have in common an electron-rich aromatic system.

2.2 Design of the molecular structure

The p-type discotic semiconductors studied in this work derive from the phthalocyanine Pc aromatic structure 17.



Figure 2.2: General chemical structure of the phthalocyanine MPc. M = H₂, Li₂, metal.

Phthalocyanines (Pcs) were discovered by accident in 1907, during the preparation of *ortho*-cyanobenzamide from phthalimide and acetic acid.[89] Braun and Tcherniac observed the unexpected formation of a dark insoluble material in their reaction medium. One had to wait until 1934 and Linstead, before having a full characterisation of the Pc's chemical structure.[90] A new class of pigments was born. Their dark blue to green colour, together with their high thermal and photochemical stabilities and their easy synthesis, have made Pcs one of the key blue to green industrial pigments for outdoor applications. In the 1940s, Eley demonstrated with a Pc derivative that organic solids can act as electronic semiconductors.[91] Moreover, the capacity of Pc derivatives to increase in conductivity when illuminated [92] is exploited commercially in devices such as photocopiers and laser printers. Pcs have also shown their potentialities in a wide variety of domains, doing from clinical phototherapy to writable compact disks.[93]

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The interest for the phthalocyanine was also dictated by the versatility of this large aromatic system. Indeed, in addition to the possibility of attaching up to sixteen chemical groups on its periphery, the Pc ring possesses a cavity in its centre that can be filled by two small, e.g. hydrogen or lithium, or one larger atom. Up to now, more than seventy different ions (M in 17, Figure 2.2) have successfully been introduced in the Pc ring.[94] All these variations in chemical structure have a dramatic influence on the material's physico-chemical properties (optoelectronic, redox, thermotropic, solubility, ...).[95]

The properties of light absorption and emission are of high importance for photovoltaic device applications. Indeed, energy, multiplicity (singlet, triplet), and geometry of the different electronic states in monomolecular (non-aggregated, in diluted solution) and in interacting systems (in the solid-state or in concentrated solution) are essential factors for a good charge photo-generation efficiency. The pigment status of the Pcs already implies a capacity to strongly absorb light in the visible. Characteristic solution absorption spectra for a metal-free phthalocyanine H_2Pc (M = H_2) and a metal-containing phthalocyanine MPc are given in Figure 2.3.



Figure 2.3: The visible absorption spectra of (a) H₂Pc and (b) CuPc.[96]

In both cases, a strong absorption ($\varepsilon \approx 2 \ge 10^5 \text{ L.cm}^{-1} \text{ .mol}^{-1}$ [96]) in the red, between 670 and 720 nm, is responsible for the colour of the dye. These low-energy absorption bands, commonly termed the Q-bands, result from an efficient $\pi - \pi^*$ transition from the HOMO to the LUMO. The splitting obtained in the case of H₂Pc (Figure 2.3a) is attributed to the lower symmetry (D_{2h}) of H₂Pc compared to that of planar MPcs (D_{4h}), and the subsequent loss of degeneracy of the LUMO orbital. Introduction of substituents can greatly influence the molecular energy levels. For example, the Q-band of an octa-alkoxysubstituted CuPc (CuPc(OR)₈) is red-shifted of 70 nm compared to the non-substituted CuPc.[96]

The phthalocyanine absorption spectrum is also characterised by the presence of the Bband, also called Soret band, located between 320 and 370 nm, in the UV region. This last is known to be less sensitive to the number, the position, and the nature of substituents.

As mentioned in the previous chapter (Section 1.3.2), the introduction of long flexible chains as substituents has not only an impact on the optical properties, but also on the material's thermotropic behaviour.

The first mesogenic Pc derivative was characterised in 1982 by Piechocki and Simon.[97] Since then, many Pc-based mesogens have been studied.[96] Their large aromatic system making them ideal discotic molecules, they use to form highly stable columnar mesophases, over very extended ranges of temperature (sometime, more than 300 °C of mesophase). When it is surrounded by long flexible side-chains, the large rigid core has a strong tendency to micro-segregation, giving to the material a propensity to crystallise at low temperature and preventing the melting of the LC phase into isotropic liquid. Indeed, Pcs that form isotropic melts below their decomposition temperature, which occurs at 250 - 500 °C under air depending on the nature of the substituents, are rare.

The close packing in Pc aggregates has also for consequence to give them high onedimensional charge carrier mobility μ and long exciton diffusion length L_e along the columnar axis. Charge carrier mobility has been measured on octa-sulfanyl substituted metalfree and metal Pcs, giving values of 0.2 to 0.5 cm².V⁻¹.s⁻¹ in the columnar and the crystalline phases respectively,[75] using the PR-TRMC technique (see section 1.3.4, page 45). It has to be noticed that, for the most commonly used ones (Cu, Fe, Zn, ...), the metal has no significant influence on the material's charge carrier mobility. This experimental observation can be explained by the weak influence of the metal on the HOMO and LUMO levels. By replacing the bulky sulfanyl (S–R) groups by the smaller ether (O–R) chains, a decrease in μ is observed (down to 0.06 cm².V⁻¹.s⁻¹).[75] The exciton diffusion length of substituted crystalline Pc has been estimated by Blanzat *et al.*, using the fluorescence quenching technique explained in section 1.3.4. The experiment estimated L_e in columnar crystalline state of substituted H₂Pc to 100 - 200 Å.[79] However, diffusion lengths up to 300 - 500 Å have already been reported for the (crystalline) unsubstituted Pc.[98] Crystalline and mesomorphic phthalocyanines have already proven their photovoltaic abilities. Because of their high red light absorption and their close packing, they are key materials for small molecules electronic device applications, [94] and more particularly in solar energy conversion. Pc materials have already been used in the two main solar cell configurations: the Schottky and the p/n junction devices. In the former overall power conversion efficiencies of 0.02 - 0.03 % have been reported. [99] The later have given some of the best power-conversion efficiencies (typically 0.4 - 1.0 %) of small organic moleculesbased solar cells [100, 39, 101, 31] up to date, by blending Pc materials with n-type (electron accepting) semiconductors such as perylene or soluble fullerene derivatives.

For this work, we want to obtain materials that show specific thermotropic properties, in order to make them more suitable for photovoltaic applications. These properties are as follows: a non-crystalline phase at room temperature RT, a columnar LC phase, and an isotropic phase below 200 °C.



Figure 2.4: Chemical structures of the two phthalocyanine derivatives that show the set of thermotropic properties searched in this work.

| Compound | phase | $T/^{\circ}$ C [ΔH /kJ.mol ⁻¹] | phase | $T/^{\circ}C ~[\Delta H ~/kJ.mol^{-1}]$ | phase |
|----------|--------------------|---|---------------------------|---|-------|
| 14a | Colho ^a | 34 (12.6) | Colhd | 185 (4.9) | Ι |
| 15f | Solid | 11 (47.4) | Col_{ho} | 170-180 (< 0.2) | I |

^a Col_{ho}, Col_{hd}: ordered and disordered hexagonal columnar mesophase. I: isotropic phase.

Table 2.1: Thermotropic properties of the two phthalocyanine derivatives having noncrystalline phase at RT and an isotropic phase below 200 °C. Up to now, only two Pc derivatives exhibiting the thermotropic properties searched in this work are known (Figure 2.4). Table 2.1 summarises the thermotropic behaviour of these two materials.

The first product 14a, made by Schouten *et al.*,[102] shows an ordered columnar hexagonal mesophase Col_{ho} at RT which is transformed into a disordered hexagonal mesophase Col_{hd} above 34 °C. Isotropisation occurs at 185 °C. The material is highly soluble in a wide variety of organic solvents. Unfortunately, the synthesis is long and not efficient. Six synthetic steps are required from commercially available reagents, and the global yield is low (only 2.8 %).

The second material 15f, made by McKeown *et al.*, shows a solid phase at low temperature. A melting to an ordered columnar hexagonal mesophase is observed at 11 °C. The mesophase remains until 170 - 180 °C, where isotropisation takes place. This material is obtained *via* a two step synthesis. No reaction yields are given by the authors.[103] Unfortunately, the purification of oligoether-containing materials is usually difficult as these chains act as traps for ions such as potassium K⁺ or sodium Na⁺.[104] The presence of ions in the resulting materials may randomly change its electronic properties.

As we will discuss in the next sections, the molecular structure of **15f** is of high interest. Several reasons allow us to consider that a tetra-alkoxy metal-free phthalocyanine derivative **15** (Figure 2.5), substituted with adequate alkyl side-chains, might fit all our physical and chemical criteria.

In this work, we have then chosen to study the tetra-alkoxy-substituted metal-free phthalocyanine **15** as potentially p-type semiconductor.





2.2.1 Why a tetra-substituted phthalocyanine?

The phthalocyanine aromatic core 14 can be substituted by up to 16 substituents. Practically, except for unusual "exotic" structures (such as perfluorinated Pc [105]), the Pcs are 4 or 8 folds substituted at two main positions: peripheral (*p*-Pcs, substituted on carbon n° 2, (3), 9, (10), 16, (17), 23, (24)) and non-peripheral (*np*-Pcs, substituted on carbon n° 1, (4), 8, (11), 15, (18), 22, (25)) substitutions. The figures in brackets correspond to optional positions in case of tetra-substitution.



Figure 2.6: General structure of the peripherally 14 and non-peripherally 18 substituted phthalocyanines.

Non-peripherally substituted Pcs are the less usual. They are obtained *via* a three or four steps synthesis from commercially available reagents, depending on the nature of the link between the Pc ring and the flexible side-chains. Two general synthetic routes are depicted in Figure 2.7.

They use to show more disordered mesophases and lower phase transition temperatures than their peripheral counterparts. This observation has been explained by steric effects. Indeed, single-crystal X-ray diffraction analysis of some non-peripherally substituted Pcs have shown that the proximity of the flexible side-chains makes them unable to remain in the plain of the aromatic core. They lie at right angle to it, alternatively up and down.[106] It results for that the formation of disordered columnar mesophases. Even if no conductivity measurement has ever been performed on this type of material yet, the large distance between neighbouring molecules (8.5 Å [107]) is anticipated to be highly detrimental to charge carrier and exciton mobilities.



Figure 2.7: Synthetic schemes leading to peripherally 14 and non-peripherally 18 octasubstituted Pcs. R_1 is an aliphatic chain. i. Appropriate alkyl halide, potassium hydroxide and phase transfer catalyst, 100 °C. ii. Bromine, dichloromethane, 0 °C. iii. Copper(I) cyanide, dimethylformamide, reflux (150 °C). iv. Phthalonitrile cyclotetramerisation. v. *N*-bromosuccinimide, light, benzoyl peroxide, tetrachloromethane. vi. Appropriate alcohol, base catalyst. vii. Acetone, 0 °C. viii. Lithium bis(trimethylsilyl)amide, tetrahydrofuran, -78 °C, aqueous work-up. ix. Sodium metabisulfite reduction in aqueous solvent. x. Appropriate alkyl halide, refluxing acetone, potassium carbonate.[96]

The most widely used Pc derivatives are the height-fold peripherally substituted ones 14. Their highly symmetrical shape makes them ideal discotic materials. And indeed, their mesophases are of exceptional stability. Most of them do not melt into an isotropic phase below their decomposition temperature. Except when highly bulky groups are attached to the molecule, they also tend to crystallise at low temperature. Octa-*p*-Pcs are usually obtained from a four-step synthetic route from commercially available products (Figure 2.7).

Certain four-fold peripherally substituted Pcs can be synthesised in two steps, depending on the nature of the substituents. They are not obtained as a single product,



Figure 2.8: The four structural isomers of tetra-substituted Pcs. The product ratio from a statistical cyclotetramerisation of 4-alkyl-phthalonitrile is $C_{4h}:D_{2h}:C_{2v}:C_s = 1:1:2:4$.

but as a mixture of the four structural isomers accessible from the cyclotetramerisation (Figure 2.8).[108] Indeed, during the cyclisation, a random distribution of the four substituents leads to the formation of four distinct position isomers (their molecular formula are identical, but they differ in the sequence of the links between the atoms). Each of them is obtained with a certain probability according to symmetry equivalences (C_{4h} : D_{2h} : C_{2v} : $C_s = 1 : 1 : 2 : 4$). Separation of the different isomers is hard, due to their high structural similarities. Nevertheless, it has been achieved by HPLC, using specifically graft columns. A quasi-statistical isomers distribution has been demonstrated by identifying the different products by ¹H-NMR, directly coupled to the HPLC.[109]

It is anticipated that the presence of a mixture of isomers has for consequence to decrease the phase transition temperatures in comparison to their octa-substituted counterparts.

2.2.2 Why alkoxy branched side-chains?

In this section, two different aspects are discussed: the choice of oxygen atom as link between the rigid and the flexible parts of the molecule, and the nature of the flexible side-chains.

| Compound | Transition temperatures (°C) | | | $\Sigma \mu_{1D} \ (cm^2.V^{-1}s^{-1})$ | | | |
|-------------------|--|-----------------------------|-----------------------------|---|---------------------------------------|----------------------------------|--|
| | $\mathrm{K} \to \mathrm{D}^\mathrm{a}$ | $\mathrm{D} \to \mathrm{K}$ | $\mathbf{D} \to \mathbf{I}$ | K phase | D phase | D phase | |
| R | | | | RT | $\mathbf{T}_{K \rightarrow D} + 10$ | $T\approx 200^{\circ}\mathrm{C}$ | |
| O-C ₆ | 119 | 86 | > 350 | 0.20 | 0.06 | 0.06 | |
| O-C9 | 101 | 71 | > 350 | 0.30 | 0.08 | 0.05 | |
| 0-C ₁₂ | 91 | 65 | 309 | 0.27 | 0.05 | 0.06 | |
| O-C ₁₈ | 98 | 65 | 247 | 0.20 | 0.07 | 0.05 | |
| S-C8 | 68 | ь | > 300 | 0.55 | 0.16 | 0.24 | |
| $S-C_{12}$ | 77 | ь | 286 | 0.26 | 0.22 | 0.28 | |
| S-C16 | 95 | b | 228 | 0.14 | 0.12 | 0.15 | |

^a K: crystal phase. D: columnar mesophase. I: isotropic phase.

^b no crystallisation observed on cooling.

Table 2.2: Influence of the linking heteroatom and the side chains length on charge carrier mobility of the phthalocyanine **14** (with $M = H_2$) (measured by PR-TRMC).[110]

A p-type semiconductor is characterised by its ease of being oxidised (i.e. to accept positive charges h^+) at the interface with an electrode, e.g. in OLEDs or in FETs, or by an excited n-type semiconductor (i.e. an electron accepting compound), e.g. in PVCs. This electron donating ability is enhanced if the ionisation potential IP of the molecule is low.

In order to facilitate oxidation of molecules, electron withdrawing linking groups (such as ester, amide, ...) have to be avoided. In the electron donor groups, the ethers (oxygen as linking atom) and sulfanyls (also called thioethers, sulfur as linking atom) groups are the more common in substituted Pcs. Ether-substituted Pcs are well known for their tendency to form homeotropically aligned films,[69, 111] which is anticipated to increase the macroscopic conductivity between the interface and the electrodes, in the case of bilayer solar cell configuration. Even if charge carrier mobility in sulfanyl substituted Pcs is two to six times higher than their ether equivalents (see Table 2.2), the capacity of oxygen substituted Pcs to spontaneously form homeotropic alignments upon slow cooling from isotropic melt, is a considerable advantage.

The capacity to reach an isotropic liquid phase at relatively low temperature is mainly given by the structure and length of the side-chains. The importance of this factor has been discussed in Section 1.3.2, page 30. In order to decrease the clearing temperature (transition between the liquid crystal phase and the isotropic melt), two different strategies can be followed: the use of high flexibility chains such as the oligoether moieties, or the use of more bulky groups such as branched aliphatic chains. The former has already been explored by McKeown *et al.*,[103] giving rise to molecule **15f**. Even if the thermotropic properties reported are compatible with what we are searching, the high affinity of oligoether chains to positive ions (Na⁺, K⁺, ...), makes them difficult to purify at the level needed for electronic device applications.

The use of branched side-chains has a double advantage: the branching makes the chains more bulky, increasing the space-filling around the rigid core, and destabilising the columnar packing. This effect is already marked with branching as short as methyl groups. For example, the comparison between 14a and $H_2Pc(OC_{12})_8$ (Table 2.2), which differs only by two methyl groups in each chain, shows that the branching causes a decrease in clearing temperature of 124 °C! Moreover, the branching permits to increase the chains flexibility, without increasing their length. Indeed, the global diameter of 14a is the same as of $H_2Pc(OC_{12})_8$, but by adding three carbon atoms in each side-chain, the number of degree of freedom accessible is increased.

The presence of an asymmetric centre in each flexible chain has for consequence to create a large number of diastereoisomers (in this case, 39), multiplying the number of slightly different molecules in the final pure product. The use of racemic mixture in state of stereochemically pure chains has no impact on the materials clearing points, but helps to decrease the crystallisation temperature.[112, 113]

Regarding to these considerations, we have chosen to study a new family of Pc derivatives, with an homologous series of side-chains (Figure 2.9). Phthalocyanine derivatives as p-type semiconductors



Figure 2.9: Structure of the five peripherally tetra-alkoxy-substituted Pcs 15a-e studied in this work.

2.2.3 Why a metal-free phthalocyanine?

The phthalocyanine aromatic ring is characterised by the presence of a cavity, in its centre, that permits the incorporation of small atoms or different metal atoms in the molecule. The central metal ion exerts a strong influence on the material thermotropic properties (interactions between the molecules by changing the ring planarity and/or by the metal - metal interactions), the molecular energy levels and, by the way, the materials optoelectronic properties (absorption, fluorescence and phosphorescence intensities and energies).[94]

The most complete study of this effect, published up to date, involves the homologous series of octa-alkyl-substituted np-Pcs 18 (with R = alkyl) and reveals that the magnitude of the increase (ΔT) in clearing temperature, compared with that of the metal-free series, is in the following order (Figure 2.10):[114, 115]

$$(H^+)_2 < Ni^{2+}(\Delta T \approx 2^\circ \mathrm{C}) < Co^{2+} \approx Cu^{2+}(\Delta T \approx 60^\circ \mathrm{C}) < Zn^{2+}(\Delta T \approx 100^\circ \mathrm{C})$$
(2.1)

The melting point (K \longrightarrow LC transition) is less affected by the nature of the central metal ion. These data are consistent with the the properties recorded with other Pc deriva-



Figure 2.10: Influence of the central metal ion on the clearing point of the octa-alkylsubstituted np-MPc 18 (with R = alkyl).[96]

tives. The influence of the presence of a metal ion on the thermotropic properties highly depends on the nature of this last. Even if metal-free Pcs have the lowest clearing points, nickel(II), which favours planar tetra-coordination, has a little impact on the thermotropic properties. In the opposite, zinc(II)-containing Pcs rarely show an isotropic phase before material's decomposition. This metal is known for its propensity for penta-coordination, which helps to stabilise the columnar structure. If a metal ion of oxidation state +3 or +4 is incorporated in the cavity, the presence of out-of-plane substituents (e.g. Si(OH)₂, TiO, ...) has for impact to dramatically decrease the material's clearing point (down to 80 °C). This can be easily understood by the impossibility of close packing due to the presence of axial substituents.[116] The resulting large intra-columnar distance is highly detrimental for charge and energy transfer.

In conclusion, as we are looking for materials that combine high charge mobility and unusually low clearing temperature, we have chosen to avoid metal containing and axially substituted Pcs. The metal-free phthalocyanine has been considered as a good candidate for our purpose.

In the next sections, we report the synthesis and the chemical and physical properties characterisation of the five phthalocyanine derivatives **15a-e**.

2.3 Synthesis

Four-fold alkoxy-substituted phthalocyanines are accessible *via* a two steps synthesis, from commercially available reagents.





2.3.1 Synthesis of the 4-alkoxy-phthalonitriles



Figure 2.12: Synthesis of the 4-alkoxy-phthalonitrile 34 precursors.

The first step consists in the nucleophilic displacement of the nitro group of the commercially available 4-nitro-phthalonitrile **32** by the adequate alcohol **33**. Studies have shown that, even if the nitro group is not usually considered as a good leaving group, it becomes as reactive as some aromatic fluoride when activated by an electron withdrawing group such as a nitrile in *para* position.[117] Aromatic nucleophilic substitutions require a polar and aprotic solvent such as N,N-dimethylformamide (DMF), methyl sulfoxide (DMSO), 1,3-dimethyl-2-imidazolidinone (DMI), 1-methyl-2-pyrrolidone (NMP), acetone, acetonitrile, ..., and a base, having for purpose to enhance the nucleophilic power of the alcohol.[118] The most wildly used conditions consist in reacting the 4-nitro-phthalonitrile **32** with 2 equivalents of the corresponding alcohol **33** in the presence of a large excess of anhydrous potassium carbonate (K_2CO_3), in DMF.[119] The reaction is remained 3 days at 50 °C. Under these conditions, the maximum yield obtained for the synthesis of 4-(2-ethylhexyloxy)-phthalonitrile **34a** has never been higher than 8 % although yields of 80 - 90 % have already been reported for similar reactions.

In order to improve the yield of this reaction, other conditions have been found.[120] The use of DMSO as solvent in aromatic nucleophilic substitutions by an alcohol is dictated by its known ability to help the deprotonation of alcohols ($pK_b \approx 16$) without using strong basic conditions. This effect is explained by the strong interactions that takes place between the alcohol function and the dipole moment of the solvent, and by the DMSO ability to form H-bonds with the remaining not deprotonated alcohol, breaking the alcoholate solvent shell according to Equation 2.2.[121]

$$RO^{\ominus} \cdots H - OR + (CH_3)_2 S^{\delta \oplus} = O^{\delta \ominus} \implies RO^{\ominus} + (CH_3)_2 S^{\delta \oplus} = O^{\delta \ominus} \cdots H - OR$$
(2.2)

The reaction kinetic is then accelerated, permitting to carry out the reaction at room temperature, with a reaction time of 2 to 3 days.

Nevertheless, the solvent effect is not sufficient to avoid the presence of a base. The use of lithium hydroxide LiOH has been dictated by its capacity to enhance the reactivity of alkoxide ions in DMSO.[122]

The best results have been obtained by dissolving the 4-nitro-phthalonitrile **32**, with 1.5 equivalent (eq.) of the corresponding alcohol **33**, in carefully dried DMSO. After two hours, 2 eq. of LiOH powder are added. The reaction is then left three days at RT, under magnetic stirring and under dry nitrogen atmosphere. Purification consists in an extraction with ethyl acetate followed by a column chromatography. These reaction conditions have given the different 4-alkoxy-Pns **34** with yields of 50 to 57 %, when yields up to 68% were reported earlier.[120] The chemical structure and the purity (> 99 %) of the phthalonitriles **34** were proven by MS, ¹H-NMR, and, for one of them, ¹³C-NMR. The proton and carbon 13 chemical shifts of **34a** were attributed, using the increments method. The results are given in Figure 2.13.

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Figure 2.13: Experimental chemical shifts of the different (a) protons and (b) carbons 13 of **34a**, attributed using the increments method.* Estimation due to peak superimposition.

Two side-products **35** and **36** have been isolated and characterised by MS and ¹H-NMR (Figure 2.14). Compound **35** is the product of a side-reaction of the 4-nitro-phthalonitrile with hydroxide ions. A proposed mechanism is given in Figure 2.15. The formation of **35** has been prevented by drying the solvent by distillation under vacuum over sodium hydroxide NaOH and by storing it in the fridge, it its solid state. This precaution permits to completely avoid this first side-reaction. Compound **36** results from the nucleophilic substitution of the activated nitrile group in *para versus* the nitro. It is present in small quantity (less than 5 %) in all the reactions and has been isolated as a slightly yellow oil by column chromatography.



Figure 2.14: Structure of the two characterised side-products of the synthesis of 4-alkoxyphthalonitriles.

The products are obtained as colourless oils at room temperature. After a long time (1 week), the oils become slightly green, showing that uncontrolled cyclotetramerisation occurs even at low temperature. All the products have then been stored at -20 °C, in their solid state, in order to avoid this spontaneous reaction.

Table 2.3 summarises the average yields obtained for the target products. As both reagents and products are highly soluble in the solvent used, and that the reactivity of the alcohols does not depend on the length of the alkyl chain attached to it, no chain-length dependence of the reaction yield was expected. It is indeed what has been observed.



Figure 2.15: Proposed mechanism for the synthesis of 35.

| compound | yield (%) | | |
|----------------------|-----------|--|--|
| 34a Pn(6,2) | 52 | | |
| 34b Pn(8,4) | 50 | | |
| 34c Pn(10,6) | 55 | | |
| 34d Pn(12,8) | 57 | | |
| 34e Pn(14,10) | 50 | | |

Table 2.3: Average yields obtained for the synthesis of the 4-alkoxy-phthalonitriles 34.

2.3.2 Synthesis of the phthalocyanines



Figure 2.16: Second step of the synthesis of the phthalocyanines 15: cyclotetramerisation of the 4-alkoxy-phthalonitriles 34.

The phthalonitrile Pn cyclotetramerisation reaction, leading to the formation of the Pc ring, has been extensively used on numerous Pn derivatives.[96]

Surprisingly, the mechanism of this reaction has never been fully elucidated. It has been briefly discussed by Christie *et al.*,[123] who studied the synthesis of unsubstituted CuPc from phthalonitrile, using differential scanning calorimetry DSC. The mechanism proposed by the authors is depicted in Figure 2.17. The previous isolation and characterisation of two intermediate species of the reaction (**42** and **44**, with $Y = OCH_3$ and with Na⁺ and Li⁺ instead of Cu²⁺, respectively) by other groups,[124] corroborates this proposed mechanism. When the reaction is carried out with Cu⁰ or Cu^I, a preliminary metal oxidation is required, for example, by the oxygen present in the atmosphere. The final step of the mechanism consisting in the elimination of the nucleophile Y and in the reduction of the macrocycle, a reducing agent is needed. The scheme suggests that the presence of a metal ion during the cyclisation stabilises the different intermediates, giving rise to higher yields and faster kinetics in comparison with the use of small monovalent ions such as lithium.

For the synthesis of metal-free phthalocyanine H_2Pc , two main strategies can be envisaged: directly introducing the two protons in the centre of the aromatic Pc system, or putting atoms that can be removed from the centre and replaced by protons.

The stability of the link between the central atom(s) and the macrocycle dramatically depends on the nature of the atom(s). Relatively small bivalent metals such as Cu, Zn, Co, ... are difficult or even impossible to remove from the cavity without breaking the

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Figure 2.17: Mechanism proposed for the cyclotetramerisation of the phthalonitrile **40** in presence of copper (II). " $Y^{(-)}$ " is a nucleophilic specie such as methanolate when methanol is used as solvent.[123]

molecule. When the metal atomic radius is larger than the cavity (for Pt, Pd, Pb, ...), the stability of the metal - macrocycle bonds, however still very large, is decreased. Lithium phthalocyanine Li_2Pc is commonly used as intermediate in the synthesis of metal or metal-free Pcs. The weakness of the chemical bond between lithium atoms and the Pc ring, makes Li easy to exchange by a metal (in presence of the corresponding metal salt, in solution), or by two hydrogen atoms (under acid conditions).

The synthesis of H₂Pcs via Li₂Pcs raises a problem: metal lithium can not be obtained commercially totally free of metal traces. The risk of metal contamination has encouraged us to first try fully metal-free synthetic methods. Phthalocyanine derivatives as p-type semiconductors

| Solvent | reagent (eq.) | temperature | reaction time | yield |
|---------------------|---------------------|--------------------------------|---------------|-----------|
| - (in mass) | hydroquinone (0.55) | $180^{\circ}\mathrm{C}$ | 4 hours | 0 % |
| 1-chloronaphthalene | hydroquinone (0.55) | $200^{\circ}\mathrm{C}$ | 30 hours | 0 % |
| 1-pentanol | DBU (2.5) | $140\ ^{\rm o}{\rm C}^{\rm a}$ | 140 hours | 7.7 % |
| 1-pentanol | Li (large excess) | $140^{\circ}\mathrm{C}$ | 4 hours | 33 - 50 % |
| | + acetic acid | | | |

^a Oil bath temperature. Boiling point of 1-pentanol: 136 - 138 °C.

Table 2.4: Reaction conditions and best results obtained for the different synthetic methods used for the formation of metal-free phthalocyanine derivatives **15**.

The use of hydroquinone as reducing agent and as source of protons has given high yields for the synthesis of high purity unsubstituted H₂Pc.[125] The reaction, performed in absence of any solvent, consists in mixing the phthalonitrile **40** with hydroquinone and to heat them to 180 °C, in the Pn melt (melting point: 138 - 142 °C), where the reaction takes place (yield: 53%). We have unfortunately not been able to reproduce this reaction with the flexible chain substituted Pns **34a**. Indeed, the presence of alkyl chains on the Pn decreases its melting and vaporisation temperatures, which occurs below 180 °C for **34a**. The addition of a high boiling point solvent (1-chloronaphthalene) to the reaction medium did not give the wanted product, no reaction being observed. The method has then been left.

An other known metal-free synthesis of H_2Pcs consists in the use of a strong nucleophilic base, the 1,8-diazabicyclo[5.4.0]undec-7-ene (also called DBU), in reflux 1-pentanol. The mechanism of this reaction has never been studied. In the literature, yields up to 90 % have been reported by use of DBU and 1-pentanol as solvent.[126] Despite five attempts, using different quantities of DBU and reaction times, we have been unable to achieve such high yields with the Pn **34**. In the best case (Table 2.4), maximum yield of only 7.7 % has been obtained. This yield is not high enough to envisage larger scale production, *sine qua non* condition for further physical properties investigations. Other conditions had to be found.

As none of the most promising alternatives to the lithium based route has given satisfactory results, this last has been tried. In order to minimise metal contamination, the lithium used is of the highest purity available by Aldrich, which certifies that no detectable metal traces are present in the product. The 1-pentanol used as solvent was freshly dried and cleaned by careful distillation over magnesium 1-pentanolate, and the glassware used was new and exclusively reserved to this reaction in order to minimise the eventual presence of metal traces resulting from other reactions in micro-scratches in the glassware. The reaction conditions have been inspired by the literature.[127] A large excess of lithium is added to a mixture of 1-pentanol and the corresponding phthalonitrile derivative 34. When the reaction medium is heated to reflux $(136 - 138 \,^{\circ}\text{C})$, its rapidly turns from colourless to dark green. After 4 hours, the reaction is cooled down and a large quantity of acetic acid is added. This acidification has for effect to quantitatively exchange the lithium atoms by protons, forming the corresponding metal-free phthalocyanine derivative 15. The product is recovered by precipitation in water and subsequent filtration over fritted glass. It is then purified by column chromatography, using a 50:50 mixture of toluene and hexane as eluent. This last procedure permits to separate the desired product (RF 0.9 with this eluent) from unidentified side-products that remain at RF 0.

Table 2.5 summarises the average yields obtained for the different products. No chainlength dependence is observed, the differences being attributed to the small number of reactions made for the short-chains substituted Pcs, and to the higher materials fluidity of these last, leading to some losses during product purification. These yields are sufficient to open the way to physical properties characterisation. The most interesting products have been synthesised by batches of 1 or 2 g. The easy synthetic method and purification procedure allow us to envisage future up-scaling.

| compound | yield (%) | |
|---|-----------|--|
| 15a $H_2Pc(6,2)_4$ | 40 | |
| 15b H ₂ Pc(8,4) ₄ | 38 | |
| $15c H_2Pc(10,6)_4$ | 33 | |
| $15d H_2Pc(12,8)_4$ | 43 | |
| 15e $H_2Pc(14,10)_4$ | 50 | |

Table 2.5: Average yields obtained for the synthesis of the H₂Pcs 15.

The chemical structures were probed by MS, ¹H-NMR, and UV-visible absorption spectroscopy. The materials purity has been checked by high performance liquid chromatography HPLC.



Figure 2.18: FD-MS spectrum of $H_2Pc(8,4)_4$ 15b with proposed peaks attribution.

The high molecular weight of the substituted Pcs makes them unable to sublimate at reasonable temperatures, even under high vacuum. The electron impact EI ionisation method used for the Pns mass spectrometry measurement, which requires preliminary sublimation of the sample, was then not adapted to the Pcs. Field desorption FD has been chosen. This method consists in placing the sample on a tungsten filament (called the emitter), which acts as electrode, and to heat it. The charged particles are desorbed and flight through the electric field created between the tungsten filament and a second electrode. FD can be applied on high molecular weight molecules (up to 10000 Da)[128] and can be considered as a smooth ionisation method since nearly no fragmentation is observed. The mass spectrum consists in peaks of masses corresponding to

$$\frac{m}{z} = \frac{aM}{b} \tag{2.3}$$

The detected particles, at masses corresponding to m/z (z being the charge), are composed on charged clusters of molecules. The clusters can be of 1, 2, 3, ... molecules (a in Equation 2.3) and charged 1, 2, 3, ... times (b).

The mass spectra of **15a-f**, obtained in collaboration with the Max-Planck Institute for Polymer Research of Mainz (D), are in full agreement with the structure. No trace of metal-phthalocyanine derivative has been observed. A representative example of FD-MS spectrum is given in Figure 2.18.



Figure 2.19: ¹H-NMR spectrum of $H_2Pc(8,4)_4$ **15b** in concentrated benzene solution (about 15 g.L⁻¹), with proposed peaks attribution. Data recorded at 300 MHz, at 25 °C.

The ¹H-NMR spectrum of the Pc derivatives **15** is rich in information. A representative example is given in Figure 2.19. In the aromatic region (above 7 ppm), three groups of peaks are observed (around 8.7, 8.1, and 7.2 ppm) in addition the the solvent signal (benzene C₆H₆, at 7.15 ppm). They have been assigned, according to the literature,[109] to the three families of magnetically distinct aromatic protons of the Pc ring. Görlach *et al.* have succeeded to isolate the four different position isomers of some tetra-substituted Pcs.[109] They showed that the ¹H-NMR signals of the aromatic protons are slightly different for each isomer. The RMN spectrum consisting in the sum of the four isomers spectra, no clear multiplicity can be observed. Nevertheless, the separation of the peaks is too small to permit an unambiguous identification nor to determine the isomer distribution.

Around 4 ppm, two broad signals are observed. They are attributed to the protons of the O–CH₂. The origin of the presence of two singlet where one doublet is expected is still under investigation.

The region between 2.1 and 0.8 is difficult to analyse since a lot of signals are superimposed. The overall integral of this region is significantly higher (137 H) that what expected (92 H) from the chemical structure. This difference is explained by the presence of impurities in the benzene used as solvent, as evidenced by the blank spectrum.

An additional peak is observed at -4.3 ppm, in negative chemical shifts (i.e. upfield of the protons of tetramethylsilane TMS, which are, by definition, at 0 ppm). This signal is attributed to the two protons located in the centre of the molecule, in the cavity. They are in the shielding zone of the aromatic ring current. The chemical shift recorded for this signal is concentration dependent. It is found at -3.2 ppm in relatively dilute solution (about 1 g.L⁻¹ in benzene), and goes down to -4.3 ppm in highly concentrated solution (about 15 g.L⁻¹). This effect can be explained by the presence of aggregates in the later case. Indeed, when two Pc rings stack on each other, the resulting extended π -system gives rise to a higher shielding. In the extreme case of solid-state NMR, this peak is observed at -7 ppm for **15d**.[129] The peak integral is consistent with a fully metal-free Pc.



Figure 2.20: Absorption spectrum of $H_2Pc(14,10)_4$ 15e in dilute toluene solution.

The UV-visible light absorption properties of the five Pc derivatives 15 have been

studied in dilute toluene solution. As expected the absorption characteristics do not depend on the length of the alkyl side-chains, since the last carbon atoms of the aliphatic chains are not part of the chromophore. A characteristic absorption spectrum is given in Figure 2.20. The Soret band is composed of three absorption bands, at 289, 344, and 390 nm. In the long wavelength region, the main peak of the Q-band is split in two (at 671 and 707 nm). This splitting is characteristic of metal-free phthalocyanines. The absorption coefficient ε is also identical (within the experimental error) for the five products. It has been estimated to about 140000 dm³.mol⁻¹.cm⁻¹ at 707 nm. A more detailed study of Pcs optoelectronic properties is given in Chapter 2.5.



Figure 2.21: HPLC elution curve of $H_2Pc(14,10)_4$ 15e, using a 9:1 mixture of hexane and toluene as eluent, and a TSK-SEC column.

Finally, the purity of the Pc materials has been probed, using HPLC on a randomly chosen sample of $H_2Pc(14,10)_4$ **15e**. This experiment was done by Niels Holst, at the Nano-Science Center of the University of Copenhagen (DK). The elution curve, given in Figure 2.21, reveals a purity of about 99.8 %. This value has to be taken with care since only one measurement on one batch has been performed. Nonetheless, it gives a good indication of the efficiency of the purification procedure.

2.3.3 Conclusions

Materials synthesis is the key step of this work. They have to be accessible in a minimum number of steps, with high yields, and with a high degree of purity.

Five four-fold substituted metal-free phthalocyanines **15a-e** have been obtained *via* a two steps, from commercially available reagents.

The first step, consisting in the nucleophilic substitution of the nitro-group of the 4nitro-phthalonitrile by an alcohol has given yields of 50 to 57 % for the different products. This result is similar to what has been reported for similar reactions.

The second step has consisted in the cyclotetramerisation of the 4-alkoxy-phthalonitriles. The first attempts, using fully metal-free conditions, have been unsuccessful. No explanation has been found to understand the unexpected lack of reactivity of the Pns under DBU-based conditions. The use of high purity lithium in 1-pentanol has allowed the formation of the metal-free phthalocyanine derivatives **15** with yields of 38 to 50 %. Even if these yields are significantly lower than the ones reported for similar reactions (up to 90 %), they permit to easily obtain the desired products in large quantities, with a high degree of purity. The most promising materials have been synthesised by batches of 1 or 2 g, opening the way of further physical properties investigations. All the five Pc derivatives are highly soluble in common organic solvents such as chloroform, hexane, or toluene, making future solution-based device manufacturing easy.

The phthalocyanine derivatives **15a-e** are accessible *via* a more rapid and efficient synthesis than the four-steps route used to obtain **14a**. Contrary to **15f**, in which the oligo-ether side-chains act as traps for ions, **15a-e** are easy to obtain with the high degree of purity needed for electronic device applications.

In conclusion, the phthalocyanine derivatives **15a-e** fit all the chemical requirement of this work.

The next sections will be devoted to the study of the thermotropic, optoelectronic, and electrochemical properties of the phthalocyanine derivatives **15a-e**.

2.4 Thermotropic properties

The characterisation of the thermotropic behaviour is one of the key steps of this work. A good understanding of the mesogenic properties and of the molecular organisation is essential.

In this work, we have defined three main thermotropic requirements for each family of materials: 1) presence of a columnar mesophase; 2) clearing point below 200 °C; and 3) non-crystalline phase at room temperature. Even if it is not necessary, an homeotropic alignment of the columns at RT would be of high interest in the case of bilayer device manufacturing.

In order to determine the thermotropic behaviour of the five phthalocyanine derivatives **15a-e**, three complementary techniques have been combined: Cross polarising microscopy (CPM), Differential scanning calorimetry (DSC), and X-ray diffraction.

The results of this investigation are given in the following sections.

2.4.1 Cross polarising microscopy

Due to their deep green colour, Pcs 15 are difficult to investigate by cross polarising microscopy. For compounds 15a-c, no clearing point is observed below 250 °C, where thermal decomposition begins. Therefore, only the fluidity and the birefringence of the materials, characteristic for LC phases have been observed by shearing the materials between the two glass slides. 15a and 15c are hard to deform at room temperature. Despite a slight softening, this high material's viscosity remains until their decomposition (around 250 °C), where their colour turns to black. The material 15b is particular in that its viscosity is lower than the two others. Its fluidity is already visible in the flask, and increases upon heating. No explanation of this phenomenon has been found.

These three materials are birefringent from RT to decomposition. As specific textures are usually formed by cooling down the material from its isotropic melt, no direct phase identification was possible in this case. No visible change in texture has been observed during the heating - cooling scans.

Mesogens 15d-e exhibit fluid and birefringent phases from RT to their isotropic phase, which appears below the materials decomposition temperature. Upon cooling from the isotropic melt, areas of pseudo focal conic fan-shaped texture, specific for hexagonal colum-



(a)

(b)



Figure 2.22: Textures observed under CPM for the phthalocyanine derivative $H_2Pc(14,10)_4$ **15e**. (a) at 165 °C, Pseudo focal conic fan-shaped texture, specific of Col_h mesophases. (b) at 173 °C, homeotropic alignment in the Col_h mesophase. (c) at 48 °C, "fingerprint" texture, specific of Col_r mesophases. (d) at 49 °C, homeotropic alignment in the Col_r mesophase.

nar mesophases,[67] are observed below 226 and 177 °C for **15d** and **15e**, respectively (Figure 2.22a). Beside the textured zones of **15e**, large areas remain non-birefringent except some long bright lines (Figure 2.22b). The homeotropically aligned LC nature of these mm-size domains has been revealed by shearing the sample between the two glass slides. The resulting disruption of the columnar organisation leads to the appearance of a large and uniform bright area, which disappears afterward with a temperature (and a viscosity) dependent kinetic.

When temperature is decreased, the optical texture of **15d-e** changes to a "fingerprint" texture (Figure 2.22c), specific for rectangular columnar mesophases.[130] The change in texture occurs at 68 and 57 °C for **15d** and **15e**, respectively. The large homeotropically

aligned mono-domains of **15e** remain below the phase transition (Figure 2.22d), and are still present at RT.

2.4.2 Differential scanning calorimetry

In order to confirm the thermotropic behaviour observed by CPM, and to detect possible other phase transitions that would not be observed by this first technique, differential scanning calorimetry DSC has been applied to the five phthalocyanine derivatives **15a-e**.



Figure 2.23: DSC curve obtained for $H_2Pc(14,10)_4$ 15e. Second heating and cooling scans, at 10 °C.min⁻¹. The dotted arrows correspond to the transitions observed by CPM.

For 15a-b, flat DSC curves have been recorded. No transition is detected from -20 to 260 °C, where decomposition takes place. For 15c, one transition is observed over the same temperature range, at $84 \,^{\circ}C^1$ upon heating (83 °C upon cooling). The enthalpy associated to this transition, 0.05 kJ.mol⁻¹, is very small and is characteristic for a transition between two mesophases (LC \longrightarrow LC transition), also called mesomorphism.

 $H_2Pc(12,8)_4$ **15d** and $H_2Pc(14,10)_4$ **15e** show two transitions between -20 and 250 °C. A first transition is detected at 68 and 57 °C for **15d** and **15e**, respectively. The same small transition enthalpy is associated to these two phase transitions, 0.05 kJ.mol⁻¹. As for **15c**, it is characteristic for a mesomorphism. A second transition appears at 226

¹all the transition temperatures given correspond to the peak value recorded in the second heating cooling scan. For all the scans, a temperature rate of 10 °C.min⁻¹ has been used.

and 177 °C for 15d and 15e, respectively. The 3.2 and 3.3 kJ.mol⁻¹ associated to these transitions are typical values for clearing points (LC \longrightarrow I transitions).

2.4.3 X-ray diffraction

2-Dimensional X-ray diffraction has been used to characterise the molecular packing structure in the different phases observed by the two precedent techniques. Two diffractograms have been recorded for each material, at RT (27 °C) and 110 °C, giving rise to a global view of the materials thermotropic behaviour. A fiber of 0.7 mm in diameter has been prepared for each material, using a mini-extruder. All the measurements have then been performed on oriented samples.

For the shortest chains substituted Pc derivative 15a, which shows only one phase from RT to decomposition by DSC and CPM, two measurements have been performed, at RT (27 °C) and at 150 °C, in order to make sure that no very small enthalpy transitions that have not been observed by DSC, are present. Contrary to the other materials, this measurement has been performed at the Max-Planck Institut of Mainz (D), using a 1dimensional $\theta - \theta$ setup. The two diffractograms are characteristic for ordered columnar hexagonal mesophase col_{ho}, only one single phase is present over this range of temperature. In the small-angles region, two peaks are observed. They can be indexes as the (1,0) and (1,1) refections of an col_h. The presence at wide-angles of a peak corresponding to a repeated distance of 3.3 Å (in addition to the amorphous halo, centred at 4.6 Å, corresponding to the average distance between the molten side-chains [131]) reveals the ordered character of the mesophase. A material density at RT of 0.94 has been calculated² for this material.

The four other materials **15b-e** show a disordered centred rectangular columnar mesophase Col_{rd} at RT and an disordered hexagonal mesophase Col_{ho} at 110 °C.

This result was surprising for $H_2Pc(8,4)_4$ **15b** since no phase transition had been detected neither by CPM or DSC. X-ray diffraction is the most sensitive technique to probe changes in a molecular assembly. It shows here its usefulness in the study of material's thermotropic behaviour.

Fiber diffraction pattern of both phases is exemplified in Figure 2.24. The high tem-

²Densities ρ were calculated with $\rho = Mw.Z/(N_A V_{unitcell})$; where $V_{unitcell}(Col_h) = a^2.c.\sqrt{3}/2$ and $V_{unitcell}(Col_r) = a.b.c.$ Mw states for the molecular weight and Z corresponds to the number of molecule per unit cell. Z = 1 and 2 for the hexagonal and rectangular mesophase, respectively.



Figure 2.24: 2-Dimensional X-ray diffraction images of $H_2Pc(8,4)_4$ **15b** A) in its Col_{ho} , at 110 °C, B) at RT, in the Col_{rd} , and C) zoom of the small-angle region of B. D) Angular dispersion of the (0,0,1) (or intra-columnar) reflection for the rectangular (solid line) and hexagonal (dotted line) mesophases.

perature (at 110 °C) X-ray patterns of **15b-e** in the Col_{ho} (Figure 2.24A) mesophase show a set of reflections in the small-angle region with reciprocal spacings given by the ratio 1 : $\sqrt{3}$: 2 : $\sqrt{7}$. They can be indexed as (1,0), (1,1), (2,0), and (2,1) reflections of the hexagonal columnar LC phase. The wide-angle diffraction patterns display only two peaks. The first broad peak, situated at s = 0.23 Å^{-1 3} is supposed to reflect the

 $^{^{3}}s$ is defined as 1/d where d is the distance between two repeated plans, which states in the Bragg's law.

average distance between the side-chains in their liquid-like state. This distance ($\approx 4.5 \text{ Å}$) is in good agreement with the van der Waals radius of methylene (CH₂) groups.[132] The second wide-angle peak is assigned to the (0,0,1) reflection, corresponding to the average intra-columnar distance. The average nearest neighbour distance is of 3.5 Å. It should be noticed that the presence of a (0,0,1) reflection implies a certain degree of order in the columnar packing that permits us to identify the phase as Col_{ho} . However, the term "ordered phase" is subject to controversy. The distinction between ordered and disordered columnar phases, is more a matter of convention and despite the fact that the (0,0,1) peak in the low-temperature mesophase is characterised by about the same width at half maximum as the (0,0,1) peak of the Col_{ho} phase, it is a common practice to identify the rectangular mesophase as Col_{rd} (disordered).



Figure 2.25: Variation of the lattice parameter a of the hexagonal coulmnar mesophase with the number of carbon atoms in the longer part of each side-chain. Extrapolation of the linear fit to the data (dashed and solid lines, respectively) allows estimation of the diameter of the rigid phthalocyanine core.

The results given in Figure 2.25 and Table 2.6 show that the lattice parameter a of the Col_{ho} phase increases linearly with the length of aliphatic chains from 26.5 Å for **15b**, having short lateral chains, to 31.8 Å for **15e** molecule, with the longest ones. By modelling the variation of a as a function of the number of carbon atoms n in the main chain with a linear function and by extrapolating the fit to the intersection with the y-axis Fig 2.25), one can estimate the diameter of the molecular core including the bridging ether oxygens. This value is found to be close to the literature diameter of 16 Å.[133] Knowing



Figure 2.26: a) Illustration of the interdigitation as an explanation of the smaller experimental molecular diameter compared to (b) the all-trans conformation of the side-chains with schematic phthalocyanine octa-substituted with linear chains.[94]

the size of the core and assuming the alkyl chains to adopt the all-trans conformation, the calculated molecular diameter of the Pcs 15 was found to vary between 40.0 and 55.2 Å. Since these values are larger than the ones derived from the X-ray measurements, it is plausible that the lateral chains belonging to the molecules in the neighbouring columns are interdigitated (Figure 2.26). More insights into the lateral chain conformation can be obtained from the estimation of the molecular volume. On the one hand, using the lattice parameters determined from the X-ray measurements, the volume of one molecule in the hexagonal and rectangular mesophases reads as: $a^2.c.\sqrt{3}/2$ and a.b.c/2, respectively. On the other hand, the molecular volume V_c can be expressed as $V_c = V_0 + Z.n.V_{CH2}$, where V_0 is the volume of the aromatic core without the methylene groups, Z is the number of lateral chains and n the number of carbon atoms in each aliphatic chain. Equating both volumes, one can find the V_{CH2} value, which vary between 24.7 and 28.4 Å³ (cf. Table 2.6).

Similar estimates are also found for the low-temperature rectangular mesophase Col_{rd} . These values are in some instances smaller than those reported in the literature for the columnar mesophases (27-28 Å³);[134, 134] the discrepancy could be explained by the fact that the V_{CH2} may differ for linear and branched alkyl chains.

In the diffractograms corresponding to the low-temperature mesophase of **15b-e** derivatives six reflections are present in the small-angle region. The indexation of these reflections is given in Table 2.6. Since all (h,k,0) reflections denoted further as (h,k) with $h+k \neq 2.n$,


Figure 2.27: Different types of lattices found in columnar mesophases. Two-dimensional lattice with A) hexagonal, B) rectangular (P2₁/a), C) rectangular (P2/a), and D) centred rectangular (C2mm) symmetry. a and b are the cell parameters. In the case of A), a = b.[131]

(h,0) with $h \neq 2.n$ and (0,k) with $k \neq 2.n$ extinct, the two-dimensional space group is compatible with a C2mm rectangular mesophase (Figure 2.27).[135] At high scattering angles the diffraction patterns exhibit only a broad peak reflecting the disordered state of the lateral chains and the (0,0,1) reflection corresponding to the stacking of disks in the column. The tilt of the molecules with respect to the columnar axis was measured from the angular dispersion of the scattering intensity pertinent to the (0,0,1) peak (Figure 2.24D). It was observed that the disks are inclined at an angle ϕ ranging between 15 and 18°.

| Compound | phase | indices | d_{exp} (Å) | d_{cal} (Å) | lattice param. | V_{CH2} (Å ³) | density |
|----------|---------------------------|---------|-------------------|---------------|--------------------|-----------------------------|---------|
| 15a | Colho | (1,0) | 0) 21.8 21.8 | | $a=25.2~{\rm \AA}$ | - | 0.94 |
| | | (1,1) | 12.7 | 12.6 | $c=3.3~{\rm \AA}$ | | |
| | | | 4.6 (halo) | | | | |
| | | | 3.3 $(\pi - \pi)$ | | | | |
| 15b | Col_{rd} | (1,1) | 22.3 | 22.3 | $a=42~{\rm \AA}$ | 29.6 | 1.07 |
| | $27^{\circ}\mathrm{C}$ | (2,0) | 21.0 | 21.0 | $b=26.3~{\rm \AA}$ | | |
| | | (0,2) | 13.1 | 13.0 | $c=3.6~{\rm \AA}$ | | |
| | | (3,1) | 12.3 | 12.3 | | | |
| | | | 4.8 (halo) | | | | |
| | | | 3.4 $(\pi - \pi)$ | | | | |
| | Col_{ho} | (1,0) | 23.0 | 23.0 | $a=26.5~{\rm \AA}$ | 28.4 | 1.04 |
| | $110^{\circ}\mathrm{C}$ | (1,1) | 13.2 | 13.3 | $c=3.4~{\rm \AA}$ | | |
| | | (2,0) | 11.5 | 11.5 | | | |
| | | (2,1) | 8.6 | 8.7 | | | |
| | | | 4.8 (halo) | | | | |
| | | | 3.4 $(\pi - \pi)$ | | | | |
| 15c | Col_{rd} | (1,1) | 24.0 | 24.0 | $a=45.5~{\rm \AA}$ | 24.2 | 1.09 |
| | $27^{\circ}\mathrm{C}$ | (2,0) | 22.5 | 22.7 | $b=28.5~{\rm \AA}$ | | |
| | | (0,2) | 14.2 | 14.2 | $c=3.5~{\rm \AA}$ | | |
| | | (3,1) | 13.2 | 13.4 | | | |
| | | (2,2) | 12.1 | 12.0 | | | |
| | | (4,0) | 11.3 | 11.4 | | | |
| | | | 4.7 (halo) | | | | |
| | | | 3.4 $(\pi - \pi)$ | | | | |
| | Col_{ho} | (1,0) | 24.5 | 24.5 | $a=28.2~{\rm \AA}$ | 25.9 | 1.07 |
| | $110^{\circ}\mathrm{C}$ | (1,1) | 14.1 | 14.1 | $c=3.4~{\rm \AA}$ | | |
| | | (2,0) | 12.2 | 12.2 | | | |
| | | (2,1) | 9.2 | 9.2 | | | |
| | | | 5.0 (halo) | | | | |
| | | | 3.4 $(\pi - \pi)$ | | | | |
| 15d | Col_{rd} | (1,1) | 25.9 | 25.9 | $a=48.6~{\rm \AA}$ | 23.8 | 1.09 |

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| Compound | phase | indices | d_{exp} (Å) | d _{cal} (Å) | lattice param. | V_{CH2} (Å ³) | density |
|----------|---------------------------|---------|-------------------|----------------------|--------------------------------|-----------------------------|---------|
| | $27^{\circ}\mathrm{C}$ | (2,0) | 24.4 | 24.3 | $\mathbf{b}=30.6~\mathrm{\AA}$ | | |
| | | (0,2) | 15.3 | 15.3 | $c=3.5~{\rm \AA}$ | | |
| | | (3,1) | 14.2 | 14.3 | | | |
| | | (2,2) | 13.1 | 13.0 | | | |
| | | (4,0) | 12.1 | 12.2 | | | |
| | | | 4.7 (halo) | | | | |
| | | | 3.4 $(\pi - \pi)$ | | | | |
| | Col_{ho} | (1,0) | 26.4 | 26.4 | a = 30.5 Å | 26.5 | 1.00 |
| | $110^{\circ}\mathrm{C}$ | (1,1) | 15.2 | 15.2 | $c=3.5~{\rm \AA}$ | | |
| | | (2,0) | 13.1 | 13.2 | | | |
| | | (2,1) | 9.9 | 10.0 | | | |
| | | | 4.8 (halo) | | | | |
| | | | 3.5 $(\pi - \pi)$ | | | | |
| 15e | Col_{rd} | (1,1) | 27.5 | 27.4 | $a=52.5~{\rm \AA}$ | 23.7 | 1.07 |
| | $27^{\circ}\mathrm{C}$ | (2,0) | 26.4 | 26.3 | $\mathbf{b}=32.1~\mathrm{\AA}$ | | |
| | | (0,2) | 16.0 | 16.1 | $c=3.5~{\rm \AA}$ | | |
| | | (3,1) | 15.2 | 15.4 | | | |
| | | (2,2) | 13.7 | 13.7 | | | |
| | | (4,0) | 13.0 | 13.1 | | | |
| | | | 4.6 (halo) | | | | |
| | | | 3.4 $(\pi - \pi)$ | | | | |
| | Col_{ho} | (1,0) | 27.6 | 27.6 | $a=31.8~{\rm \AA}$ | 24.7 | 1.04 |
| | $110^{\circ}\mathrm{C}$ | (1,1) | 15.9 | 15.9 | $c=3.5~{\rm \AA}$ | | |
| | | (2,0) | 13.7 | 13.8 | | | |
| | | (2,1) | 10.4 | 10.4 | | | |
| | | | 4.8 (halo) | | | | |
| | | | $3.5 (\pi - \pi)$ | | | | |

Table 2.6: Powder X-ray diffraction data of the phthalocyanine derivatives **15a**e. Results obtained in collaboration with Dr Matthias Lehmann and Mrs Ioana Raluca Gearba.

2.4.4 Conclusions

By putting together the data obtained by CPM, DSC, and X-ray diffraction, a clear view of the thermotropic behaviour of the different phthalocyanine derivatives **15a-e** can be obtained. Table 2.7 summarises these conclusions.

| Compound | phase | T, °C ^ ($\Delta H)^{\rm b}$ | phase | T, °C ^ ($\Delta H)^{\rm b}$ | phase |
|--|---------------------------|----------------------------------|---------------------------|----------------------------------|-------|
| $\mathbf{15a} \; \mathrm{H_2Pc}(6,\!2)_4$ | Col_{ho} | - | - | - | - |
| ${\bf 15b} \; {\rm H_2Pc}(8,\!4)_4$ | Col_{rd} | ? | Col_{ho} | - | - |
| ${\bf 15c} \; {\rm H}_2{\rm Pc}(10,\!6)_4$ | Col_{rd} | 84 (0.05) | Col_{ho} | - | - |
| $15d H_2Pc(12,8)_4$ | Col_{rd} | 68(0.05) | Col_{ho} | 226 (3.2) | Ι |
| ${\bf 15e} \; {\rm H_2Pc}(14,\!10)_4$ | Col_{rd} | 57 (0.05) | Col_{ho} | 177 (3.3) | Ι |

^a Heating and cooling rate: 10°C.min⁻¹. Peak values from the second heating scan.

^b transition enthalpy in kJ.mol⁻¹

Table 2.7: Calorimetric data of the phthalocyanine derivatives **15a-e**, obtained by combining cross polarising microscopy, differential scanning calorimetry, and X-ray diffraction.

Despite the high number of isomers present in the materials, the five phthalocyanine derivatives studied in the work show quite simple thermotropic behaviour in comparison with many Pcs substituted by height linear alkyl side-chains (e.g. see [136]).

All the five materials show a LC phase from RT to their decomposition (around $250 \,^{\circ}$ C) or to their isotropic phase. Except for H₂Pc(6,2)₄ **15a**, which shows a single columnar hexagonal mesophase over the entire temperature range, all the Pc materials are in a columnar rectangular mesophase at RT, which changes into hexagonal at higher temperature. Only the two longest-chains substituted Pc derivatives **15d** and **15e** have a clearing point below their decomposition temperature.

The evolution of the transition temperatures by increasing the length of the side-chains in illustrated in Figure 2.28a. A linear increase in chain-length leads to a quasi-linear decrease in transition temperature. From the longest chains substituted Pcs, we can conclude that the clearing temperature decreases more rapidly than the Col_{ho} to Col_{rd} transition (49 and 11 °C for the two transitions, respectively).

Figure 2.28b summarises the evolution of the different lattice parameters in function of the chain-length. We can clearly observe that the Col_{ho} to Col_{rd} transition leads to a



Figure 2.28: a) Evolution of the transition temperature by increase of the length of the flexible alkyl side-chains. The target temperature of the dotted line is uncertain since no phase transition has been observed by CPM or DSC for $H_2Pc(8,4)_4$ **15b**. b) Variation of the lattice parameters in function of the length of the side-chains, in the Col_{rd} mesophase at RT and in the Col_{ho} mesophase, at 110 °C.

change of only one parameter. This fact is in good agreement with a C2mm rectangular mesophase, since in this phase the molecules are all tilted in the same direction, changing only the lattice parameter a. The tilt angle is small (15 - 18°) compared to the literature, where values of 46° are commonly encountered.[133] This small phase distortion is responsible for the low transition enthalpy observed by DSC, both mesophases being close in geometry. Moreover, it is consistent with the fact that large homeotropic areas remain in the tilted Col_{rd} mesophase, at RT for $\text{H}_2\text{Pc}(14,10)_4$ **15e**.

As anticipated, the introduction of a mixture of isomers and of diastereoisomers in metal-free phthalocyanine materials has led to a decrease in transition temperatures.

Finally, the thermotropic behaviour of $H_2Pc(14,10)_4$ **15e** fits all the criteria fixed at the beginning of this work: a non-crystalline phase at RT, a columnar LC phase, and an isotropic phase below 200 °C. For this reason, **15e** will be more extensively studied in the next sections.

2.5 Optoelectronic properties

The phthalocyanines are known for their capacity to strongly absorb light in the visible range of the electromagnetic radiation, making them extensively used as blue or green pigments.

The optoelectronic properties of a material can be seen as a signature of its electronic levels.[18] The study of the energy and intensity of light absorption and emission provides important information concerning the structure, energetics, and dynamics of electronically excited states. The comparison between dilute solution (in absence of intermolecular interactions) and solid-state (where molecules can interact with each other) properties is used to probe the molecular interactions and geometry in the condensed phases.

2.5.1 In dilute solution



Figure 2.29: a) Absorption, emission (excitation at 343 nm), and excitation (emission at 717 nm) spectra of the phthalocyanine **15e** in dilute toluene solution. b) Schematic representation of the energetic levels in H_2Pc **17**. Figure reproduced from [137].

Figure 3.25a summarises the photo-physical properties of the phthalocyanine derivative $H_2Pc(14,10)_4$ **15e** in dilute solution. In the absorption spectrum, two main domains can be distinguished: the B-band (also called Soret band), from 280 to 500 nm, and the Q-band, between 500 and 750 nm. The optoelectronic properties of the unsubstituted H_2Pc

17 have been extensively studied by Orti *et al.* [137] Since the presence of four alkoxy side-chains does not affect much the molecular energy levels, this article has been taken as reference in the following discussion.

In the literature, the Q-band absorption has been assigned to a $\pi - \pi^*$ transition from the highest occupied molecular orbital (HOMO), of $4a_u$ symmetry (see Figure 3.25b), to the lowest unoccupied molecular orbital (LUMO) of $4b_{2g}^*$ and $4b_{3g}^*$ symmetry. In the H₂Pcs, the lower molecular symmetry compared to MPcs leads to a loss of degeneracy of the LUMO. The unique, degenerated LUMO level e_g^* is then split in two, forming the $4b_{2g}^*$ and $4b_{3g}^*$ molecular orbitals. Two transitions are then allowed, giving rise to a splitting of approximately 0.17 eV of the Q-band.[137] In H₂Pc(14,10)₄, these two transitions appear at 707 and 671 nm respectively. The two additional peaks, visible in the Q-band region at 642 and 607 nm, may be attributed to transitions from the HOMO to higher energy vibrational states of the split LUMO level. The Soret band, composed here of three peaks at 390, 344 and 289 nm, comes from higher energy transitions such as HOMO - LUMO+1 (e.g. $4a_u \rightarrow 7b_{2g}^*$) and HOMO-1 - LUMO (e.g. $7b_{1u} \rightarrow 4b_{3g}^*$).

The absorption spectrum is not chain-length dependent, the same spectrum has been recorded for the five Pc derivatives **15a-e**. A maximum absorption coefficient ε (at 707 nm, in toluene) of 140000 ± 14000 L.mol⁻¹.cm⁻¹ has been calculated for all of them. This value is in good agreement with the literature. Indeed, absorption coefficient of 120000 to 2000000 L.mol⁻¹.cm⁻¹ are commonly encountered for metal-free Pc derivatives in dilute solution.[96]

In solution, $H_2Pc(14,10)_4$ is weakly luminescent in the red. The fluorescence spectrum shown in Figure 3.25a is composed of two peaks, at 717 and 799 nm. The former is attributed to the radiative 0-0 transition corresponding to the desexcitation of the ground vibrational state of the LUMO to the ground vibrational state of the HOMO. The difference in energy between the 0-0 transition in absorption (at 707 nm) and the 0-0 transition in emission (at 717 nm) is called the Stokes shift. This value is directly correlated to the changes in molecular geometry between the unexcited and the excited species. A small Stokes shift, as observed here (only 10 nm), is obtained when the molecular geometry is only slightly modified after the transition, and corresponds to a highly rigid system.

The second emission peak, at 799 nm may be attributed to a radiative 0-X transition, from the ground vibrational state of the LUMO to an excited vibrational state (X) of the

HOMO.[138] The fluorescence spectrum is not excitation energy dependent. According to the Kasha's rule,[139] fluorescence is only observed from the first (in energy) singlet excited state. The more energetic states decay non-radiatively to the first singlet excited state prior radiative desexcitation.

The excitation spectrum is a plot of emission intensity as a function of the excitation light wavelength, at fixed emission energy and constant excitation light intensity. When the absorption and emission species are identical, the excitation spectrum has the same spectral appearance as the corresponding absorption spectrum. As this is the case in Figure 3.25a, the fluorescence spectrum does not result from the presence of a fluorescent impurities, aggregates or excimers to which energy would have been transferred.

2.5.2 Concentration dependence



Figure 2.30: Concentration dependence of the absorption spectrum of the phthalocyanine derivative **15e** in dichloromethane solution. The arrows show the evolution with increasing concentration. The solid-state absorption spectrum has been obtained from a thin film made by spin-coating from chloroform solution.

Phthalocyanines are well known for their tendency to strongly interact with one an-

other. The main illustration of this is the highly stable columnar packing observed in the solid-state. This propensity to aggregation has an impact on the photo-physical behaviour of the material in solution. $\pi - \pi$ interactions are still present in highly dilute solution, but the probability of meeting is to low to have a significant impact on the spectra. When the material's solubility is low, aggregation can be observed even at very low concentration. For example, aggregation is observed for certain HBC derivatives **12** at concentrations as low as 10^{-9} mol.L⁻¹.[140] When solution concentration is increased, the probability of meeting grows. Aggregates (dimers, trimers, ...) can then be observed. In the case of the phthalocyanines, the difference between the absorption spectrum of isolated (monomeric) and aggregated species is large. Nevertheless, it has been shown that the absorption patterns of the different aggregated species (dimers, trimers, ...) are very close.[141]

Figure 2.30 shows the evolution of the absorption spectrum of a dichloromethane solution of $H_2Pc(14,10)_4$ **15e** in function of solution concentration. The plot has been obtained by normalising the spectra recorded with the most adapted pathlength cells (from 0.01 to 10 mm) to 1 at the highest energy transition (around 344 nm). At low concentrations (<10⁻⁵ mol.L⁻¹), the absorption spectra are fully superposable. No aggregation is observed. At concentrations higher than 10⁻⁵ mol.L⁻¹, the absorption spectrum changes gradually (as shown by the arrows in Figure 2.30). This evolution is attributed to the disappearance of the monomer species due to aggregates formation. No energy shift is observed, except for the Soret band, at 340-344 nm. We can conclude that the molecular orbitals are not modified, but replaced by different ones. Indeed, formation of aggregates leads to a complete change in the Pc orbitals. The similarity between the absorption patterns of the different aggregated species makes us unable to distinguish them. They are seen as an only specie. The energy shift of the Soret band is also attributed to the appearance of a new transition, but the energy and intensity closeness of the two transitions leads to a gradual shift in energy. The aggregation phenomenon of the Pcs in solution has already been studied in function of solution concentration [141], of solvent composition, [57] and of temperature.[142] The same effects on the absorption characteristics were observed.

2.5.3 In the solid state

The differences in absorption spectra obtained for solid-state Pc materials, compared to dilute solutions spectra, can be understood using the exciton coupling theory.[143] In this theory, Kasha *et al.* studied the interactions between the transition moments of adjacent molecules (dimers) as a function of the magnitude of the transition moments (in the plane of the aromatic ring) and the distance between the interacting molecules.



Figure 2.31: Comparison between the absorption spectra of the phthalocyanine **15e** in dilute toluene solution and in the solid-state (film obtained by spin-coating from chloroform solution).

For MPcs, the formation of dimers leads to a slitting of the LUMO level. In the case of H_2Pcs , the LUMO orbital is already split. Aggregation will then lead to the formation of four distinct energy levels.[144] The relative orientation of the transition dipole moments determines which electronic transitions are permitted (Figure 2.32). In the case of a columnar packing, two molecular arrangements are privileged: the face-to-face (2.32a) and the shifted cofacial (2.32b). In the face-to-face arrangement, transitions to the higher energy levels are allowed and the Q-band of the absorption spectrum is blue-



Figure 2.32: Exciton energy diagrams for various dimer interactions. Figure reproduced from [136].

shifted (hypsochromic shift) relative to the dilute solution situation. The lower energy levels do not produce a net transition dipole and, therefore, transition to these states is not permitted. In the shifted cofacial molecular organisation, the transition energy shift depends on the angle θ formed between the columnar axis and the ring plane. Both cases are commonly encountered in columnar molecular organisation, the later case being usually observed for columnar oblique phases (Col_{ob}) and for most of the columnar rectangular phases (Col_r).

In the solid-state, the fluorescence of the Pcs is totally quenched.

In dilute solution, the absorbed light intensity is guide by the Beer-Lambert law $(A = \varepsilon lC)$. This equation can easily be transformed to estimate the absorption coefficient in the solid-state. Solution concentration C (in mol.L⁻¹) corresponds to the number of absorbing molecules per volume unit, which corresponds to the molar density ρ (in mol.dm⁻³) of the material in the solid-state. ρ is experimentally accessible by X-ray diffraction. The pathlength l in solution is determined by experimental conditions. It corresponds to the distance covered by the light through the solution, and is given by the size of the cell used in the experiment. In thin films, this parameter becomes the average thickness of the absorbing layer. In the case of liquid crystalline materials, a smooth and precise method of thickness determination is needed. In this case, we have chosen the X-ray reflectometry. This method is based on the Bragg's law, applied on the distance between two constructive interferences of X-beams reflected by the film surface and by the substrate (Figure 2.33a). This experiment has been performed by Raluca Gearba (Physics department, ULB).

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Figure 2.33: (a) Principle of the X-ray reflectometry as a method of thickness measurement.(b) Tapping mode AFM image of a film of $H_2Pc(14,10)_4$ **15e** (spin-coated from chloroform solution). Colour scale: 0 - 30 nm. (c) Plot of the absorbance at 615 nm as a function of the thickness of the films of **15e**. The slope of the tendency straight line is directly proportional to the solid-state absorption coefficient.

A plot of the film absorbance A at a specific excitation wavelength (here 615 nm) as a function of its thickness d can then be drawn (Figure 2.33c). The straight line obtained has as equation:

$$A = (\epsilon \rho)l$$
 (2.4)

In the case of $H_2Pc(14,10)_4$, the volumetric mass has been estimated by X-ray to 1.07 kg.dm⁻³ at RT, giving a molar density of 0.56 mol.dm⁻³. The solid-state absorption coefficient ε of $H_2Pc(14,10)_4$ can then be estimated to 32000 dm³.mol⁻¹.cm⁻¹ at 615 nm. This value is quite low compared to the 140000 L.mol⁻¹.cm⁻¹ measured in solution. Unfortunately, the lack of references in organic materials solid-state absorption properties, and more particularly in the estimation of their solid-state absorption coefficients, makes

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us unable to go confidently further in this discussion.

Atomic force microscopy AFM has been used to probe the roughness of the surface of the film. Figure 2.33b shows a smooth surface with maximum roughness amplitude of 25 nm.



Figure 2.34: Temperature dependence of the solid-state absorption spectrum of the phthalocyanine in spin-coated thin film. The arrows show the evolution with increase in temperature. Heating and cooling at $10 \,^{\circ}\text{C.min}^{-1}$. a : spectra obtained during the cooling.

As we have seen, solid-state spectroscopy can be very useful to probe the arrangement of the molecules in condensed phases. Up to now, all the measurement were done at room temperature, in the columnar rectangular mesophase of $H_2Pc(14,10)_4$ **15e**. As shown in section 2.4, the molecular organisation of the phthalocyanines changes with temperature. A mesomorphism is observed at 57 °C from a tilted rectangular to a non-tilted hexagonal mesophase. When a thin film of $H_2Pc(14,10)_4$, spin-coated on a glass substrate (from 50 g.L⁻¹ chloroform solution, spinning rate: 1500 rpm during 30 sec.) is heated, the absorption spectra of Figure 2.34 are obtained. An increase in temperature has for consequence to slightly decrease the light absorption intensity (hypochromic shift) in the whole spectrum, and to slightly decrease the energy of the Q-band (bathochromic shift of 5 nm from 25 to 145 °C). The absorption spectrum steadily changes with temperature, no abrupt modification is observed before and after the phase transition. The tilt has non noticeable impact on the material's absorption characteristics. This conclusion is in good agreement with a small change in molecular organisation between the two phases, and with the low transition enthalpy observed by DSC.

The changes cannot be attributed to a difference in film thickness due to a flowing out of material at high temperature, because the initial RT spectrum is recovered after cooling.

In the solid-state, the fluorescence of $H_2Pc(14,10)_4$ **15e** is completely quenched. This quenching, already observed for other Pc materials in concentrated solutions,[57] may be due to interactions between the transition moments of adjacent molecules that prevent fluorescence from the LUMO band. This effect, called "concentration quenching", is commonly encountered in ordered materials.[145]

2.5.4 Conclusions

In the perspective of photovoltaic applications, the materials have to strongly absorb light in the visible. Phthalocyanines were chosen for their known propensity to light absorption. In this section, the optoelectronic properties of the phthalocyanine derivatives **15** have been developed.

As expected, the five phthalocyanine derivatives 15 have shown the same optoelectronic properties in dilute solution. The absorption spectra recorded are in full agreement with metal-free Pc derivatives. An absorption coefficient ε (at 707 nm, in toluene) of 140000 dm³.mol⁻¹.cm⁻¹ has been estimated for all the five materials. This values is not chainlength dependent, and is in good agreement with the literature, where ε of 120000 to 200000 dm³.mol⁻¹.cm⁻¹ are commonly reported.[96] The materials weakly fluoresce in the red (maximum at 717 nm) in solution.

A study of the absorption characteristics in function of solution concentration has been performed. A change in the absorption pattern is already observed at low concentrations $(10^{-5} \text{ mol.L}^{-1} \text{ for } 15e \text{ in dichloromethane solution})$. This result shows the strong tendency to aggregation of these molecules. The same aggregation effect has been reported in the literature by changing solution concentration, solvent polarity, and temperature.

Finally, the solid-state absorption properties of $H_2Pc(14,10)_4$ **15e** have been studied in thin films, in function of temperature. The intermolecular interactions present in the solid-state, as a dramatic effect on the absorption pattern of **15e**. The resulting blue-shift of the HOMO - LUMO transition band is consistent with a tilted face-to-face molecular organisation in the condensed state, which is in good agreement with the tilted (15°) Col_{rd} mesophase characterised at RT for this compound.[69] An absorption coefficient of 32000 dm³.mol⁻¹.cm⁻¹ at 615 nm has been estimated for **15e** in the solid-state. Even if this value is significantly lower than in solution, it is still sufficient for photovoltaic device applications.

When temperature is increased, a slight gradual bathochromic and hypochromic shifts of the absorption spectrum are observed from RT to 145 °C. The initial spectrum is recovered after cooling. No discontinuity in the spectral changes is observed before and after the phase transition. Such an effect has already been reported for similar phase transitions [69], and is consistent with a small change in molecular interactions between the two mesophases, corroborating the conclusions of the thermotropic behaviour characterisation.

2.6 Electrochemical behaviour

The electrochemical behaviour of $H_2Pc(14,10)_4$ **15e** has been investigated in order to estimate the HOMO and LUMO energy levels of the material. $H_2Pc(14,10)_4$ has been taken as representative of the five Pc derivatives studied in this work. Indeed, the HOMO and LUMO bands are characteristic of the Pc ring and its direct substituents. The alkyl side-chains does not participate to these energy levels.

This investigation has been performed by Dr Rafael Gómez Aspe (from our group), in collaboration with Professor Buess (analytical and interfaces chemistry laboratory, ULB).



Figure 2.35: Oxidation and reduction cyclic voltammograms recorded at room temperature for a dichloromethane solution ($\approx 10^{-4} \text{ mol.L}^{-1}$) of H₂Pc(14,10)₄ **15e**, using glassy carbon, platinum wire and SCE as working, counter and reference electrodes, respectively. tetran-butylammonium perchlorate Bu₄NClO₄ was used as supporting electrolyte.

In the reduction part of the voltammogram (at negative voltages), two quasi-reversible reduction waves can be detected, at around $E_{1/2}^1 = -0.72$ V and $E_{1/2}^2 = -1.05$ V. The dependence of the reduction potentials with the scan rate is small. The difference between forward and backward scan peaks is of about 80 mV. This value allows us to guess that only one electron (theoretically, 60 mV) is involved in each process. Taking into account this fact, we can assign the observed waves to the formation of the mono and dianion, respectively. According to the literature, [146, 147] relationship between oxidation potential of single molecules in solution and the material's electron affinity EA corresponding to the energy of the LUMO, $\text{EA} = (\text{E}_{red} + 4.75) = 4.0 \text{ eV}$. This method takes into account the presence of intermolecular interactions and the absence of solvent – material interactions in the solid-state. From the chemical point of view, the processes are quite reversible, as can be stated from the reproducibility of scans.

In the oxidation part of the voltammogram (at negative voltages), **15e** shows a relatively complex behaviour, with three quasi-reversible oxidation processes at potentials E_{ox} around + 0.64, + 1.03 and + 1.24. The materials's ionisation potential, corresponding the the energy of the HOMO, can be estimation to IP = (E_{ox} + 4.75) = 5.7 eV.

These values have to be taken with care. Indeed, the high concentration needed to obtain a sufficient signal intensity has obliged us to use solutions in which aggregates are present. The measured redox potentials may be these of aggregates and not of single molecules, making the model used to estimate the frontier orbitals energy no more applicable. Nevertheless, these values are in good agreement with the literature.

Indeed, oxidation and reduction potentials of +1.10 and -0.66 V, respectively, are usual values for the metal-free phthalocyanine in solution.[96, 94] The HOMO and LUMO levels can then be estimated to 4.1 and 5.8 eV, respectively, using the same model as above.

2.7 General conclusions

The goal of this part of the work was to obtain a potentially p-type semiconducting material that strongly absorbs light in the visible, that shows high exciton and hole mobility, that is highly soluble in common organic solvents, and that has a specific thermotropic behaviour: 1) a non-crystalline phase at room temperature, 2) a columnar liquid crystal phase, and 3) an isotropic phase below 200 °C. Even if an homeotropic alignment of the columns would be highly preferred, it has been proven to be not essential to give efficient photovoltaic devices.[148] Finally, the material has to be obtainable with a high degree of purity, in relatively high quantity to allow further physical properties characterisation.

To fill these criteria, five potentially p-type semiconducting discotic materials have been synthesised. The series of tetra-substituted metal-free phthalocyanine derivatives 15 have been obtained via a two step synthesis, with a global yield of 18 to 25 % from commercially available reagents, allowing the synthesis of the product in large quantities (up to 2 g of pure final product in one batch). The materials have been purified by column chromatography in order to reach purity of > 99 %. They are all highly soluble in common organic solvents (chloroform, toluene, hexane, ...).

Their ease of synthesis and of purification makes them more suitable for device manufacturing than the two phthalocyanine derivatives **14a** and **15f**, that possess the wanted thermal behaviour.

The thermotropic properties of the five materials have been studied by combining the data of CPM, DSC, and X-ray diffraction. If all the five materials 15 show a columnar mesophase down to room temperature, only the longest-chains substituted Pc derivative $H_2Pc(14,10)_4$ 15e shows an isotropic phase below 200 °C (at 177 °C) together with a Col_{rd} LC phase at RT. Moreover, this material has the capacity to spontaneously form homeotropic alignments, when sandwiched between two glass slides.

As expected, the five phthalocyanine derivatives 15 have shown the same optoelectronic properties in dilute solution. They all strongly absorb light in the visible, with a maximum absorption coefficient of about 140000 L.mol⁻¹.cm⁻¹ at 707 nm (in toluene). They are weakly fluorescent in solution.

The solid-state absorption properties of $H_2Pc(14,10)_4$ **15e** have been studied in thin films, in function of temperature. The molecular interactions have an important impact on the absorption properties. The solid-state absorption coefficient has been estimated, using X-ray reflectometry to determine the film thickness, to 32000 dm³.mol⁻¹.cm⁻¹ at 615 nm. In thin films, the fluorescence is completely quenched.

Finally, the electrochemical properties of 15 have been studied in solution. The electron affinity and the ionisation potential have been estimated to 4.0 and 5.7 eV, respectively. These values are consistent with the literature.

The phthalocyanine derivative 15e combines all the criteria defined at the beginning of this work. In addition to an easy and relatively efficient synthesis, it strongly absorb light in the visible, in solution and in the solid-state. It is liquid crystalline at RT and melts into an isotropic phase below 200 °C. The formation of homeotropic alignments over large areas (mm-size) upon cooling, and that remain at RT, is a non-negligible advantage for future electronic device applications. Moreover, its high solubility in common organic solvents allows the use of solution-based device processing. With that all, **15e** can be seen as a highly promising material for future solar cells manufacturing.

2.8 Experimental part

2.8.1 General

¹H-NMR and ¹³C-NMR spectra were recorded in DMSO-d₆ and C₆D₆ on a Bruker Avance 300 with solvent signal as internal standard. Mass spectra were recorded on a VG Micromass 7070F instrument (electron impact EI, 70 eV) and a VG analytical ZAB 2-SE-FPD (field desorption FD, 8 kV). UV/Vis absorption measurements were carried out in solution with a HP 8453 spectrophotometre and in the solid-state with a Perkin-Elmer Lambda 5 spectrophotometre equipped with a Mettler PF - hot stage. The emission measurements were carried out with a SLM-Aminco 3000 diode array spectrophotometre. Thin solid films have been obtained by spin casting, with a Chemat Tech. Spin-Coater KW-4A, from chloroform solutions of the corresponding compound(s) onto quartz or glass slides. Thin Layer Chromatographies (TLC) were performed on Silicagel 60 T_{254} . The thermal behaviour of all the synthesised materials have been investigated by polarising optical microscopy (JENA microscope equipped with a Mettler FP 52 hot stage) and differential scanning calorimetry (Mettler Toledo DSC 821, 2-6 mg samples in closed Al pans) with heating and cooling scans performed at 10 °C.min⁻¹ (peak values are given). X-ray diffraction measurements were performed on BM26 beamline of the European Synchrotron Radiation Facility, E.S.R.F, Grenoble using X-ray photons with energy of 10 KeV. The diffraction pattrens were collected in transmision. The temperature of the sample was controlled with a Linkam heating stage. The s-axis was calibrated using silver behenate. The electrochemical features of these derivatives were probed by cyclic voltammetry at room temperature. A dichloromethane solution $(10^{-4} \text{ mol.L}^{-1})$ and tetra-n-butylammonium perchlorate as supporting electrolyte were used in a conventional three-compartment cell, equipped with a glassy carbon, SCE and platinum wire as working, reference and auxiliary electrode, respectively. Measurements were carried out under inert atmosphere and using an Autolab (Eco Chemie) PGSTAT 30 potentiostat with a Scan-Gen module at a scan rate of 200 mV.s⁻¹.

All the reagents were purchased from Aldrich or Acros Organics and used as received. DMSO (A.C.S. reagent, Aldrich) was reflux over NaOH and distilled under vacuum freshly before use. 1-pentanol (A.C.S. reagent, Aldrich) was reflux over magnesium 1-pentanolate and distilled freshly before use. The solvents for the photo-physical study were of spectroscopic grade and used as received. Column chromatographies were performed on silica gel (Merck silica gel 60, mesh size 0.2 - 0.5 mm).

2.8.2 General procedure for the synthesis of the 4-alkoxy-phthalonitriles

This procedure has been adapted from the literature.[120] A mixture of 4-nitrophthalonitrile (4.50 g, 26 mmol) and the appropriate alcohol (39 mmol) in 100 mL anhydrous dimethyl-sulfoxide was stirred during two hours at RT. Lithium hydroxide powder (1.25 g, 52 mmol) was then added with stirring. The reaction medium turned from yellow to black, and was stirred 3 days at RT. The solution was poured in water and extracted three times with ethyl acetate. The combined organic fractions were dried on Na₂SO₄, filtrate, and evaporated. The crude products (a dark green-yellow oil) were purified on a silica gel column chromatography with toluene as eluent to afford the pure 4-alkoxy-phthalonitrile as a viscous light yellow oil, with yields of \approx 50 %. The compounds have to be stored in the freezer, in their solid-state, to avoid uncontrolled cyclotetramerisation.

4-(2-ethylhexyloxy)-phthalonitrile (Pn(6,2)₄, 34a):

Yield 52 %. ¹H NMR (DMSO-d₆, 300 MHz): δ (ppm) 0.87 (t, J = 7 Hz, 3 H), 0.89 (t, J = 7.4 Hz, 3 H), 1.2 - 1.5 (m, 8 H), 1.71 (q, J = 6.0 Hz, 1 H), 4.02 (d, J = 5.8 Hz, 2 H), 7.45 (dd, J = 8.8 and 2.7 Hz, 1 H), 7.78 (d, J = 2.7 Hz, 1 H), 8.03 (d, J = 8.8 Hz, 1 H). ¹³C NMR (DMSO-d₆, 75.4 MHz): δ (ppm) 10.6, 13.8, 22.3, 23.0, 28.2, 29.6, 38.2, 71.4, 105.6, 115.6, 116.1, 116.2, 119.9, 120.2, 135.6, 162.1. MS (EI) m/z = 256 (M+, calculated 256), 127, 100, 71, 57. RF (silica gel, toluene) : 0.55.

4-(2-butyloctyloxy)-phthalonitrile (Pn(8,4)₄, 34b):

Yield 50 %. ¹H NMR (DMSO-d₆, 300 MHz): δ (ppm) 0.86 (m, 6 H), 1.2 - 1.5 (m, 16 H), 1.76 (br, 1 H), 4.01 (d, J = 5.9 Hz, 2 H), 7.44 (dd, J = 8.8 and 2.6 Hz, 1 H), 7.76 (br, 1 H), 8.03 (d, J = 8.8 Hz, 1 H). MS (EI) m/z = 312 (M+, calculated 312), 169, 157, 144, 127, 113, 99, 85, 71, 57. RF (silica gel, toluene) : 0.55.

4-(2-hexyldecyloxy)-phthalonitrile (Pn(10,6)₄, 34c):

Yield 55 %. ¹H NMR (DMSO-d₆, 300 MHz): δ (ppm) 0.84 (t, J = 6.6 Hz, 6 H), 1.15 - 1.45 (m, 24 H), 1.75 (br, 1 H), 4.01 (d, J = 5.5 Hz, 2 H), 7.43 (dd, J = 8.8 and 2.6 Hz, 1 H), 7.76 (d, J = 2.6 Hz, 1 H), 8.03 (d, J = 8.8 Hz, 1 H). MS (EI) m/z = 368 (M+, calculated 368), 225, 157, 144, 127, 113, 99, 85, 71, 57. RF (silica gel, toluene) : 0.55.

4-(2-octyldodecyloxy)-phthalonitrile (Pn(12,8)4, 34d):

Yield 57 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.88 (m, 6 H), 1.2 - 1.5 (m, 32 H), 1.81 (m, 1 H), 3.93 (d, J = 5.5 Hz, 2 H), 7.19 (dd, J = 8.8 and 2.6 Hz, 1 H), 7.27 (d, J =2.6 Hz, 1 H), 7.71 (d, J = 8.8 Hz, 1 H). MS (EI) m/z = 424 (M+, calculated 424), 281, 183, 169, 155. RF (silica gel, toluene) : 0.55.

4-(2-decyltetradecyloxy)-phthalonitrile (Pn(14,10)₄, 34e):

Yield 50 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.88 (t, J = 6.6 Hz, 6 H), 1.2 (br m, 40 H), 1.81 (m, 1 H), 3.91 (d, J = 5.6 Hz, 2 H), 7.17 (dd, J = 8.7 and 2.4 Hz, 1 H), 7.25 (d, J = 2.2 Hz, 1 H), 7.69 (d, J = 8.7 Hz, 1 H). MS (EI) m/z = 480 (M+, calculated 480), 337, 155, 141, 127, 113, 99, 85, 71, 57. RF (silica gel, toluene) : 0.55.





Phthalocyanine derivatives as p-type semiconductors



Figure 2.37: ¹³C-NMR spectrum of Pn(6,2) **34a** in DMSO with proposed peaks attribution. Data recorded at 25 °C, at 75.4 MHz.

2.8.3 General procedure for the synthesis of the phthalocyanines:

This procedure has been adapted from the literature.[127] 4-alkoxy-phthalonitrile (1g) was mixed with a large excess of metal lithium, in 6 mL of dry 1-pentanol. The reaction mixture was then heated to reflux under an inert atmosphere. After 4 hours, 30 mL of acetic acid was added to the dark green solution. The formed precipitate was collected by filtration, and washed with water and methanol. The pasty green material obtained was then dissolved in methylene chloride, and the solvent was evaporated under vacuum. The pure product was obtained after purification on silica gel column chromatography (toluene/hexane 1:1 as eluent) to afford the corresponding H₂Pc in ≈ 40 % yield.

2,9(10),16(17),23(24)-Tetra(2-ethylhexyloxy)-phthalocyanine (H₂Pc(6,2)₄, 15a):

¹H NMR (C₆D₆, around 4 g.L⁻¹, 300 MHz): δ (ppm) -3.2 (br, 2 H), 0.93 (t, J = 7.0 Hz, 24 H), 1.5 - 1.9 (m, 32 H), 2.03 (m, 4 H), 3.87 (s, 4H), 4.08 (s, 4 H), 7.20-7.45 (m, 4 H), 8.05-8.25 (m, 4 H), 8.55-8.60 (m, 4 H). MS (FD) m/z = 513 (M+/2), 1027 (M+, calculated 1027.42), 1541 (3M+/2), 2055 (2M+), 3082 (3M+). UV-vis (toluene): λ_{max}

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 $(\varepsilon) = 707 \text{ nm} (140000 \pm 14000 \text{ dm}^3.\text{mol}^{-1}.\text{cm}^{-1}).$

2,9(10),16(17),23(24)-Tetra(2-butyloctyloxy)-phthalocyanine (H₂Pc(8,4)₄, 15b):

Due to the high fluidity of this material at RT, filtration was not possible. An extraction (water-methylene chloride) was necessary in order to remove the 1-pentanol. The organic solutions were combined, dried over Na₂SO₄, filtrated, and evaporated under vacuum. The green oil was purified by column chromatography on silica gel with toluene-hexane 1:1 as eluent, to afford the H₂Pc in 38 % yield. ¹H NMR (C₆D₆, around 15 g.L⁻¹, 300 MHz): δ (ppm) -4.3 (s br, 2 H), 0.8-2.2 (m, 92 H), 3.89 (m br, 4H), 4.12 (m br, 4 H), 7.15-7.45 (m, 4 H), 8.01-8.15 (m, 4 H), 8.54-8.73 (m, 4 H). ¹³C NMR (C₆D₆, around 15 g.L⁻¹, 75.4 MHz): δ (ppm) 161.3, 148.1, 138.5, 129, 123.3, 118.8, 104.9, 71.5, 39.0, 32.6, 31.8, 30.6, 30.2, 30.0, 27.8, 23.9, 23.4, 14.7, 14.6. MS (FD) m/z = 626 (M+/2), 1252 (M+, calculated 1251.85), 2504 (2M+), 3756 (3M+). UV-vis (toluene) : λ_{max} (ϵ) = 705 nm (131000 ± 14000 dm³.mol⁻¹.cm⁻¹).

2,9(10),16(17),23(24)-Tetra(2-hexyldecyloxy)-phthalocyanine (H₂Pc(10,6)₄, 15c):

Yield 33 %. ¹H NMR (C₆D₆, around 4 g.L⁻¹, 300 MHz): δ (ppm) -3.34 (s br, 2 H), 1.00 (t, J = 6.5 Hz, 12 H), 1.09 (t, J = 6.5 Hz, 12 H), 1.3-2.0 (m, 96 H), 2.08 (m br, 2 H), 2.21 (m br, 2 H), 4.05 (m br, 4H), 4.28 (m br, 4 H), 7.48-7.71 (m, 4 H), 8.43-8.63 (m, 4 H), 8.91-9.13 (m, 4 H). MS (FD) m/z = 1476 (M+, calculated 1476.29), 2215 (3M+/2), 2461 (5M+/3), 2953 (2M+), 3703 (5M+/2). UV-vis (toluene): λ_{max} (ε) = 705 nm (140000 ± 15000 dm³.mol⁻¹.cm⁻¹).

2,9(10),16(17),23(24)-Tetra(2-octyldodecyloxy)-phthalocyanine (H₂Pc(12,8)₄, 15d):

Yield 43 %. ¹H NMR (C₆D₆, around 4 g.L⁻¹, 300 MHz): δ (ppm) -3.24 (s br, 2 H), 0.94 (t, J = 6.5 Hz, 12 H), 1.00 (t, J = 6.8 Hz, 12 H), 1.3-2.0 (m, 112 H), 2.1 (m br, 2 H), 2.2 (m br, 2 H), 4.08 (m br, 4H), 4.30 (m br, 4 H), 7.51-7.75 (m, 4 H), 8.49-8.69 (m, 4 H), 8.97-9.17 (m, 4 H). MS (FD) m/z = 1700 (M+, calculated 1700.72), 2268 (4M+/3), 2551 (3M+/2), 2836 (5M+/3), 3402 (2M+). UV-vis (toluene): λ_{max} (ε) = 705 nm (132000 ± 13000 dm³.mol⁻¹.cm⁻¹). 2,9(10),16(17),23(24)-Tetra(2-decyltetradecyloxy)-phthalocyanine (H₂Pc(14,10)₄, 15e):

Yield 50 %. ¹H NMR (C₆D₆, around 15 g.L⁻¹, 300 MHz): δ (ppm) -4.3 (s br, 2 H), 0.91 (m, 24 H), 1.3-2.0 (m, 120 H), 2.0 (m br, 2 H), 2.1 (m br, 2 H), 3.9 (m br, 4H), 4.1 (m br, 4 H), 7.15-7.45 (m, 4 H), 8.0-8.15 (m, 4 H), 8.5-8.7 (m, 4 H). MS (FD) m/z = 962 (M+/2), 1924 (M+, calculated 1925.15), 2564 (4M+/3), 2886 (3M+/2), 3207 (5M+/3), 3366 (7M+/4). UV-vis (toluene): λ_{max} (ε) = 705 nm (149000 ± 15000 dm³.mol⁻¹.cm⁻¹).



Figure 2.38: ¹³C-NMR spectrum of $H_2Pc(8,4)_4$ **15b** in benzene (around 15 g.L⁻¹), with proposed signals attribution. Spectrum recorded at 25 °C, at 75.4 MHz.



Chapter 3

Hexaazatrinaphthylene derivatives as n-type semiconductors

3.1 Introduction

An efficient n-type organic semiconductor is characterised by a high electron affinity, combined with a good electron mobility.

Up to date, only a few families of n-type discotic materials have been studied. Discotic materials with low first reduction potential are usually constituted by a electron-poor (π -deficient) aromatic core or that is surrounded by electron-withdrawing functional groups such as esters or amides.



Figure 3.1: Common n-type semiconducting discotic materials.

Figure 3.1 shows the chemical structures of the most wildly studied electron-poor discotic mesogens. Perylene tertracarboxdiimide PTCDI derivatives **47** have already been extensively studied.[149] Some of them can be synthesised in one step from commercially available reagents. Their easy synthesis, their intense red colour and their high fluorescence quantum yield, have led to the commercialisation of some of them as pigments. Crystalline PTCDI derivatives have been used as n-type semiconductor in solar cells, giving the most efficient mesogens containing PVCs.[40] To the best of our knowledge, mesogenic perylene derivatives have never been used in PVCs yet.

Several mesogenic tricycloquinazoline TCQ derivatives have already been synthesised, either with alkylthio **48** [150] and alkoxy **49** [151] substitution. This electron-poor aromatic system requires a long synthesis (five to six steps). Despite conductivity investigations for extrinsically doped mesogenic TCQ derivatives, [152] these materials have never been used in photovoltaic applications.

More recently, a new promising family of electron-deficient discotic mesogens, based on the hexaazatrinaphthylene HATNA aromatic core **50**, has been reported.[153]

3.2 Design of the molecular structure

In this work, we have chosen to study the 2,3,8,9,14,15-hexa-alkoxy-5,6,11,12,17,18- hexaazatrinaphthylene HATNA-OR derivatives **16**. Different reasons justify this choice. They are developed in the following sections.



Figure 3.2: General structure of the hexa-alkoxy- hexaazatrinaphthylene HATNA-OR derivatives 16 studied in this work. R = n-alkyl.

3.2.1 Why the hexaazatrinaphthylene aromatic core?

The first flexible-chains substituted HATNA derivatives were synthesised in our group, and reported in 2001.[153] Consisting in a three-arms star, HATNA is along the same lines as the well-known triphenylene 7 and the hexaazatriphenylene HAT 13.



Figure 3.3: Chemical structure comparison of hexaalkylthio-triphenylene 7, hexaalkylthio-HAT 13, and hexaalkylthio-HATNA 50.

The introduction of pyridine-like nitrogens in the aromatic structure (from 7 to 13) has for consequence to increase the electron affinity of the aromatic core, making electron injection easier, enhancing the material's n-type character. An increase in core size (from 13 to 50) is expected to enhance materials charge carrier mobility.[86]

A theoretical investigation of the potential charge carrier mobility of these three aromatic systems has reinforced the potential of the HATNA core as electron conductor.[154] Indeed, Lemaur *et al.* showed that the increase in core-size when going from HAT to HATNA significantly reduces the organisation energy λ , enhancing charge migration along the columns.

The HATNA derivatives reported in 2001 were six-fold substituted by alkylthic flexible side-chains. A complete series of chain length (from $n-C_6H_{13}$ for HATNA-SC₆ 50a to $n-C_{12}H_{25}$ for HATNA-SC₁₂ 50d) were obtained, *via* an efficient two-steps synthetic scheme (Figure 3.4), with global yields of about 60 %, starting from commercially available reagents.

All the linear alkyl-chains substituted HATNA-SR show a liquid crystalline behaviour over a wide range of temperature. The high stability of their columnar packing makes them to remain up to materials decomposition temperature, which occurs around 250 °C. They Hexaazatrinaphthylene derivatives as n-type semiconductors



Figure 3.4: Two steps synthesis of hexa-alkylthio-hexaazatrinaphthylene HATNA-SR derivatives 50.

never melt into isotropic phase. Their study also revealed a rich and complex thermotropic behaviour, with up to five different mesophases for HATNA-SC₁₀ **50c**. The strong molecular interactions also lead to materials crystallisation at relatively high temperature (never below 99 °C).

In the other hand, all the HATNA-SR derivatives **50** strongly absorb light in the visible. In solution (toluene), an absorption coefficient $\varepsilon(470)$ of 105000 L.mol⁻¹.cm⁻¹ has been reported, giving rise to yellow, slightly fluorescent, solutions.

Their charge carrier mobility have been recently studied, using the PR-TRMC technique. The best values obtained are highly encouraging. Indeed, a maximum overall charge mobility of 0.9 and $0.3 \text{ cm}^2 \text{.V}^{-1} \text{.s}^{-1}$ have been obtained for the crystalline and the columnar liquid crystalline phases of HATNA-SC₁₀ **50c**, respectively. This values correspond to the sum of the e⁻ and h⁺ mobilities, no distinction being possible by this method. Even if no electron mobility measurement has ever been performed on these materials, HATNA-based discotic mesogens seems to be good candidates for our study. Indeed, their capacity to strongly absorb light in the visible, combined with their high tendency to form columnar aggregates, their electron-deficient character, and their potential high electron mobility, make them promising materials for our purpose.

3.2.2 Why alkoxy side-chains?

We have shown in the introduction that the thermotropic properties of a material is highly influenced by the nature of the link between the aromatic core and the flexible chains. For HATNA-SR 50 the sulfanyl (S-R) group was chosen for two reasons: the presence of a sulfur directly linked to the aromatic systems, decreases the material's reorganisation energy, increasing its potential charge carrier mobility. The second aspect was the possibility of obtaining the material in only two efficient synthetic steps. Unfortunately, in addition to a complicated thermotropic behaviour, all the resulting linear-chains substituted materials are in a crystal phase at RT, and do not melt into an isotropic phase below their decomposition temperature.

In the case of n-type semiconductors, an electron withdrawing group would be preferable. Indeed, materials electron affinity increases when the electron density in the aromatic core is lower. By grafting highly electronegative functional groups such as ester or amide, around the aromatic moieties, the charge density is expected to be high on the substituents, and low on the aromatic core. In theory, these chemical functions seems to be more favourable in terms of electron injection. Nevertheless, even if a strong n-type character is one of the requirements of this part of the work, we also want the n-type material to show a specific thermotropic behaviour.



Colho 47 Colho

3b with R = C₁₂H₂₅ K 80 I

Figure 3.5: Chemical structure and thermotropic behaviour of the hexa-(N-(n-dodecyl))carboxamido-HAT **55a**,[61] and of the hexa-n-dodecylthio-HAT **13b**.[155]

The comparison of the thermotropic behaviour of amide- and sulfanyl-substituted HAT

derivatives (Figure 3.5), clearly demonstrate that the presence of H-bonding between the amide functions act as "clams" between adjacent molecules in the column.[61] If the stacking order is improved, the clearing temperature is increased to above the decomposition temperature (approximately 250 °C).

In the case of esther groups, no H-bonding is possible. Nonetheless, regarding to the impact of these highly polarisable functions on the thermotropic properties of octa-substituted phthalocyanines 14 (see Table 1.2, page 29), we can confidently expect that hexa-estersubstituted HATNA will not melt into an isotropic phase before decomposing.

In order to reach our thermotropic properties requirements, we have chosen to attach six alkoxy chains around the HATNA system. Theoretical investigations, performed in Mons (B) by Vincent Lemaur, have shown that replacing the sulfanyl groups by alkoxy does not change much the properties of single (isolated) molecules.[156] We can then expect to keep the high light absorption ability of HATNA-SR, and in the same energy range. When molecules are in interaction, the theory foresees a decrease in charge mobility by going from HATNA-SR to HATNA-OR.[154] This result is in good agreement with experimental investigations on triphenylene derivatives **7** and **11**.[75]

Interestingly, the thermotropic behaviour of HATNA-OR derivatives is expected to be less complicated than the one of HATNA-SR. Indeed, the energy gain achieved by putting in their lowest energy interacting conformation two isolated HATNA-OR derivatives (with $R = C_2H_5$ for the calculations), is of 89.5 kJ.mol⁻¹. In the case of HATNA-SR, the gain is only of 52.4 kJ.mol⁻¹. A change of conformation in HATNA-SR is then expected to be less energy demanding than in HATNA-OR.[156]

In a chemical point of view, a two steps synthesis to HATNA-OR can be envisaged. Indeed, the replacement of the thiolates used in Figure 3.4 by alcoholates, leads to the synthesis of 16.

All these facts make us confident to the chance of HATNA-OR derivatives to behave according to the requirements fixed in this work.

3.3 Synthesis

3.3.1 First synthetic routes

The synthetic route leading to 2,3,8,9,14,15-hexaalkoxy-5,6,11,12,17,18-hexaazatrinaphthylene derivatives **16** has been first copied from the simple two steps synthetic scheme used to obtain their sulfanyl analogs (Figure 3.6).[153]



Figure 3.6: Two steps synthetic route to six-fold alkoxy-substituted hexaazatrinaphthylene HATNA-OR 16.

The first step consists in the three-fold condensation of 1,2-dichloro-4,5-phenylenediamine **51** (5 equivalents eq.) with hexaketocyclohexane **52** in reflux acetic acid. the reaction is remained 2 hours under magnetic stirring. The product is then precipitate by addition of water, and washed overnight, using a Soxhlet of methanol. The pure hexachlorohexaazatrinaphthylene HATNA-Cl **53** is obtained quantitatively (yield: 97 %) as a green solid.

The nucleophilic displacement of chlorine atoms on an activated aromatic system is a common reaction. Moreover, HATNA-Cl has already shown its reactivity against thiolates. In the case of alkoxy substitution, a strong base is required to deprotonate the alcohol **33**.

The alcoholate is formed in a flask by reaction with sodium hydride NaH (and subsequent formation of hydrogen H₂) in dry N,N-dimethylformamide DMF, under nitrogen Hexaazatrinaphthylene derivatives as n-type semiconductors

| Product | reagents | solvent | $T ^{\circ}\mathrm{C}$ | time | comment |
|---------------------------|-------------------------|---------|------------------------|--------|---------|
| | (eq.) | | | | |
| HATNA-OC $_8$ 16b | octanol (12) & NaH (15) | DMF | 25 | 2 h | |
| | + 53 | DMF | 80 | 4 days | no re- |
| | | | | | action |
| HATNA-OC $_8$ 16b | octanol (12) & NaH (15) | DMF | 25 | 2 h | |
| | + 53 | DMF | 110 | 5 days | dec. |
| HATNA-OC ₈ 16b | octanol (30) & NaH (41) | DMF | 25 | 2 h | |
| | + 53 | DMF | 140 | 6 days | dec. |

Table 3.1: Reaction conditions and results of the first route used to synthesise HATNA-OR derivatives. "dec." states for "decomposition".

atmosphere. The reaction medium is then filtrated to remove the excess of base, and transferred to a second flask where **53** is in suspension in DMF. All the transfer process is done under inert atmosphere. After four to six days of reaction at 80 to 140 °C, the resulting products are precipitated by addition of water and recovered by filtration. The different reaction conditions and their results are summarises in Table 3.1. MS analysis reveals that, when the reaction is performed at low temperature, the reagent **53** is recovered unchanged. No reaction is then observed. When higher temperatures are used, neither the reagent **53** nor any substituted products are observed. Only fragments with masses lower than the hexaazatrinaphthylene aromatic system are detected, showing that the reagent has decomposed in the reaction medium.

This unexpected lack of reactivity and reagent unstability in hot basic medium, obliged us to find other conditions for the nucleophilic substitution.

The use of transition metals as catalyst in organic synthesis is in a constant evolution. Up to recently, high efficiency substitution of chloroarenes by metal catalysis was rare.[157] Actual developments in the use of palladium-based catalysts in the substitution of aryl chlorides by amines or alcohols have led to reactions such as Figure 3.7, where DPPF stands for 1,1'-bis(diphenylphosphino)ferrocene **58** (Figure 3.8).[158]

The proposed mechanism of this reaction is complicated and still uncertain. [160] The authors propose that the reactive form of the catalyst is produced *in situ* by exchanging the acetate ligands by DPPF. Sodium alcoholates are needed for this reaction.

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Figure 3.7: Nucleophilic substitution of a chloride by a sodium tetrio-butylate (t-Bu-ONa) by use of transition metal catalysis. Reaction yield: 89 %.[159]



Figure 3.8: Chemical structure of 1,1'-bis(diphenylphosphino)ferrocene DPPF 58.

The similitude of the HATNA system with 56, both being electron-poor, made us optimistic about the chances of the substitution to proceed efficiently. The reaction has been performed in two steps, as for the previous method. The alcoholate is first synthesised in a flask, in dry toluene solution and under nitrogen atmosphere, using NaH (12 eq.) as base. In order to decrease the reaction basicity and, by the way, to reduce reagent decomposition, an excess of alcohol (18 eq.) has been used. This reaction has been performed at reflux of toluene (111 °C) in order to make sure all the NaH has reacted. The other reagents (HATNA-Cl, DPPF (20 mol%), and palladium II acetate $Pd(OAc)_2$ (10 mol%)) are then added to the reaction medium. After 4 hours at reflux, a thin layer chromatography TLC and a MS analysis were done, showing that that HATNA-Cl was decomposed. The different product of decomposition have not been isolated and identified.

After two other failed attempts, at lower temperature and with a larger quantity of alcohol and of catalyst, only degradation products were obtained. The strong basic conditions needed for the reaction to proceed are certainly the origin of the problem.

An other synthetic route, avoiding the use of base on the HATNA aromatic system had to be found.



3.3.2 Second synthetic route

Figure 3.9: Four steps synthetic route to six-fold alkoxy-substituted hexaazatrinaphthylene HATNA-OR 16. R = n-alkyl.

Nucleophilic substitution of the chloride of HATNA-Cl 53 by alcoholates has not been successful. A radical change in the synthetic strategy has been decided. Instead of grafting the chains on the HATNA system, the new synthetic route consists in grafting the chains on the precursors and forming the aromatic HATNA core in a final reaction (Figure 3.9).

This new route has advantages and inconveniences. By grafting the chains in the first reaction, synthesis of new potentially mesogenic materials involves three synthetic steps for each chain, when only one was required in the previous scheme, from the common reagent **53** that was produced in large quantity (up to 10 g per reaction). In the other hand, the introduction of the chains before ring formation makes high purity materials easier to achieve. Indeed, the last reaction of the two-steps route consisting in a six-fold substitution, an incomplete reaction would lead to chemically similar compounds. The separation of penta- and hexa-substituted HATNA-SR **50** has been found difficult either by column chromatography or recrystallisation. In the new route, the structural differences between the desired product **16** and the by-products increase the ease of materials purification.
Synthesis of the 1,2-bis-alkoxy-benzenes



Figure 3.10: Synthesis of the 1,2-bis-alkoxy-benzene precursors 60. R = n-alkyl.

The first step consists in a double nucleophilic substitution. The etherification by action of an alcohol (or a phenol) on an alkyl halide is know as the Williamson reaction. For the conversion of catechol **59** into 1,2-bis-alkoxy-benzene **60**, we have chosen solvent-free conditions.[161] The reaction medium consists in two liquid phases: the melted catechol **59** and the alkyl bromide **63** in excess. The reaction has been carried out in presence of potassium hydroxide KOH, base capable of deprotonating the phenol function, and of a catalytic amount of aliquat 336 (methyltrioctylammonium chloride) as phase transfer agent. Indeed, the formation of a quaternary ammonium catecholate, allows this last to be transferred in the alkyl bromide phase where nucleophilic substitution takes place. After four hours at 120 °C and a purification by column chromatography or recrystallisation, depending of the RT state of the product **60**, yields of 48 to 56 % have been obtained for the different chains (Table 3.2). No evidence of chain length dependence on the reaction yields has been observed.

This reaction can easily be scaled up. Indeed, in this work, up to 5 g of final product has been synthesised at once.

| compound (R) | yield (%) | | | | |
|--|-----------|--|--|--|--|
| 60a (n-hexyl, C_6H_{13}) | 53 | | | | |
| $60b$ (n-octyl, C_8H_{17}) | 52 | | | | |
| $60c$ (n-decyl, $C_{10}H_{21}$) | 55 | | | | |
| $60d$ (n-dodecyl, $C_{12}H_{25}$) | 48 | | | | |
| 60e (n-tetradecyl, C ₁₄ H ₂₉) | 56 | | | | |
| 60f (n-hexadecyl, C ₁₆ H ₃₃) | 53 | | | | |

Table 3.2: Average yields obtained for the synthesis of the 1,2-bis-alkoxy-benzene precursors 60.



Synthesis of the 1,2-bis-alkoxy-4,5-dinitro-benzenes

Figure 3.11: Synthesis of the 1,2-bis-alkoxy-4,5-dinitro-benzene precursors 61 from 1,2-bis-alkoxy-benzenes 60. R = n-alkyl.

The second step consists in the dinitration of the 1,2-bis-alkoxy-benzene precursors **60**.[162] The nitration of an aromatic compound is an electrophile substitution. It is activated by the presence of a mesomere donor substituent in the aromatic system. The reaction is then directed to the *ortho* and *para* positions relative to the substituent. Due to steric effect, no substitution is observed in *ortho* of an alkoxy group. As this reaction operates on an activated position, pure nitric acid is strong enough to do the first substitution. Indeed, the active specie for electrophile aromatic nitration is the nitronium ion NO_2^+ , which is naturally present in concentrated nitric acid (Equation 3.1).[118]

$$2 HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \tag{3.1}$$

After the first substitution, the deactivation due to the presence the electron withdrawing nitro group in ortho of the substitution site prevents the second reaction. In order to increase the medium reactivity, sulfuric acid is added to the solution when the first substitution is achieved. The presence of sulfuric acid increases the concentration in NO_2^+ , according to Equation 3.2.

$$HNO_3 + 2 H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2 HSO_4^-$$
 (3.2)

When an aromatic ether is dissolved in a strong acid (pH < 1), it can be cleaved, reforming the phenol function.[163] To avoid this cleavage, the reaction is carried out using biphasic conditions (dichloromethane - acid aqueous). The concentration in acid is then reduced in the organic phase, wherein the organic compounds are dissolved.

After two hours of reaction at RT, the organic products are precipitate in water and purified by recrystallisation. Under these conditions, high yields (67 to 96 %) have been obtained for all the compounds (Table 3.3). No chain-length dependence on the reaction yields has been observed. The lower yields are attributed to the higher solubility of short-chains substituted compounds in the solvent of recrystallisation. When the use of dilute nitric acid (70 %) leads exclusively to the mono-nitrated product, this last is not observed by use of concentrated acids.

| compound (R) | yield (%) | | | | |
|--|-----------|--|--|--|--|
| 61a (n-hexyl, C_6H_{13}) | 67 | | | | |
| 61b (n-octyl, C_8H_{17}) | 80 | | | | |
| $61c$ (n-decyl, $C_{10}H_{21}$) | 92 | | | | |
| 61d (n-dodecyl, $C_{12}H_{25}$) | 94 | | | | |
| 61e (n-tetradecyl, $C_{14}H_{29}$) | 93 | | | | |
| 61f (n-hexadecyl, $C_{16}H_{33}$) | 96 | | | | |

Table 3.3: Average yields obtained for the synthesis of the 1,2-bis-alkoxy-4,5-dinitrobenzene precursors **61**.

Synthesis of the hexa-alkoxy-hexaazatrinaphthylenes



Figure 3.12: Two-steps synthesis of the hexa-alkoxy-hexaazatrinaphthylenes 16 from 1,2bis-alkoxy-4,5-dinitro-benzenes 61. R = n-alkyl.

The two last steps consist, firstly, in the reduction of the two nitro groups of **61** into amines, and secondly, in the HATNA-ring formation by three-fold condensation of the 4,5-dialkoxy-benzene-1,2-diamine precursors **62** with hexaketocyclohexane **52**. These two reactions have been managed straightaway after the other, without purification of

the diamino-compound **62**. Indeed, the presence of four electron donating groups on the phenyl ring of **62** makes it highly sensitive to oxidation. After about ten minutes under air, its colour turns from white to black, making decomposition process visible.

Catalytic hydrogenation of aromatic nitro compounds into amines by use of palladium on activated charcoal Pd/C 10 %, has been wildly used in organic synthesis.[118] This reaction is known for its high efficiency and selectivity. Acids, amides, esters, nitriles and ethers are not affected by this reagent. The ease of product purification due to the heterogenous character of the catalyst, makes this reaction ideal for the synthesis of air sensitive products.

The reaction has been done under anhydrous conditions. The entire setup has been dried at 130 °C during at least twenty-four hours before use. Methanol has been chosen as solvent for two reasons: it can easily be dried by distillation over magnesium methanolate (storage over molecular sieves 3 Å) and its low boiling point makes it easy to remove under vacuum. In this case, hydrogen (H_2) has been used as source of hydrogen atoms. The hydrogen atmosphere has been installed by putting the setup under vacuum and refilling it with hydrogen (1 atm) three times, in order to minimise the presence of residual oxygen. The evolution of the reduction reaction has been followed by eyes, since the light yellow colour of 61 is rapidly replaced by the dark yellow colour of the nitro-amino intermediate. The reaction is complete when the reaction medium is completely decolourised, 62 being colourless. The reaction time varies with the quantity of catalyst and with the length of the side-chains. Indeed, the lower solubility of long-chains substituted 61 in hot methanol decreases the reaction kinetic. After removing of the catalyst by filtration over celite, the solvent is removed by vacuum evaporation. The second part of the reaction is started directly, without further purification. In the literature, similar reactions have led to a maximum of 93 % of conversion.[164]

Due to the instability of **62**, the last reaction is started directly after the reduction. It consists in the three-fold condensation of 4,5-dialkoxy-benzene-1,2-diamines **62** with hexaketocyclohexane **52**. In order to minimise reagent decomposition, this reaction is performed under inert atmosphere (argon). The optimised reaction conditions use a mixture of dry ethanol and acetic acid (5:5) as solvent. After twenty hours of reaction, the products **16** are purified by column chromatography directly followed by precipitation in ethanol and filtration over fritted glass. Purity of > 99 % has been achieved, as proven by

¹H-NMR (Figure 3.35) and MS analysis. Conversions of 35 to 63 % have been obtained for the different compounds (Table 3.4). No chain-length dependence on the yield has been observed. It has to be noticed that no aggregation has been observed by ¹H-NMR in chloroform for concentrations between 1 and 20 g.L⁻¹.

| compound | yield (%) | | | | |
|----------------------------|-----------|--|--|--|--|
| 16a HATNA-OC $_6$ | 64 | | | | |
| 16b HATNA-OC $_8$ | 40 | | | | |
| 16c HATNA-OC $_{10}$ | 63 | | | | |
| 16d HATNA-OC ₁₂ | 50 | | | | |
| 16e HATNA-OC ₁₄ | 61 | | | | |
| 16f HATNA-OC ₁₆ | 35 | | | | |

Table 3.4: Average yields obtained for the synthesis of the 2,3,8,9,14,15-hexaalkoxy-5,6,11,12,17,18-hexaazatrinaphthylene derivatives **16**. Global yields for the two last steps.



Figure 3.13: ¹H-NMR spectrum of HATNA-OC₆ **16a** in chloroform solution, with proposed signals attribution. Spectrum recorded at 25 °C, at 300 MHz.

3.3.3 Conclusion

In the view of possible future large scale synthesis, the materials has to be accessible in a minimum number of efficient steps. As purity is a critical issue in molecular electronics, the products must be easy to purify (> 99 %).

The HATNA aromatic system has been found unstable under strong basic conditions. This lack of stability made us unable to directly graft the alkoxy side-chains around it.

By grafting the alkoxy side-chains at the beginning, and forming the aromatic HATNA system in the final reaction, global yields of 17 to 32 % have been achieved for the different HATNA-OR materials 16, allowing large scale production (up to 1 g of final material produced in one batch) for physical properties characterisation. This result has to be compared to the two step synthetic scheme leading to the HATNA-SR derivatives 50 (Figure 3.4), which gives the final product with a global yields of 63 % in the best case.[153] Nevertheless, the two steps synthetic route used for the HATNA-SR 50 requires careful purification by column chromatography to make sure all the products of uncomplete reaction (penta- or tetra-substituted products) have been removed. The last reaction of the four steps scheme leading to HATNA-OR 16 allows significantly easier purification procedure.

Finally, all the HATNA-OR derivatives are highly soluble in common organic solvents (chloroform, toluene, ...). Contrary to the HATNA-SR,[165] no concentration dependence of the chemical shift of the aromatic proton has been observed for the HATNA-OR derivatives by ¹H NMR. This fact suggests that there is no aggregation in chloroform solution, even with concentrations of 20 g.L⁻¹.

3.4 Thermotropic properties

As for the phthalocyanine derivatives, in the previous chapter, the thermotropic behaviour of the HATNA-OR 16 has been studied by combining three complementary techniques: Cross polarising microscopy (CPM); Differential scanning calorimetry (DSC); and X-ray diffraction.

The thermotropic requirement defined for the work are: 1) presence of a columnar mesophase; 2) clearing point below 200 °C; and 3) non-crystalline phase at RT.

The results of are given in the following sections.

3.4.1 Cross polarising microscopy



Figure 3.14: Textures observed under CPM for HATNA-OC₆ **16a** upon cooling at $10 \,^{\circ}\text{C.min}^{-1}$ from the isotropic melt. (a) at 200 $^{\circ}\text{C}$, growth of the pseudo focal conic fan-shaped liquid crystal texture. (b) at 84 $^{\circ}\text{C}$, crystal phase.

When a film of HATNA-OC₆ 16a, placed between two glass slides and is heated, isotropisation arises around 227 °C. The cooling of the phase gives rise to the appearance of a fluid and birefringent mesophase at 226 °C (Figure 3.14a). This pseudo focal conic fan-shaped texture usually corresponds to a Col_h LC phase.[67] If the material is further cooled down, a change in texture appears at 187 °C. The material becomes solid and breakable (Figure 3.14b), which is characteristic for a crystal phase. A second change in texture is observed at 94 °C. The same behaviour is observed during the second heating scan.

HATNA-OC₈ 16b and HATNA-OC₁₀ 16c show the same thermotropic behaviour under CPM, expect for the transition temperatures. When they are cooled from their isotropic phase, a fluid and birefringent mesophase appears at 229 and 224 °C for 16b and 16c, respectively. The texture formed is not specific to a particular mesophase. At 195 °C for 16b (153 °C for 16c), the large domains are parcelled out giving small birefringent domains. The colour of the birefringent mesophase changes from yellow - green to red - brown at 65 and 42 °C for 16b and 16c, respectively. Even if the texture is kept, the matter becomes breakable and rigid. The phase is characterised as crystalline.

Upon heating, the green colour is recovered at 72 °C for 16b and 54 °C for 16c, but the material is still solid. At 118 and 159 °C for 16b and 16c, respectively, an increase in brightness and in domain size mark the transition to a liquid crystal phase. A rapid increase in domain size is observed at 199 °C for 16b, thirty degrees below its isotropisation, which occurs at 228 - 232 °C. The clearing point of 16c is observed at 227 - 229 °C.

When HATNA-OC₁₂ **16d** and HATNA-OC₁₄ **16e** are cooled from their isotropic phase, birefringence appears at 203 and 199 °C for **16d** and **16e**, respectively. A texture, typical for an hexagonal columnar mesophase is observed for both materials (Figure 3.15a).[67] At 93 °C for **16d** (88 – 83 °C for **16e**), the different domains are broken, forming a nonspecific texture. The pseudo focal conic fan-shaped texture, typical for hexagonal lattice is recovered at 50 and 55 °C for **16d** and **16e**, respectively. Surprisingly, a phase transition giving rise to a slow disappearance of the birefringence is observed from 43 °C for **16d** (49 °C for **16e**). At 38 °C (45 °C for **16e**), the material is fully non-birefringent and behave under shearing as a non-breakable and non-deformable solid. Only three molecular organisations can give rise to non-birefringent phases: the cubic phase, a perfect homeotropic arrangement, and a non-ordered (amorphous) phase.

The first possibility can be rejected since the rare discotic cubic phases, resulting from a separation of the aromatic moieties in the columns, are usually observed at temperatures close to the clearing point, when thermic energy permits to the disks to separate from one another.[57] At low temperature, the disks separation would break the highly stabilising $\pi - \pi$ interactions between neighbouring molecules, and would be too expensive in energy to occur in the case of discotic materials.

In order to test the second possible explanation, an additional experiment has been done. As homeotropic alignment is a highly ordered molecular organisation, it can only be obtained by slow cooling. When **16d** is cooled down rapidly (about $20 \,^{\circ}\text{C.min}^{-1}$), the birefringence disappears, giving rise to a fully "black phase" upon CPM. When the mesophase



(a) 185 °C

(b) 90°C



(c) 49°C

(d) 42°C



Figure 3.15: Textures observed under CPM for HATNA-OC₁₂ **16d**. Upon cooling: a) pseudo focal conic texture at 185°C, b) non-specific texture at 90°C, c) pseudo focal conic texture at 49°C, d) disappearance of the birefringence at 42°C, e) non-birefringent "black" phase at 38°C (overexposed). Upon heating f) LC phase at 196°C.

is slowly cooled down (about $2 \,^{\circ}$ C.min⁻¹), some birefringence is conserved (Figure 3.16. As a better alignment can not result from faster cooling, this explanation has to be re-



Figure 3.16: Persistence of a birefringence under CPM for HATNA-OC₁₂ 16d. Picture taken at RT, after slow cooling (about 2 °C.min⁻¹).

jected as well. The results of this last experiment vouches for a molecular disorganisation upon cooling. Indeed, if we consider that, at 43 °C, the columnar organisation of HATNA- OC_{12} becomes unstable and tries to crystallise into a completely different structure, the molecules have to move from their columnar assembly to their new equilibrium position. If their energy or freedom of motion is not sufficient, they can be frozen in an intermediate, disorganised (isotropic) fashion upon fast cooling. Upon slow cooling, the molecules have more longer more freedom to move. They can then more easily reach their new equilibrium position, giving rise to a birefringent (partially) crystalline state. It has to be noticed that no birefringent phase has been observed for HATNA- OC_{14} 16e at RT, even after slow cooling from the LC phase.

When temperature is increased, birefringence comes back at 59 °C for 16d and 60 °C for 16e, forming an uniformly bright area. A texture, typical for an hexagonal mesophase is gradually formed. Isotropisation occurs at 201-209 and 199 °C for HATNA-OC₁₂ and HATNA-OC₁₄, respectively.

Finally, HATNA-OC₁₆ **16f** becomes birefringent upon cooling at 177 °C. The texture of the mesophase is characteristic for columnar hexagonal LC phase. No further transition is observed until 51 - 48 °C where birefringence disappears, giving rise to the same "black phase" as of **16d** and **16e**.

Upon heating, the birefringence reappears at $62 - 63 \,^{\circ}\text{C}$. The specific Col_h texture is gradually recovered until $168 - 182 \,^{\circ}\text{C}$, where gradual clearing is observed.

3.4.2 Differential scanning calorimetry

The thermotropic behaviour of a material can not be unambiguously characterised only by CPM. In order to detect possible additional phases, that have not been observed by the first technique, at least two DSC experiments have been performed, on at least two different batches of the six HATNA-OR derivatives **16a-f**. The results are summarised hereafter¹.



Figure 3.17: DSC curve of HATNA-OC₆ 16a. Heating and cooling rate: 10° C.min⁻¹. The dotted arrows correspond to the transitions observed by CPM.

Three peaks are observed in the DSC curve of HATNA-OC₆ **16a**, upon heating and upon cooling (Figure 3.17). With a transition enthalpy of 23.5 kJ.mol⁻¹, the first transition (maximum at 97 °C) is attributed to a crystal to crystal (K \longrightarrow K) phase transition. The second transition (3.3 kJ.mol⁻¹), at 187 °C, is attributed to the melting of the crystal phase to a liquid crystal mesophase (K \longrightarrow LC). Finally, the higher temperature transition (peak at 230 °C) is a clearing point (LC \longrightarrow I), with a transition enthalpy of 1.3 kJ.mol⁻¹. The same transitions are observed, upon heating and cooling, with a slight overcooling of about 4 °C.

¹In the text, peak values are given.



Figure 3.18: DSC curve of HATNA-OC₈ 16b. Heating and cooling rate: 10 °C.min⁻¹. The dotted arrows correspond to the transitions observed by CPM.

The DSC curves of HATNA-OC₈ 16b are more complicated (Figure 3.18). Upon heating, five transitions can be observed. The product first melts (at 35 °C, ΔH 22.3 kJ.mol⁻¹) before crystallising (at 59 °C, ΔH -21.9 kJ.mol⁻¹). At 116 °C, a melting of 72.7 kJ.mol⁻¹ indicates the transition from the crystalline solid state to the liquid crystal phase. At higher temperature, two small transitions are observed, at 196 and 217 °C. Even if they are close to the detection limits of the apparatus (ΔH of 0.11 and 1.2 kJ.mol⁻¹, respectively), they are present in all the DSC traces. Such small enthalpy values usually correspond to a mesomorphism (LC \rightarrow LC) or a clearing (LC \rightarrow I).

The cooling trace is slightly different. The two small transitions at high temperature are still observed, with no significant overcooling. At lower temperature, crystallisation occurs at 67 °C (ΔH -39.2 kJ.mol⁻¹). A transition between two crystal phases is also observed at 24 °C (ΔH -21.8 kJ.mol⁻¹).

When we compare the DSC and CPM experiments, the lowest temperature transition can not be observed by CPM, since no cooling system is attached to the heating plate. The crystallisation upon heating does not give rise to a change in optical texture, or is

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not present when the material is not cooled down below the low temperature $K \longrightarrow K$ transition. If the very low enthalpy transitions are observed under CPM, the highest temperature transition does not appear at the clearing temperature determined under microscope. This difference in temperature is observed in all the DSC curves of **16b**. A possible explanation could be that even if the clearing occurs at 217 °C, birefringence is conserved until the end of the transition, which could be 10 °C higher.



Figure 3.19: DSC curve of HATNA-OC₁₀ **16c**. Heating and cooling rate: $10 \,^{\circ}\text{C.min}^{-1}$. The dotted arrows correspond to the transitions observed by CPM.

The thermotropic behaviour of HATNA-OC₁₀, studied by DSC, can be seen as the link between short and long side-chains substituted materials. Indeed, when the short chains substituted compounds show relatively narrow transitions due to the long range organisation created by the capacity of the chains to order themselves in highly ordered fashion, longer chains are more difficult to stretch and can not form highly ordered crystal phases. This conformation disorder prevents formation of an unique molecular packing structure, giving rise to a set of slightly different domains in the sample that melt at different temperatures. The transitions observed by DSC are then broader and, by the way, less intense. Upon heating, three transitions are observed for HATNA-OC₁₀ (Figure 3.19). The first broad peak (at 38 °C, ΔH 8.3 kJ.mol⁻¹) is directly followed by a smaller transition (at 68 °C, ΔH 0.54 kJ.mol⁻¹). No further phase identification is possible only with DSC. At higher temperature, a low intensity broad transition is observed at 207 °C (ΔH 0.46 kJ.mol⁻¹). It certainly corresponds to the clearing transition.

Upon cooling, the corresponding isotropic to liquid crystal transition appears with an overcooling of 5 °C, at 202 °C (ΔH -0.62 kJ.mol⁻¹). At lower temperature, two superimposed transitions are observed, with maxima at 44 °C (ΔH -1.7 kJ.mol⁻¹) and around 40 °C (ΔH -6.9 kJ.mol⁻¹), respectively, showing the complexity of this thermotropic behaviour.

By comparing the DSC data with the CPM observations, we can conclude that the lower temperature transitions correspond to the crystal to liquid crystal transitions. The medium temperature transitions observed only by CPM certainly results from very low energy transitions between two mesophases, close in molecular organisation. They have not been detected by DSC. As observed for HATNA-OC₁₀, the transition corresponding to the clearing of the LC phase appears at lower temperature in the DSC curves than under CPM. The same explanation can be invoked.



Figure 3.20: DSC curve of HATNA-OC₁₂ 16d. Heating and cooling rate: 10 °C.min⁻¹. The dotted arrows correspond to the transitions observed by CPM.

A lot of small broad transitions are observed in the heating DSC curve of HATNA-OC12

16d (Figure 3.20). At low temperature, four transitions can be identified, at 33, 54, 79, and 96 °C, respectively. They are associated to ΔH of 2.0, 4.2, 1.9, and 4.7 kJ.mol⁻¹, respectively. These values have to be taken as an image of the complexity of the thermotropic behaviour of this compound, since some of the transitions are not single. At higher temperature, a fifth transition occurs at 198 °C (ΔH 1.7 kJ.mol⁻¹). It is attributed to the clearing of the LC phase.

As observed for the previous material **16c**, less phase transitions are visible in the cooling DSC trace. In addition to the isotropic to liquid crystal transition, which occurs at 198 °C (ΔH -0.75 kJ.mol⁻¹), only one broad peak is observed, with a maximum at 38 °C (ΔH -3.4 kJ.mol⁻¹). Such a broad peak can be obtained if the phase transition kinetic is slow. Indeed, due to the principle of the DSC measurement, a slow kinetic transition does not appear as a narrow peak at 10 °C.min⁻¹. The transition takes place during a certain time, corresponding to a certain temperature range.

The comparison between the DSC data and the CPM observations shows that the optical transition observed at 93 °C upon cooling is not visible by DSC. The enthalpy change associated to this transition is very low, as it is usually the case for a mesomorphism. At the onset of the low temperature transition upon cooling, a texture, characteristic of Col_h LC phase is observed. The transition to the black phase nicely coincides with the one observed by DSC. Upon heating, not all the transitions give rise to a visible change in optical texture. The appearance of the LC phase can not be assigned to one particular variation in enthalpy. Finally, the difference in clearing temperature between the DSC and CPM measurements, observed for the two previous materials, in less marked in this case. The LC \longrightarrow I transition under CPM occurs only 3 °C above the peak value of the corresponding DSC transition.

The heating DSC scan of HATNA-OC₁₄ **16e** consists in a superposition of melting and crystallisation processes (Figure 3.21). The peaks position has no physical meaning since they depend on the intensity and position of the different simultaneous processes. Only the sum of the different positive and negative contributions can give an indication of the material's enthalpy change before and after all the transitions. Here, an global enthalpy change of 19.6 kJ.mol⁻¹ has been measured. As expected, the global change consists in a melting. No further transition is observed, meaning that the clearing point is under the detection limits of the apparatus. Hexaazatrinaphthylene derivatives as n-type semiconductors



Figure 3.21: DSC curve of HATNA-OC₁₄ 16e. Heating and cooling rate: $10 \,^{\circ}C.min^{-1}$. The dotted arrows correspond to the transitions observed by CPM.

Upon cooling, no transition is observed. This result shows that many phase transitions, that lead to a change in texture or in birefringence brightness, result from small changes if the molecular organisation, or operate too slowly to make transition visible by DSC. Indeed, by definition, the global enthalpy change of a back and forth scan must be equal to 0 kJ.mol⁻¹. Therefore, we can conclude that signals for ΔH of about -19.6 kJ.mol⁻¹ are merged with the baseline.

Upon heating, the melting of the black phase to the LC phase coincides with the centre of the superimposed transitions zone. The clearing are not observed by DSC.

Finally, HATNA-OC₁₆ **16f** shows the same complex thermotropic behaviour as **16e**, by DSC (Figure 3.22). Upon heating, a large number of superimposed transitions is observed from 30 to 108 °C. A global enthalpy change of 9 kJ.mol⁻¹ can be estimated by summing all the transition enthalpy changes. This value has to be taken with care since the baseline is not completely flat. No transition is observed at higher temperature.

In the cooling trace, one broad peak is visible, at 51 °C (ΔH -0.99 kJ.mol⁻¹).

None of the clearing transition are visible in the DSC traces. Upon cooling, the small transition at 51 °C nicely coincides with the LC \rightarrow black phase transition observed by

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Figure 3.22: DSC curve of HATNA-OC₁₆ 16f. Heating and cooling rate: 10° C.min⁻¹. The dotted arrows correspond to the transitions observed by CPM.

CPM. As for **16e**, the corresponding black phase disappearance upon heating does not clearly correspond to one single peak.

3.4.3 X-ray diffraction

X-ray diffraction has been used to determine the nature of the phases of the different HATNA-OR derivatives 16. In order to see all the phases of each compound, temperaturedependent synchrotron X-ray diffraction measurements on non-oriented samples (powders diffraction) were performed and resolved by Raluca Gearba (Polymer Physics Laboratory, ULB), using the synchrotron facilities of Hamburg (D). This experiment consists in using the high intensity X-beam of the synchrotron to measure the diffraction at all angles simultaneously. One diffractogram is then recorded at each degree upon heating and cooling with a temperature rate of 10 °C.min⁻¹. All the phases can then be identified, together with an estimation of their phase transition temperature.

| Compound | program | phase | T ^a | phase ^b | т | phase | т | phase | т | phase |
|----------|----------------|--------------|----------------|------------------------|-----|---------------------------|-----|-------|-----|-------|
| 16a | h ^c | K | 95 | К | 168 | Col_x | - | - | 235 | I |
| | с | К | 90 | к | 180 | Col_x | - | - | 235 | I |
| 16b | h | K | 115 | - | - | Col_x | 185 | х | 230 | Ι |
| | с | к | 62 | - | - | Col_x | 186 | х | 230 | I |
| 16c | h | К | 60 | к | 89 | Col_x | 162 | х | 220 | Ι |
| | с | \mathbf{L} | 45 | - | - | Col_x | 148 | х | 235 | I |
| 16d | h | К | 58 | Col_{hd} | - | - | - | - | 210 | Ι |
| | с | \mathbf{L} | 45 | Col_x | 110 | Col_{hd} | - | - | 200 | Ι |
| 16e | h | \mathbf{L} | 60 | Col_{hd} | - | - | - | - | 198 | I |
| | с | \mathbf{L} | 65 | Colhd | - | - | - | - | 210 | I |
| 16f | h | \mathbf{L} | 58 | Col_{hd} | - | - | - | - | 188 | I |
| | с | \mathbf{L} | 55 | Colhd | - | - | 160 | х | 200 | Ι |

The results of this investigation are summarised in Table 3.5.

^a approximative transition temperature in °C.

^b K: crystal phase; L: lamellar phase; Col_x: columnar oblique Col_{ob} or disordered columnar rectangular Col_{rd} phase; Col_{bd} disordered columnar hexagonal phase; X: undetermined phase; I: isotropic phase.

^c h: heating scan; c: cooling scan. Heating and cooling rate: 10°C.min⁻¹.

Table 3.5: Summary of the thermotropic behaviour of the HATNA-OR derivatives 16a-f, studied by temperature-dependent X-ray diffraction on non-oriented samples.



Figure 3.23: Temperature dependent X-ray powder diffraction patterns of HATNA-OC₆ **16a** ((a) and (b)) and HATNA-OC₁₆ **16f** ((c) and (d)) at a heating rate of $10 \,^{\circ}\text{C.min}^{-1}$.

The small-angle X-ray scattering SAXS and wide-angle X-ray scattering WAXS of HATNA-OC₆ **16a** and HATNA-OC₁₆ **16f** at three different temperatures are given in Figure 3.23.

For HATNA-OC₆ 16a, three phases have been identified. The large number of diffrac-

tions at small-angles (Figure 3.23a) recorded at RT, is attributed to the long-distance order of a crystalline phase. At 95 °C, the diffraction pattern changes to a second crystal phase. The disappearance of many peaks at 168 °C reveals the transition to a columnar LC phase. The choice between Col_{rd} and Col_{ob} was not possible since only two peaks are remained in the SAXS region. This not fully identified mesophase will be noticed as Col_x in this discussion. In the LC phase, only one diffraction, corresponding the the amorphous halo is observed at wide-angles (Figure 3.23b). This phase can not be qualified as ordered. Upon cooling, the same phases are observed.

For HATNA-OC₈ 16b, the crystal phase present at RT melts into a Col_x phase at 115 °C. At 185 °C, only one peak is observed. This phase can then not be identified. This type of phase will be noticed as X in this discussion. The same behaviour is observed upon cooling.

The particularity of HATNA-OC₁₀ **16c** comes from the presence, at low temperature upon cooling, of a molecular disordering. Indeed, at 45 °C, the peaks become less intense and broader. Such a phenomenon is usually observed upon heating, at the clearing point, where the isotropisation comes with a decrease in correlation distance. In this case, three low intensity broad peaks are kept in the SAXS region (Figure 3.23c at 35 °C). Their reciprocal spacing ratio 1 : 2 : 3 could be consistent with a lamellar L mesophase. Such a phase can be seen as a superposition of layers (or lamellas) of columns or of disks with no positional order between the layers.

16d-f have in common to show, in addition to other phases (see Table 3.5), a Col_{hd} phase in their thermotropic behaviour, upon heating and cooling. The lattice parameter a has been estimated to 30.6, 33.5, and 35.8 Å (at 75, 70, and 65 °C, respectively) for 16d-f, respectively. An intra-columnar distance of 3.6 Å has been measured for 16d-e. No (0,0,1) diffraction was found for 16f. At low temperature, the three compounds show a disordered phase that could be identified as lamellar. The distance between two layers has been estimated to 32.2 and 35.2 Å for 16e-f, respectively.

As the transition temperatures mentioned in Table 3.5 have been estimated by looking at changes in the diffraction patterns, they are marred by a large error. Due to the small differences between the diffractograms at the clearing points, their values can only be seen as rough estimations.

3.4.4 Conclusions

In this section, the thermotropic properties of the six HATNA-OR derivatives **16a-f** studied in this work has been investigated by combining CPM, DSC, and X-ray diffraction.





Table 3.24 shows a comparison of the thermotropic behaviour of HATNA-SR derivatives 50a-d (where R = n-hexyl in 50a, n-octyl in 50b, n-decyl in 50c, and n-dodecyl in 50d) and of HATNA-OR derivatives 16a-f. Contrary to the HATNA-SR, where no clearing point is observed below the materials decomposition temperature (which occurs around 250 °C), all the HATNA-OR melt into isotropic liquid at reasonable temperatures. The decomposition temperature of HATNA-OR has never been clearly measured. It can be estimated to 250 °C by comparison with HATNA-SR.

All the materials of the two families show at least one columnar LC phase in their thermotropic behaviour. The HATNA-SR derivatives use to form more ordered mesophases than HATNA-OR, as evidenced by the higher number of diffractions observed in the SAXS region of the X-ray diffractogram. This higher order leads to crystallisation of the HATNA-SR derivatives at relatively high temperature. Finally, the high number of crystal phases observed for some HATNA-SR derivatives is an indication of the closeness in energy of the different molecular packing. Such a high tendency to polymorphism has not been observed for the HATNA-OR. This fact is in good agreement with the theoretical investigations performed in Mons by Vincent Lemaur.

Interestingly, the long-chains substituted compounds (16c-f by X-ray, 16d-f by CPM) have shown a phase disordering upon cooling. The nature of the non-birefringent or "black" phase has not been fully elucidated. By CPM, it could be assigned as an amorphous phase arising from a too rapid cooling through a LC \longrightarrow K transition. X-ray diffraction has identified this phase as a lamellar L mesophase. These two results are not in contradiction. The broadening of the peaks in the SAXS region of the X-ray patterns reveals a decrease in correlation length between the columns. In the WAXS region, no diffraction corresponding to $\pi - \pi$ stacking has been observed. These two facts demonstrate that the materials might be no longer ordered enough to induce birefringence. They might be isotropic regarding to polarised light.

In this work, three technics have been combined to determine the thermotropic behaviour of the six mesogens. None of these three methods can be taken reference to obtain an unambiguous characterisation. Indeed, we have shown that, even if HATNA-OC₆ 16a forms a texture specific for hexagonal mesophase upon cooling, this phase has been characterised as Col_x (Col_{ob} or Col_{rd}) by X-ray diffraction. The DSC curves of 16c-f are complicated and can not give a comprehensive phase identification. Finally, even if X-ray diffraction is a very powerful technique to investigate the molecular organisation, it might give rise to mis- or over-interpretations.

Despite this uncertainty about the nature of the phase present at RT, HATNA-OC₁₆ 16f shows the thermotropic behaviour searched in this work. Indeed, it has a clearing point at 177 °C (< 200 °C), a columnar hexagonal mesophase, and a non-crystalline phase at RT. For this reason, this material will be more extensively studied in the following physical properties characterisation.

3.5 Optoelectronic properties

The absorption and emission properties of mesogenic hexa-alkoxy-hexaazatrinaphthylene HATNA-OR derivatives **16** have been studied in dilute solution and in the solid-state.

3.5.1 In dilute solution



Figure 3.25: Absorption, emission (excitation at 338 nm), and excitation (emission at 460 nm) spectra of the HATNA derivative **16a** in dilute toluene solution.

Optoelectronic properties of the six HATNA-OR derivatives 16 have been studied in dilute solution. As anticipated, no chain-length dependence has been observed. Indeed, since the alkyl chains are not part of the chromophore, their length was expected to have no influence on the materials photo-physical properties in solution. Figure 3.25 summarises the absorption, emission and excitation characteristics of 16a in solution in toluene. In absorption, two regions can be distinguish. At low energies, two transitions are observed, at 427 and 402 nm, with a maximum absorption coefficient $\varepsilon(427)$ of 98000 \pm 2500 L.mol⁻¹.cm⁻¹. The absorption spectrum of HATNA-OR in solution has been theoretically simulated by Vincent Lemaur (University of Mons Hainaut). Due to the high number of atoms in the chromophore, many molecular orbitals, close in energy, can give rise to light absorption. The peak assignment is then difficult. Nevertheless, the main contribution to the lowest energy absorption band comes from a electronic transition from the HOMO to the LUMO, consisting a π - π^* transition.[156] The optical gap can then be estimated to 2.90 eV. The high intensity of the 0-0 transition suggests that the ground state molecular geometry is conserved in the first excited state, showing a high molecular rigidity. At lower energies the more complex structure can be attributed to an overlap of higher energy transitions. Two main peaks are observed at 338 and 303 nm.



Figure 3.26: Comparison of the absorption spectra of HATNA-OC6 16a and HATNA-SC6 50a, in solution in toluene and chloroform.

The attribution of the absorption bands to π - π^* transitions, is reinforced by the global red-shift (about 12 nm, 80 meV) of the absorption spectrum, by increasing solvent polarity from toluene to chloroform (Figure 3.26). An increase in solvent polarity would have the opposite effect on a n - π^* transition, where n stands for a nonbonding molecular orbital.[18] This bathochromic shift goes with a decrease in absorption intensity

(hypochromic effect), since the maximum ϵ (439) falls down to 69000 ± 2500 L.mol⁻¹.cm⁻¹ in chloroform. The same solvent effect has been observed for the HATNA-SR derivatives.

As expected from theoretical calculations, the same absorption pattern is obtained for the two series of materials. Due to the presence of nonbonded electrons on the oxygen and sulfur atoms, the ether and sulfanyl functions can be qualified as "auxochromes". Such a group is known displace (through resonance) and usually intensifies the absorption of a chromophore.[118] The bathochromic shift observed going from HATNA-OR to HATNA-SR is consistent with the literature.[166]

In solution, the HATNA-OR derivatives 16 fluoresce in the yellow under UV light. The fluorescence spectrum is given in Figure 3.25. No excitation wavelength dependence has been observed, the same luminescence being observed with different excitation energies. Two peaks are visible, at 434 and 457 nm (in toluene). They might be attributed to transition from the ground vibrational state of the lowest π^* molecular orbital, to the ground (0-0 transition) and higher vibrational (0-X transition) states of the highest π level, respectively. The small Stokes shift (only 7 nm) reveals a highly rigid chromophore. In chloroform, the entire fluorescence spectrum is red-shifted of 15 nm versus toluene solution. Even if no fluorescence quantum efficiency measurement has been performed on 16 and 50 in solution, the fluorescence intensity is clearly higher for HATNA-OR than for HATNA-SR.

The excitation spectra of the two emissions are identical and have the same spectral appearance than the absorption spectrum. The absorbing and emitting species are then identical.

3.5.2 In the solid state

In order to study the changes in molecular orbitals due to interactions between molecules in the solid-state, a study of the absorption and emission properties of **16f** in thin films has been performed. A comparison of the spectra obtained in toluene solution and in thin spin-coated film is given in Figure 3.27.



Figure 3.27: Comparison between the absorption and emission spectra of the HATNA derivative **16f** in dilute toluene solution and in the solid-state (film obtained by spin-coating from chloroform solution).

In the solid-state, the presence of intermolecular interactions leads to a splitting of the different energy states. The resulting absorption spectrum is constituted of broader bands and are, by the way, less resolved (Figure 3.27). A slight blue-shift is observed for the lowest energy transition ($\lambda_{HOMO-LUMO}$ (toluene solution) = 427 nm; λ_{max} (solid) = 415 nm). This hypsochromic shift is general for the all spectrum. Indeed, two high energy transitions shift from 338 and 303 nm in toluene solution to 301 and 226 nm in the solid-state. The blue-shift induced by material condensing is attributed, according to the exciton coupling theory mentioned in the previous chapter (page 96), to the presence of columnar aggregates in the solid-state. In the solid-state, an additional low intensity transition can be observed at longer wavelength (at 530 nm). It might attest to the presence of a transition from the π molecular orbital a nonbonding *n* molecular orbital.

HATNA-OR derivatives 16 are slightly fluorescent in the solid state under UV illumination. The same broad emission peak, centred at 565 nm is obtained by shining a film of 16f at different wavelengths. The solid-state fluorescence quantum efficiency has been roughly estimated, using an integrating sphere and a multi-line UV laser light of 10 mW,[167] to 2.5 % at RT. Note that the same experiment, performed on a film of HATNA-SC₁₆ 50e, has given a fluorescence quantum efficiency of about 2 %.

The shape and the low energy of the fluorescence spectrum might be explained in two ways. In the solid-state, the formation of closely packed aggregates induces a systematic red-shift of the fluorescence spectrum.[168] The presence of conformation disorder in then responsible for the loss of resolution and for the band broadening. Another explanation might be that the fluorescence does not result from a $\pi^* - \pi$ transition, but from a radiative $\pi^* - n$ transition. Such a behaviour has been reported previously for trans- β -hydrindanone in solution.[18] Hence, the observation of a low-intensity $n - \pi^*$ absorption in the solid-state is consistent with this hypothesis.

The excitation spectra, recorded at different emission wavelength (at 515, 567, and 626 nm), are all identical. They have the same spectral appearance than the solid-state absorption spectrum.

In order to probe a possible change in molecular interactions in the different phases, a study of the absorption characteristics in the solid-state, as a function of temperature, has been performed. The results are summarised in Figure 3.28. A clear change in the absorption spectrum is observed between 28 and 50 °C. At RT, only one peak is visible in the range 350 - 500 nm. When temperature is increased, two peaks appear, with maxima at 410 and 432 nm. In order to determine more precisely the transition temperature, the first derivative of the absorbance at 419 nm as a function of temperature has been plotted. The wavelength has been chosen for its high amplitude of change at the optical transition. The results are given in Figure 3.28b. The absorbance changes faster at 62 °C upon heating and does not change afterward. Upon cooling a similar spectral modification is observed at 56 °C. The optical transition is then fully reversible, as confirmed by the full spectra. These temperatures nicely coincide with the transition between the black



Figure 3.28: (a) Temperature dependence of the solid-state absorption spectrum of HATNA-OC₁₆ 16f (spin-coated from chloroform solution). The arrows show the evolution with increase in temperature. Heating and cooling rate : $10 \,^{\circ}\text{C.min}^{-1}$. ^a : spectrum obtained after cooling. (b) First derivative of the absorbance at 419 nm in function of the temperature (dA/dT). Second heating (below) and cooling (above) at $10 \,^{\circ}\text{C.min}^{-1}$.

phase and the columnar hexagonal mesophase, observed under CPM and by X-ray. The two spectra are then characteristic for each phase. This modification might be due to a change in relative intensity between the two peaks visible at high temperature. As phase transition goes with a change in molecular assembly, the different electronic states and the probability of transition between them can be modified.

Has we have seen, long chains substituted HATNA-OR derivatives 16d-f form a disordered non-birefringent phase at 50 - 60 °C upon cooling at 10 °C.min⁻¹. For 16d, it was observed that this black phase is only obtained upon fast cooling by CPM. The birefringence remains if the cooling is slow. When the chains are longer (for 16e-f), the black phase is obtained even with cooling rate of 0.5 °C.min⁻¹. Absorption spectroscopy has shown its usefulness in the characterisation of molecular organisation in the solid-state. An experiment has then been done in order to probe possible crystallisation after long thermal annealing.

A thin film of 16f, spin-coated from chloroform solution (50 g.L⁻¹, 1500 rpm during 30 sec.), has been heated to 75 °C at 10 °C.min⁻¹, where it has been left for 20 hours. After this annealing time, the film has been cooled down to RT, where an absorption spectrum

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Figure 3.29: Comparison between the absorption spectra of a spin-coated film of HATNA-OC₁₆ **16f**, recorded before annealing, at 75 °C (upon heating), and at RT after 1 night of thermal annealing at 75 °C.



Figure 3.30: CPM pictures of a spin-coated film of HATNA-OC₁₆ **16f**, taken at RT (a) just after film spin-coating, and (b) after one night of thermal annealing at $75 \,^{\circ}$ C.

has been recorded. Surprisingly, it is similar to the one recorded at temperatures higher than the optical transition. The splitting of the two peaks observed at high temperature attests of the presence of two distinct well defined molecular interactions.[73] It might be due to the formation of an ordered crystal crystal structure. This conclusion is reinforced by the presence of light scattering at long wavelength, which is commonly attributed to light refraction on micro-crystals. Moreover, after annealing, the film is birefringent under CPM, showing crystal-like texture (Figure 3.30). The relative intensity at long wavelength suggests that columnar organisation is kept in the crystal phase.

In order to estimate the absorption coefficient of HATNA-OC16 16f in the solid-state, thickness measurements have been perform, using contact mode AFM (Figure 3.31a,b). Topology images (in tapping mode) have also been taken on a crude film, spin-coated from chloroform solution (Figure 3.31c,d), showing a smooth surface consisting in small needles. A plot of the film absorbance A as a function of its thickness d is given in Figure 3.31e. It has been done by recording the absorption spectra of two film, spin-coated at 1500 rpm from 10 and 50 g.L⁻¹ chloroform solutions. Unfortunately, the disordered phase present at RT for this material makes us unable to estimate its density ρ . Nevertheless, if we consider that the density does not change much from RT to 65 °C, and that the average intracolumnar distance c at that temperature is of the same order for 16f than for 16d-e, it can be roughly estimated to 3.6 Å. With a lattice parameter a of 35.8 Å, a density of 0.76 can be calculated according to the equation $\rho = a^2 \cdot c \cdot \sqrt{3}/2$. This value seems to be reasonable since the LC phase density of HATNA-SR derivatives 50a-d decreases with increase in chain-length (1.03, 0.92, 0.91 in the Colhd phase of 50a, 50c, and 50d, respectively). In other words, with a molar density of 0.416 mol.dm⁻³, the solid-state absorption coefficient of 16f can be roughly estimated to 40000 and 77000 dm^3 .mol⁻¹.cm⁻¹ at 417 and 300 nm, respectively.



Figure 3.31: a) and b) Section analysis of a spin-coated thin film of HATNA-OC₁₆ **16f** by contact mode AFM (colour depth: 1 μ m). c) and d) Tapping mode AFM image HATNA-OC₁₆ **16f** (colour depth: 40 and 30 nm, respectively). e) Plot of the absorbance at 417 and 300 nm as a function of the film thickness.

3.5.3 Conclusions

In the photovoltaic applications point of view, both p- and n-type materials must strongly absorb light in the visible. A complementarity in light absorption range would be highly preferred.

The optoelectronic properties of the HATNA-OR derivatives 16 have been investigated in solution and in the solid-state. In both cases, the absorption coefficient has been estimated.

As expected, regarding to the optoelectronic properties of the HATNA-SR derivatives **50**, the six HATNA-OR derivatives **16a-f** have shown the same high intensity absorption spectrum in solution. With an absorption coefficient of $\varepsilon(427)$ of 98000 \pm 2500 L.mol⁻¹.cm⁻¹ in toluene solution, they can be qualified as yellow dyes. This value is not chain-length dependent. The materials weakly fluoresce in the yellow (maximum at 434 nm in toluene).

In thin film, the absorption pattern of **16f** is modified. The aggregation effect results in a broadening of the different absorption bands, together with slight blue-shift. According to the exciton coupling theory, such an energy shift in characteristic for (tilted) face-to-face aggregation. An additional low intensity absorption band is observed at long wavelength. Such a signal might come from a $n - \pi^*$ transition. The shape of the emission band is completely modified in the solid-state. Two explanation has been proposed: a redshift with a loss of fine structure due to aggregation, or a radiative $\pi^* - n$ transition. A fluorescence quantum yield of 2.5 % has been measured for **16f** in the solid-state (rough estimation).

When the film is heated, a change in absorption spectrum occurs at $62 \,^{\circ}\text{C}$ (56 $^{\circ}\text{C}$ upon cooling). This optical transition can confidently be attributed to the transition between the black phase present at RT and the higher temperature Col_{hd} mesophase. This change is fully reversible. Interestingly, when the film is thermally annealed at a temperature close to this last transition (at 75 $^{\circ}\text{C}$) during a long time, the absorption spectrum obtained after cooling at RT is characteristic for a material in which no intra-molecular motion is present. Moreover, a crystalline birefringent texture in observed under CPM. This experiment gives additional arguments for the amorphous nature of the black phase.

Finally, the strong absorption of HATNA-OR derivatives **16** in a region complementary to the phthalocyanines **15** absorption, makes them promising candidates for our study.

3.6 Charge carrier mobility

The charge carrier mobility is one of the key factors that show the potential of a material as organic semiconductor. The charge carrier mobility of HATNA-OC₁₆ has been measured by Dr Michael Debije (University of Delft), using the PR-TRMC technique.

This technique gives an estimation of the maximum charge carrier mobility μ in the material, but is not able to distinguish electron and hole mobilities. The μ value is given as the sum of the positive and negative charges contributions.



Figure 3.32: One-dimensional, intra-columnar charge carrier mobilities as a function of temperature for HATNA-OC₁₆ 16f.

At RT, the pristine (as obtained after material purification, not heated) material HATNA-OC₁₆ gives a μ of 0.02 cm².V⁻¹.s⁻¹ with an estimated first half-life of ≈ 10 ns. This value is quite low in comparison to HATNA-SC₁₀ **50c**, where a μ of 0.59 cm².V⁻¹.s⁻¹ has been obtained for the pristine material. It has to be noticed that this specific value highly depend on the supramolecular organisation obtained during the purification process. Indeed, the same material, purified by an other method, may gives totally different results. This fact is illustrated by the μ values obtained for the different HATNA-SR derivatives at RT, where μ of < 0.01, 0.07, 0.59, and 0.27 cm².V⁻¹.s⁻¹ have been obtained for the RT crystal phase of **50a-d**, respectively.[165] It results from this observation that the values on pristine materials highly depend on the purification procedure and not only on the material itself.

The best fit of the data gives a mobility $\Sigma \mu_{1D}$ of 0.03 cm².V⁻¹.s⁻¹ for 16f, which can



Figure 3.33: Room temperature microwave conductivity transients for a pristine sample of 16f.

be seen as roughly a maximum mobility for this material.

Surprisingly, this initial value is kept up to $100 \,^{\circ}$ C, in the LC phase. Upon transition from the crystalline to liquid crystalline phases, the side chains become more liquid-like, this melting of the side-chains has for consequence to reduce the hopping rate between neighbouring aromatic cores within the columnar stack. An abrupt decrease in charge mobility is usually observed at the transition temperature.[75] For HATNA-OC₁₆, the different mesophases do not seems to influence the charge mobilities.

After heating to just beyond 100 °C (still in a LC phase), the sample has been cooled to 60 °C, where the transients were completely gone (i.e. $< 0.01 \text{ cm}^2 \text{.V}^{-1} \text{.s}^{-1}$). The signal did not return upon cooling to RT. This result is consistent with the idea of molecular disordering in the black phase, as the abrupt decrease in mobility coincides with this phase transition.

If we compare the charge carrier mobility in HATNA-OC₁₆ with the values obtained for other discotic materials, we can conclude that, the pristine crystal state's charge mobility in **16f** is low for a crystal phase. Indeed, some hexabenzocoronene HBC derivatives have already shown μ of 1.13 cm².V⁻¹.s⁻¹ [169] in their K phase. But it is at same level as the mobilities recorded in the LC states of some triphenylene derivatives (0.002 - 0.025 cm².V⁻¹.s⁻¹).[83]

3.7 Electrochemical properties

As far as the n-type (or electron accepting) character of the HATNA-OR derivatives 16 will enable their application as electron carriers in electronic devices, we have carried out electrochemical studies to determine their reduction potential, which can be considered as an evidence of their π -deficient character.

This study has been Dr Rafael Gómez Aspe (from our group), in collaboration with Professor Buess (analytical and interfaces chemistry laboratory, ULB).

This investigation has been performed on two HATNA-OR derivatives (HATNA-OC₆ 16a and HATNA-OC₁₂ 16d). As it could be expected from their structures, the redox behaviour of 16 in solution is independent of the length of the lateral chains. Contrary to the phthalocyanine derivatives 15, no evidence of aggregation, even in concentrated chloroform solution, has been observed neither by 1H-NMR nor by UV-visible absorption spectroscopy.



Figure 3.34: Oxidation and reduction cyclic voltammograms recorded at room temperature for a dichloromethane solution ($\approx 10^{-3} \text{ mol.L}^{-1}$) of HATNA-OC₁₆ **16d**, using glassy carbon, platinum wire and SCE as working, counter and reference electrodes, respectively. Bu₄NClO₄ was used as supporting electrolyte.

It has been found that these molecules show a single non reversible oxidation process at +1.33 V. Three mono-electronic and reversible reduction waves can be observed centred at -1.20, -1.44 and -1.67 V, which can be accounted by the formation of the corresponding mono-, di- and triradical species. Despite the higher electronegativity of oxygen (in HATNA-OR) with respect to sulfur (in HATNA-SR), the first reduction wave of **16d** appears cathodically shifted that corresponding to the sulfur substituted analogs. Indeed, HATNA-SR **50** shows three quasi-reversible reduction waves centred at around -1.09, -1.35 and -1.60 V. No oxidation waves have been observed below +2 V.[165]

To a first approximation, the first reduction potential can be related to the electron affinity EA and thus to the LUMO energy level according to the following equation $EA = (E_{red} + 4.7) = 3.5 \text{ eV}.[146, 147]$ A similar relationship can be established for the oxidation potential, the ionisation potential IP and HOMO energies. The calculation shows that 16 has an IP of around 6.0 eV, what allows to estimate an electrochemical bandgap of around 2.5 eV. The high tendency of HATNA-SR derivatives 50 to aggregation even in dilute solution, has made estimation of the material's EA and IP difficult, since the equation was determined for solvated single molecules.

The shown high electron affinity suggests that electrons can be easily injected in these disc-like molecules and therefore these compounds could be good candidates for their application in water and oxygen free electronic devices as electron conducting layers.
3.8 Conclusions

The purpose of this chapter was the synthesis and the characterisation of n-type (electron accepting) mesogens. In addition to the high electron affinity, the searched material had to strongly absorb light in the visible and to possess a specific set of thermotropic properties: 1) a non-crystalline phase at room temperature, 2) a columnar liquid crystal phase, and 3) an isotropic phase below 200 °C. Furthermore, the material had to be highly soluble in common organic solvents and to be accessible in a minimum number of efficient synthetic steps.

A complete series of six hexa-alkoxy-hexaazatrinaphthylene HATNA-OR derivatives have been synthesised before having a material that fit our criteria the best. This structure has been chosen by comparison with the properties of their hexa-sulfanyl substituted counterparts HATNA-SR. Indeed, these materials, studied in our laboratory by Gaël Kestemont, have demonstrated the high tendency of the HATNA system to form columnar stacks, over extensive temperature ranges. They strongly absorb light in the visible $(\varepsilon(470) = 105000 \text{ L.mol}^{-1} \text{ cm}^{-1})$ and are accessible *via* an efficient two steps synthesis. But none of them melts into an isotropic phase before decomposing (around 250 °C) and their thermotropic behaviour is complicated (up to five different mesophases for HATNA-SC₁₀ **50c**). They are all in a crystalline state at RT.

All the HATNA-OR derivatives 16 have been obtained via a four steps synthetic route. Global yields of 17 to 32 % have been achieved. Even if this yield is significantly lower than the one obtained for the HATNA-SR derivatives (maximum 63 %), it is still sufficient to allow large scale synthesis. In this work, more than 1 g of final product has been produced in one batch. Moreover, the materials obtained after the last reaction of this four steps synthesis are easy to purified by column chromatography followed by precipitation. Even if no precise purity measurement has ever been performed on these materials, the absence of unassigned signals in the ¹H RMN spectra reveals a minimum purity of 99 %. All the HATNA-OR derivatives are highly soluble in common organic solvents (chloroform, hexane, toluene, ...).

The optoelectronic properties of the synthesised materials have been studied in solution and in the solid-state. As predicted by the theory, all the six HATNA-OR derivatives strongly absorb light in the visible. A maximum absorption coefficient of $\varepsilon(427)$ of 98000 \pm 2500 L.mol⁻¹.cm⁻¹ in toluene solution, has been estimated for all of them. In thin films, this strong absorption is conserved. The solid-state absorption coefficient of HATNA-OC₁₆ **16f** has been estimated to 77400 dm³.mol⁻¹.cm⁻¹ at 300 nm by measuring the films absorption spectra and their respective thicknesses (measured by AFM). Such a strong solid-state absorption makes HATNA-OR derivatives suitable for future photovoltaic applications.

In addition to the chemical and optical requirements, which are satisfied by all the six HATNA-OR derivatives, this work also includes limitations on the materials thermotropic behaviour. Three technics have been combined to investigate the mesogenic properties of the six materials. All the potentially mesogenic materials show at least one columnar LC phase over a wide temperature range. They all melt into an isotropic phase prior decomposition (which occurs around 250 °C), but only the longest-chains substituted materials HATNA-OC₁₆ **16f** has a clearing point significantly below 200 °C. Surprisingly, the long-chains substituted compounds **16d-f** show a phase disordering around 50 - 60 °C. It results from that a non-birefringent "black" phase that has not yet been fully understood. The results of X-ray diffraction are consistent with a lamellar mesophase, when the amorphous nature of this phase is corroborated by some other investigations (CPM, absorption spectroscopy on thermally annealed samples, charge mobility).

Finally, with its high electron affinity ($\approx 3.5 \text{ eV}$), its strong light absorption, its clearing point at 168 – 182 °C, its Col_{hd} mesophase, its non-crystalline (but still not fully characterised) phase at RT, and its easy synthesis, HATNA-OC₁₆ **16f** is a good n-type candidate for future photovoltaic applications.

Organic electronics is a challenging and highly promising field of science. Many groups, all around the world are working in this recent research topic. The competition is getting stronger and stronger. To illustrate that, we have to mention the recent publication, by Ong *et al.* of the synthesis of some HATNA-OR derivatives studied in this work.[170, 171]

3.9 Experimental part

3.9.1 General

The same scientific instruments have been used for the synthesis and the characterisation of the HATNA-O derivatives than for the phthalocyanine derivatives (refer to Section 2.8, except the following points:

Powder X-ray diffraction measurements were performed on the X33 camera of the European Molecular Biology Laboratory at the storage ring DORIS III of the Deutsches Elektronen Synchrotron (DESY), Hamburg. Diffraction patterns were collected in transmission in series of frames of 10 s or 6 s each with two position sensitive delay line readout detectors connected in series.[33,34] The sample temperature was controlled with a Mettler FP-82 HT heating stage under the flux of nitrogen. The data were normalized to the intensity of the primary beam using the SAPOKO program (Svergun and Koch unpublished). The scattering vector (s = $2 \sin \theta . \lambda^{-1}$, where θ is the Bragg angle and λ is the wavelength (1.5 Å)) was calibrated with tripalmitin and/or rat tail collagen in the small s-region and benzoic acid in the high s-region.

¹H-NMR and ¹³C-NMR spectra were recorded in CDCl₃.

3.9.2 General procedure for the synthesis of the 1,2-dialkoxybenzene

This procedure has been adapted from the literature.[161] A catalytic quantity (5 drops) of aliquat 336 was added to a mixture of catechol (2 g, 18 mmol), of potassium hydroxide KOH (1.8 g, 32 mmol), and of the appropriate alkyl bromide (39 mmol). The mixture was heated up to 120 °C, where the catechol melt, and stirred for 4 hours. The reaction medium turned from colourless to black. After cooling to RT, the resulting solid was dissolved by a large quantity of dichloromethane (50 mL) and the brown the solution was filtered over a column of Florisil 60-100 mesh. The resulting light yellow solution was evaporated under vacuum. Depending on the length of the alkyl chain, the crude products is an oil or a crystalline solid at RT. (Purification method A) The oils were purified on a silica gel column chromatography with a 5:5 mixture of toluene and hexane as eluent to afford the pure 1,2-dialkoxybenzene as a colourless oil, with yields of 45 to 52 %. (Purification method B) The solids were purified by recrystallisation in methanol, with a small amount of dichloromethane, afford the pure 1,2-dialkoxybenzene as white

needles, with yields of 48 to 56 %.

1,2-dihexyloxy-benzene (60a):

Purification method A. Yield 53 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.89 (t, J = 6 Hz, 6 H), 1.2 - 1.4 (m, 8 H), 1.47 (q, J = 7 Hz, 4 H), 1.81 (q, J = 7 Hz, 4 H), 3.99 (t, J = 6.6 Hz, 4 H), 6.88 (s, 4 H). ¹³C NMR (CDCl₃): δ (ppm) 14.5, 23.0, 26.1, 29.7, 32.0, 69.7, 114.5, 121.4, 149.7. MS (EI) m/z = 57, 71, 85, 110, 193, 278 (M+, calculated 278). RF (silica gel, toluene-hexane 5:5) : 0.49.

1,2-dioctyloxy-benzene (60b):

Purification method A. Yield 52 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.88 (t, J = 7 Hz, 6 H), 1.2 - 1.4 (m, 16 H), 1.47 (m, 4 H), 1.81 (q, J = 7 Hz, 4 H), 3.99 (t, J = 6.6 Hz, 4 H), 6.88 (s, 4 H). MS (EI) m/z = 57, 71, 85, 97, 110, 221, 334 (M+, calculated 334). RF (silica gel, toluene-hexane 5:5) : 0.48.

1,2-didecyloxy-benzene (60c):

Purification method B. Yield 55 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.88 (t, J = 7 Hz, 6 H), 1.2 - 1.4 (m, 24 H), 1.46 (m, 4 H), 1.81 (q, J = 7 Hz, 4 H), 3.99 (t, J = 6.6 Hz, 4 H), 6.88 (s, 4 H). ¹³C NMR (CDCl₃): δ (ppm) 14.1, 22.7, 26.0, 29.3, 29.4, 29.6, 29.6, 31.9, 69.3, 114.2, 121.0, 149.3. MS (EI) m/z = 57, 71, 85, 110, 121, 250, 390 (M+, calculated 390). RF (silica gel, toluene-hexane 5:5) : 0.45.

1,2-didodecyloxy-benzene (60d):

Purification method B. Yield 48 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.88 (t, J = 6.6 Hz, 6 H), 1.2 - 1.4 (m, 32 H), 1.46 (m, 4 H), 1.81 (q, J = 7 Hz, 4 H), 3.99 (t, J = 6.6 Hz, 4 H), 6.88 (s, 4 H). ¹³C NMR (CDCl₃): δ (ppm) 14.1, 22.7, 26.1, 29.4, 29.4, 29.6, 29.7, 29.7, 31.9, 69.3, 114.2, 121.0, 149.3. MS (EI) m/z = 57, 71, 85, 97, 110, 277, 446 (M+, calculated 446). RF (silica gel, toluene-hexane 5:5) : 0.50.

1,2-ditetradecyloxy-benzene (60e):

Purification method B. Yield 56 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.88 (t, J = 6 Hz, 6 H), 1.2 - 1.4 (m, 40 H), 1.46 (m, 4 H), 1.81 (q, J = 7 Hz, 4 H), 3.99 (t, J = 6.6 Hz, 4 H), 6.88 (s, 4 H). MS (EI) m/z = 57, 71, 83, 97, 110, 306, 502 (M+, calculated 502). RF (silica gel, toluene-hexane 5:5) : 0.52.

1,2-dihexadecyloxy-benzene (60f):

Purification method B. Yield 53 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.88 (t, J = 7 Hz, 6 H), 1.2 - 1.4 (m, 48 H), 1.46 (m, 4 H), 1.81 (q, J = 7 Hz, 4 H), 3.98 (t, J =

6.6 Hz, 4 H), 6.88 (s, 4 H). MS (EI) m/z = 57, 71, 83, 97, 110, 334, 558 (M+, calculated 558). RF (silica gel, toluene-hexane 5:5) : 0.46.

3.9.3 General procedure for the synthesis of the 1,2-bis-alkoxy-4,5-dinitrobenzenes

This procedure has been adapted from the literature.[162] The 1,2-dialkoxybenzene (10 g) in dichloromethane (40 mL) was added dropwise to magnetically stirred nitric acid (80 mL), in a water bath (≈ 20 °C). After 5 minutes stirring, sulfuric acid (40 mL) was added slowly to the biphasic medium. The mixture was stirred for 2 hours at RT, and poured into crushed ice. The dinitro compound was extracted with dichloromethane, the organic phases were washed until neutral and dried over anhydrous magnesium sulfate. After evaporation of the solvent under vacuum, the yellow solid was recrystallised from ethanol, with a small amount of dichloromethane, afford the pure 1,2-bis-alkoxy-4,5-dinitro-benzene as a yellow powder, with yields of 63 to 96 %.

1,2-bis-hexyloxy-4,5-dinitro-benzene (61a):

Yield 67 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.91 (t, J = 7.0 Hz, 6 H), 1.3 - 1.4 (m, 8 H), 1.49 (q, J = 7 Hz, 4 H), 1.87 (q, J = 7 Hz, 4 H), 4.10 (t, J = 6.6 Hz, 4 H), 7.29 (s, 2 H). ¹³C NMR (CDCl₃): δ (ppm) 13.9, 22.5, 25.5, 28.6, 31.4, 70.2, 107.9, 151.8. MS (EI) m/z = 57, 85, 184, 200, 268, 284, 368 (M+, calculated 368). RF (silica gel, toluene - hexane 5:5) : 0.46.

1,2-bis-octyloxy-4,5-dinitro-benzene (61b):

Yield 80 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.89 (t, J = 7.0 Hz, 6 H), 1.3 - 1.4 (m, 16 H), 1.48 (q, J = 7 Hz, 4 H), 1.87 (q, J = 7 Hz, 4 H), 4.10 (t, J = 6.6 Hz, 4 H), 7.29 (s, 2 H). ¹³C NMR (CDCl₃): δ (ppm) 14.0, 22.6, 25.8, 28.7, 29.2, 31.7, 70.2, 107.9, 151.8. MS (EI) m/z = 57, 71, 85, 97, 111, 184, 311, 424 (M+, calculated 424). RF (silica gel, toluene - hexane 5:5) : 0.54.

1,2-bis-decyloxy-4,5-dinitro-benzene (61c):

Yield 92 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.89 (t, J = 7.0 Hz, 6 H), 1.3 - 1.4 (m, 24 H), 1.48 (m, 4 H), 1.87 (q, J = 7 Hz, 4 H), 4.10 (t, J = 6.6 Hz, 4 H), 7.29 (s, 2 H). MS (EI) m/z = 57, 71, 85, 97, 111, 140, 184, 324, 450, 480 (M+, calculated 480). RF (silica gel, toluene - hexane 5:5) : 0.52.

1,2-bis-dodecyloxy-4,5-dinitro-benzene (61d):

Yield 94 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.88 (t, J = 7.0 Hz, 6 H), 1.3 - 1.4 (m, 32 H), 1.48 (m, 4 H), 1.87 (q, J = 7 Hz, 4 H), 4.10 (t, J = 6.6 Hz, 4 H), 7.29 (s, 2 H). ¹³C NMR (CDCl₃): δ (ppm) 14.1, 22.7, 25.8, 28.7, 29.2, 29.3, 29.6, 29.6, 31.9, 70.2, 107.9, 136.5, 151.7. MS (EI) m/z = 57, 71, 85, 97, 111, 155, 170, 198, 367, 502, 536 (M+, calculated 536). RF (silica gel, toluene - hexane 5:5) : 0.55.

1,2-bis-tetradecyloxy-4,5-dinitro-benzene (61e):

Yield 93 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.88 (t, J = 7.0 Hz, 6 H), 1.3 -1.4 (m, 40 H), 1.48 (m, 4 H), 1.87 (q, J = 7 Hz, 4 H), 4.10 (t, J = 6.6 Hz, 4 H), 7.29 (s, 2 H). ¹³C NMR (CDCl₃): δ (ppm) 14.1, 22.7, 25.8, 28.7, 29.2, 29.3, 29.5, 29.6, 31.9, 70.2, 107.9, 136.5, 151.7. MS (EI) m/z = 85, 97, 111, 141, 170, 184, 196, 366, 562, 592 (M+, calculated 592). RF (silica gel, toluene - hexane 5:5) : 0.54.

1,2-bis-hexadecyloxy-4,5-dinitro-benzene (61f):

Yield 96 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.88 (t, J = 7.0 Hz, 6 H), 1.3 - 1.4 (m, 48 H), 1.49 (m, 4 H), 1.87 (q, J = 7 Hz, 4 H), 4.10 (t, J = 6.6 Hz, 4 H), 7.29 (s, 2 H). MS (EI) m/z = 57, 71, 85, 97, 111, 170, 394, 618, 648 (M+, calculated 648). RF (silica gel, toluene - hexane 5:5) : 0.53.

3.9.4 General procedure for the synthesis of the hexa-alkoxy-hexaazatrinaphthylenes

The procedure used for the reduction has been adapted from the literature.[164] 10 %palladium on activated charcoal (0.1 g) was added to a solution of the 1,2-bis-alkoxy-4,5dinitro-benzene (1 mmol) in dry methanol (20 mL), and put under hydrogen atmosphere (1 atm). The reaction medium turns rapidly from light to dark yellow, attesting the presence of the nitro-amino compound. The mixture was reflux for 3 hours, until all the yellow colour has disappeared. Dichloromethane was added to the colourless solution in order to prevent precipitation upon cooling. The resulting solution was rapidly filtered on celite in order to eliminate to catalyst residue, and evaporated under vacuum. Hexaketocyclohexane octahydrate (100 mg, 0.33 mmol), acetic acid (10 mL) and dry ethanol (10 mL) were then added to the resulting white powder, and put under an argon atmosphere. The mixture was heated up to reflux (oil bath at 120 °C), and stirred for 20 hours. The reaction medium turned rapidly from colourless to dark red - brown. After cooling to RT, a large quantity of water (50 mL) was added to the solution which was neutralised by addition of potassium carbonate K_2CO_3 . The organic products were extracted with dichloromethane. The organic phases were washed and dried over anhydrous magnesium sulfate. After evaporation under vacuum, the crude product was purified on a silica gel column chromatography with dichloromethane – ethyl acetate (95:5) as eluent and the resulting solutions were precipitated by addition of ethanol and evaporation of the dichloromethane under vacuum. After filtration, the pure hexa-alkoxy-hexaazatrinaphthylenes is obtained as a yellow powder, with yields of 35 to 64 %.



Figure 3.35: ¹³C-NMR spectrum of HATNA-OC₆ **16a** in chloroform solution, with proposed signals attribution. Spectrum recorded at 25 °C.

2,3,8,9,14,15-hexa-hexyloxy-5,6,11,12,17,18-hexaazatrinaphthylene (16a):

Yield 64 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.95 (t, J = 7 Hz, 18 H), 1.4 -1.5 (m, 24 H), 1.60 (m, 12 H), 2.00 (q, J = 7 Hz, 12 H), 4.30 (t, J = 6.6 Hz, 12 H), 7.85 (s, 6 H). ¹³C NMR (CDCl₃): δ (ppm) 14.0, 22.6, 25.7, 28.8, 31.6, 69.5, 107.7, 141.0, 141.3, 154.5. MS (FD) m/z = 986 (M+, calculated 985.38), 1972 (2M+), 2952 (3M+). RF (silica gel, dichloromethane - ethylacetate 95:5) : 0.88. UV-vis (toluene): λ_{max} (ε) = 427 nm (98000 ± 2500 dm³.mol⁻¹.cm⁻¹). UV-vis (chloroform): λ_{max} (ε) = 439 nm (69000 ± 2500 dm³.mol⁻¹.cm⁻¹).

2,3,8,9,14,15-hexa-octyloxy-5,6,11,12,17,18-hexaazatrinaphthylene (16b):

Yield 40 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.91 (t, J = 6.6 Hz, 18 H), 1.3 - 1.4 (m, 48 H), 1.58 (m, 12 H), 2.00 (q, J = 7 Hz, 12 H), 4.30 (t, J = 6.6 Hz, 12 H), 7.85 (s, 6 H). MS (FD) m/z = 577 (M+/2), 1155 (M+, calculated 1153.7), 1732 (3M+/2), 2310 (2M+), 3463 (3M+). RF (silica gel, dichloromethane - ethylacetate 95:5) : 0.88.

2,3,8,9,14,15-hexa-decyloxy-5,6,11,12,17,18-hexaazatrinaphthylene (16c):

Yield 63 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.91 (t, J = 6.6 Hz, 18 H), 1.25 - 1.45 (m, 72 H), 1.58 (m, 12 H), 2.00 (q, J = 7 Hz, 12 H), 4.30 (t, J = 6.6 Hz, 12 H), 7.85 (s, 6 H). MS (FD) m/z = 661 (M+/2), 1320 (M+, calculated 1322.03), 2646 (2M+), 3308 (5M+/2). RF (silica gel, dichloromethane - ethylacetate 95:5) : 0.83.

2,3,8,9,14,15-hexa-dodecyloxy-5,6,11,12,17,18-hexaazatrinaphthylene (16d):

Yield 50 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.88 (t, J = 6.5 Hz, 18 H), 1.25 - 1.45 (m, 96 H), 1.56 (m, 12 H), 2.00 (q, J = 7 Hz, 12 H), 4.30 (t, J = 6.6 Hz, 12 H), 7.85 (s, 6 H). MS (FD) m/z = 746 (M+/2), 1491 (M+, calculated 1490.35), 2234 (3M+/2), 2980 (2M+), 4468 (3M+). RF (silica gel, dichloromethane - ethylacetate 95:5) : 0.87.

2,3,8,9,14,15-hexa-tetradecyloxy-5,6,11,12,17,18-hexaazatrinaphthylene (16e):

Yield 61 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.88 (t, J = 6 Hz, 18 H), 1.2 - 1.4 (m, 120 H), 1.58 (m, 12 H), 2.00 (q, J = 7 Hz, 12 H), 4.30 (t, J = 6.6 Hz, 12 H), 7.85 (s, 6 H). MS (FD) m/z = 830 (M+/2), 1660 (M+, calculated 1658.68), 3320 (2M+). RF (silica gel, dichloromethane - ethylacetate 95:5) : 0.90.

2,3,8,9,14,15-hexa-hexadecyloxy-5,6,11,12,17,18-hexaazatrinaphthylene (16f):

Yield 35 %. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 0.87 (t, J = 6 Hz, 18 H), 1.2 - 1.4 (m, 144 H), 1.58 (m, 12 H), 2.00 (q, J = 7 Hz, 12 H), 4.30 (t, J = 6.6 Hz, 12 H), 7.85 (s, 6 H). MS (FD) m/z = 917 (M+/2), 1828 (M+, calculated 1827.0), 3657 (2M+). RF (silica gel, dichloromethane - ethylacetate 95:5) : 0.82. UV-vis (toluene): λ_{max} (ε) = 427 nm (99000 ± 2500 dm³.mol⁻¹.cm⁻¹).

Chapter 4

Properties of blends of discotic materials

4.1 Introduction

The last part of this work is devoted to the study of blends of discotic materials, including the ones synthesised in this work.

As we have discussed in the introduction (Section 1.2.2), exciton dissociation in organic materials is only efficient at the interface between two materials of sufficiently different electron affinity. The semiconductors can be blended to increase the size of the interface, resulting in a so called "dispersed heterojunction cell". Such a device architecture has also the advantage of being easily manufactured when both materials are soluble in the same solvents.

In order to better understand the molecular organisation and to probe a possible phase separation in blends of discotic materials, their optoelectronic properties have been investigated in function of their composition and of temperature. Photovoltaic devices based on the discotic materials **15e** and **16f**, blended together or separately with other organic disk-like materials, have also been studied.

The results reported in this chapter were obtained in close collaboration with the Nano-Science Center of the University of Copenhagen (Denmark), and the Cavendish Laboratory of Physics of the University of Cambridge (United-Kingdom).

4.1.1 What can we learn from the photo-physical properties of blends

The influence of film morphology and phase separation on the photovoltaic efficiency is still not fully understood. Numerus interesting phenomena can be observed as changes in the blends absorption and/or emission spectra in comparison to the pure products.



Figure 4.1: Extreme molecular assemblies that can be met when two discotic materials are blended together. a) Stacking that would lead to an absorption spectrum close to the weighted sum of the pure product ones; b) Stacking that might lead to a change in the blend absorption spectra.

The absorption characteristics of a material in its condensed state mainly depends on its chemical structure and on the interactions with the surrounding molecules.[172] In blends of discotic materials, two extreme assemblies can be distinguished (Figure 4.1). In the former (Figure 4.1a), interactions between molecules of identical chemical structure are the most favourable. The two materials are then spatially separated and only interactions between molecules of the same nature are observed. In this case, the absorption spectrum of the blend is expected to be equal to the weighted sum of the pure product ones. In the later (Figure 4.1b), the lowest energy molecular assembly is obtained when molecules of different nature interact, resulting in alternating structure. Such a molecular assembly has already been reported for some pairs of n- and p-type discotic semiconductors.[173, 174, 175] The appearance of interactions that are, by definition, not present in the pure products, may have an influence on the blend's absorption characteristics.[176]

For photovoltaic device applications, the mixed structures depicted in Figure 4.1a is the most promising. Indeed, when molecular-scale mixing is present (Figure 4.1b), exciton splitting can occur anywhere in the film. In this case, exciton diffusion length is not an obstacle but the charges, are less mobile and can be more easily trapped by impossibility of being transferred to any surrounding molecules. In the case of phase separation (Figure 4.1a), the large interfacial area and the presence of continuous conducting pathways for excitons and charges, enables the excitons to dissociate into free charges, and reduces the probability of charge recombination and/or trapping.[42]

The emission spectrum may also be changed by blending two materials together, wherein at least one is luminescent in the solid-state. Different cases can be distinguished:

- No change is observed, the fluorescence spectra of both materials are conserved in the blend. This case usually results from an absence of charge or energy transfer in the system, the two materials being as alone in the blend. It might also results from a too short exciton lifetime or diffusion length. Indeed, if the exciton is unable to reach an interface, where transfer reactions take place, it can eventually be radiatively deactivated, giving the same luminescence spectrum as of the pure product.
- By illuminating one material specifically, the other material emission spectrum is recorded. This situation is usually due to an energy transfer between the two materials. Indeed, if the photo-excited material transfers its energy, its luminescence is quenched. An exciton is then created in the second (not photo-excited) material, that might be radiatively deactivated, giving rise to a luminescence spectrum characteristic of this last.[76, 177]



Figure 4.2: Excitation transfer due to energy transfer reaction. By photo-exciting one specific material, the luminescence spectrum of the other one is recorded.

• An additional low energy emission band is observed. When charge transfer takes place between a donor and an acceptor, the resulting pair of charges (e⁻ in the n-type and h⁺ in the p-type semiconductor) might lead to the formation of an exciplex. This specie results from the coulombic interactions between the two oppositely charged molecules. When an electric field is present in the device, the exciplex is usually dissociated, giving rise to a pair of free charges, according to the Onsager theory.[178, 179] In absence of external forces, they can recombine by radiative or non-radiative backward charge transfer reaction. The subsequent luminescence would appear at lower energy (\equiv longer wavelength) than the pure products 0-0 emission bands.[180]



Figure 4.3: Exciplex formation by electron transfer. The excited exciplex state might emit light by radiative electron - hole recombination, giving rise to an emission wavelength corresponding to the energy difference between the LUMO of the n-type and the HOMO of the p-type material.

 The luminescence of both materials is quenched. Such a luminescence (fluorescence and/or phosphorescence) quenching is observed when electron transfer takes place between a donor and an acceptor, leading to a pair of free charges. The excited state (exciton) is not present anymore and can not be radiatively deactivated.[181, 182] It might also result from the formation of a pair of charges, linked by coulombic interactions (corresponding to a non-luminescent exciplex).



Figure 4.4: Luminescence quenching by charge transfer. If an exciton located (a) in a p-type or (b) in a n-type semiconductor is split into a pair of free charges by electron transfer, a luminescence quenching is expected.

To be use as active layer in solar cells, a blend of two materials must allow efficient charge transfer. If it occurs, a quenching of both materials luminescence is expected. The observation of exciplex emission attests to charge transfer but is also an indication of strong coulombic interactions between the two charged species and, by the way, of more efficient charge recombination at the interface.

In conclusion, the study of the optoelectronic properties of blends might give interesting indications on the molecular-scale phase separation and on the processes that take place at the interface between the two semiconducting materials. Nevertheless, fabrication of PVCs in the best way to probe the photovoltaic abilities of a specific blend.

4.1.2 Solar cells manufacturing and characterisation

In order to study the photovoltaic abilities of the mesogens synthesised in this work, experimental solar cells have been made and characterised. In this section, the manufacturing technic is explained and the main parameters that characterise a PVC are introduced.

Device fabrication

A schematic drawing of the photovoltaic devices made in the work is given in Figure 4.5.



Figure 4.5: Typical experimental PVC structure.

They consist in dispersed hetero-junction cells obtained by spin-coating a solution of known composition on a Indium-Thin Oxide ITO -coated glass substrate. The top electrode, consisting in height aluminium fingers, is then evaporated on the film, giving height pixels (or small cells) on each device. As device manufacturing has a dramatic influence on its efficiency, a detailed procedure is given hereafter.

- Substrate cleaning: The substrates used were 12 mm wide glass squares, already coated with ITO (purchased from Cambridge Display Technology). This last was protected by a photoresist sheet. The protecting layer was dissolved in acetone, in an ultrasonic bath (twice 10 minutes). An additional ultrasonic bath cleaning (10 minutes) in high purity isopropanol IPA was then performed in order to remove any residue of the protecting sheet. The ITO-coated substrates were then cleaned by oxygen plasma treatment (250 W, 10 minutes). Indeed, oxygen plasma cleaning of ITO does not change the electrode surface nature, contrary to Piranha (4:1 H₂SO₄/H₂O₂), RCA (1:1:5 NH₄OH/H₂O₂/H₂O), or aquaregia (1:3:20 HNO₃/HCl/H₂O) surface treatment, leaving a a metal oxide-rich surface.[183, 184] Under optimised conditions, it also induces a higher surface energy and polarity, a smoother surface, a higher work-function, and a lower sheet resistance.[185] Indium-tin oxide has been widely used as anode (+) in organic solar cells. The transparency of this mixed oxide (9:1 In₂O₃/SnO₂) to light of wavelength higher than 350 nm, permits visible light to run though it, entering into the active layer with the less losses. Moreover, its high work-function (about 4.8 eV), [186, 187] corresponding to
- Solution preparation: The two materials were weighted separately in carefully cleaned bottles (with acetone, IPA, and finally chloroform), and dissolved in a known volume of chloroform in order to obtain solutions of known concentration (here, 15 and 20 g.L⁻¹).¹ The mixtures were then obtained by mixing a specific volume of each mother solutions. Parafilm sheets were laid on the bottle caps to minimise solvent evaporation during their transfer into the glovebox.

its ionisation potential, makes it ideal hole collecting contact electrode.

 Active layer fabrication by spin-coating in glovebox: In order to avoid the presence of oxygen and water, impurities that are expected to decrease electron mobility in the active layer, the rest of the manufacturing was performed under dry nitrogen atmosphere, in a glovebox.

Spin-coating was used for the films manufacturing. This technic uses the centrifuge forces, created by spinning the substrate on itself, to uniformly spread a material on a substrate. Three main parameters determine the film thickness: the solution

¹Note that all the ratios given in this chapter are by weight, except if specified.

concentration, the rotation rate, and the use of an acceleration slope. When an increase in solution concentration results in thicker films, an increase in spinning rate gives rise to thinner films. By applying an acceleration at the beginning of the spin program, more regular thicker films are usually obtained. In this work, the films were made by covering the substrate with drops of the filtrated corresponding solution (0.45 μ m pore size). All the photovoltaic devices studied in this work were obtained using an acceleration coefficient of 9 (the highest available) and a spinning rate of 1500 rpm. They were all spun during 30 seconds in order to make sure all the solvent was evaporated.

• Top electrode deposition by vacuum metal evaporation: In order to complete the photovoltaic device, an cathode (-) has to be deposited onto the active layer. In this work, we have chosen to work with aluminum Al as low work-function electrode (4.28 eV).[188]

Thin Al films ($\approx 100 \text{ nm}$) were evaporated under high vacuum (around 10^{-6} mbar during evaporation), by resistively heating a tungsten filament dressed with aluminium rod. The film thickness was monitored using a quartz crystal thickness monitor. The Al evaporation speed has a dramatic effect on the surface morphology and, by the way, on the device performances.[189] In this work, evaporation speed of about 3 Å.sec⁻¹ was used.

• Silver paste deposition: In order to improve the electric contact between the device electrodes and the sample holder used for device characterisation, a silver paste was deposited on each pixel (on the Al electrodes), and on the ITO contact.

To reduce the risk of device deterioration, its characterisation was always performed just after its fabrication.

In the following section, the main photovoltaic performance parameters are introduced.

Device characterisation



Figure 4.6: Schematic drawing of the setup used for the study of the photovoltaic devices.

The key parameter used in this work to express the performances of a photovoltaic cell is the **external quantum efficiency** EQE. The EQE is defined, at each excitation wavelength upon monochromatic light illumination, as the number of collected electrons upon short-circuit conditions (i.e. when no bias voltage is applied at the electrodes), divided by the number of incident photons:

$$EQE(\%) = \frac{I_{SC}}{eN_0} \tag{4.1}$$

where I_{SC} is the short-circuit photocurrent density, e the elementary charge and N_0 the incident photons flux density.

 I_{SC} is determined experimentally by measuring the current flowing through the device under short-circuit conditions. N_0 is calculated at each wavelength by measuring the current produced by a calibrated Si-photo-diode. The plot of EQE versus wavelength λ is also called "action spectrum". It is obtained by shinning the sample with a monochromatic light and scanning over a defined range of wavelength.

The second important device characterisation consists in analysing the current I flowing through the device when a vias voltage V is applied at the electrodes. A typical I-V curve of a solar cell upon illumination is given in Figure 4.7.

Three main parameters can be extracted from the I-V curve.

 the short-circuit current I_{SC} is defined as the current density that flows through the device when no bias voltage is applied. If a load is connected to the diode, a current will conduct in the circuit. I_{SC} corresponds to the maximum current



Figure 4.7: Current versus applied voltage curve (I-V curve) of a solar cell. The fourth quadrant represents the voltage and current that is generated by the cell upon illumination. I_{SC} : short-circuit current; V_{OC} : open-circuit voltage; FF : fill factor.

realised when an electrical short is placed across the diode terminals.[190] It has been demonstrated that the short-circuit current is sensitive to film morphology.

- the open-circuit voltage V_{OC} is defined as the bias voltage that has to be applied at the electrode to stop the current flow (I = 0).[191] It is an essential factor since it determines the upper voltage above which no current is produced by the device. The origin of the open-circuit voltage in organic PVCs has not been fully understood yet. The traditional assumption that it corresponds to the difference between the work-functions of the two electrodes is too simplistic to describe the behaviour of most organic devices. It has recently been shown that V_{OC} is also affected by the active layer morphology, [192] by variations in the electron acceptor strength, [193] and by incident light intensity.[194]
- the fill factor FF represents a measure of the quality of the shape of the I-V curve. It is calculated by

$$FF = \frac{(IV)_{max}}{I_{SC}V_{OC}}$$

$$\tag{4.2}$$

The maximum power that can be supplied by the device corresponds to the maximum product of I and V in the fourth quadrant $(IV)_{max}$. The larger is this area, the more the I-V curve resembles to a rectangle with area $I_{SC}V_{OC}$. The FF is defined as the ratio between these two areas.

A FF of 1 would signify that the PVC can supply a constant current I_{SC} up to a maximum voltage V_{OC} . The power that can be extracted from the device is then maximum.[41] Has we can see, even if it is essential, high EQE (corresponding to high I_{SC}) is not sufficient to have highly efficient solar cell. An efficient device is characterised by high values of all these parameters. In the next sections, the values of the different parameters will be given as indications. They will not be discussed in details.

For comparison, the most efficient PVC comprising discotic materials obtained up to date, has a maximum EQE of 34 % (at 490 nm), with $I_{SC} = 33.5 \ \mu A.cm^{-2}$, $V_{OC} = 0.69 \text{ V}$, and a FF of 40 %.[40] This result has been achieved with a blend of a crystalline perylene derivative PTCDI **47a** with a RT liquid crystalline HBC derivative HBC-PhC₁₂ **63** (Figure 4.8), in a ratio of 60:40.



Figure 4.8: Chemical structure and HOMO and LUMO levels for the PTCDI 47a and HBC-PhC₁₂ 63.[40]

4.2 Photo-physical and photovoltaic properties of HATNA-OR – Pc blends

4.2.1 Photo-physical properties

The photo-physical properties of five bends of different composition (20, 40, 50, 60, and 80 % of one component) have been investigated. The aim of these experiments was to probe possible changes in the absorption and/or emission spectra, due to the presence of a second material in the film.



Figure 4.9: Temperature dependence of the solid-state absorption spectrum of a 50:50 blend of $H_2Pc(14,10)_4$ **15e** and HATNA-OC₁₆ **16f** spin-coated on glass. * = spectrum recorded after two weeks at RT. Heating and cooling rates: 10 °C.min⁻¹

The changes in the small wavelength region of the absorption spectra is more difficult to interpret. Indeed, since both materials absorb in this region, the sum of the two contributions is observed. The changes in absorption intensity can not be unambiguously attributed to one of the two materials.

Figure 4.9 summarises the absorption spectra recorded for a 50:50 blend of 15e and 16f

at different temperatures. The five film compositions show exactly the same behaviour. In the long wavelength region of the pristine film absorption spectrum (just after spincoating), an absorption band characteristic for pure solid-state phthalocyanine is detected (maximum at 614 nm). Two additional bands are observed, at 676 and 713 nm. The initial intensity of these two peaks increases with the amount of HATNA in the blend. When temperature is increased, a jump in absorption intensity is observed at 649, 683, and 718 nm. The transition occurs between RT and 50 °C for all the blends. The resulting spectrum nicely coincides with the weighted sum of the solid-state and the dilute solution absorption spectra of the pure phthalocyanine derivative **15e**.



Figure 4.10: a) Temperature dependance of the absorbance of a 80:20 HATNA/Pc film at 715 nm (blue curve) and its first derivative (red curve). b) Evolution of the absorbance at 718 nm with temperature for a 50:50 film.

A time-drive absorption experiment has been performed on a 80:20 HATNA/Pc blend, in order to determine more precisely the optical transition temperature (Figure 4.10a). By recording the absorbance at 715 nm in function of temperature (heating rate: $10 \,^{\circ}\text{C.min}^{-1}$), an optical transition temperature of 38 °C has been obtained. This temperature does not correspond to any phase transition of the pure products and can then not be attributed to an abrupt increase in one material's fluidity.

We have previously shown (Section 2.5.2) that aggregation effect on the phthalocyanine absorption spectrum is clearly visible, even at low concentrations (down to 10^{-5} M). The observation of solution-like absorption pattern attests of the presence of Pc molecules that are isolated from the others. We can then conclude that the change in absorption spectrum observed at 38 °C corresponds to a transition from a structure in which most of the Pcs interact with other Pc molecules (Figure 4.1a), to a phase in which a certain amount of Pc molecules are "dissolved" in the HATNA, forming a phase where the two materials are mixed together on a molecular level (Figure 4.1b). A maximum of mixing is obtained just above the optical transition (Figure 4.10b), even if the peak intensity does not change much at higher temperature. The transition is also observed upon cooling, a drop in absorption intensity at the three "solution-like" Pcs absorption bands being observed between 50 °C and RT. Just after thermal annealing, the films still conserve a certain amount of mixing. Two weeks at RT are needed to recover the initial spectrum. The separation can be accelerated by leaving the film under toluene atmosphere (solvent annealing). One night is sufficient to recover the pristine film absorption spectrum. The two molecular organisations (separated and mixed) can also be distinguish by CPM and AFM. The RT CPM and AFM images recorded at RT before and after thermal annealing are given in Figure 4.11 and 4.12.



Figure 4.11: CPM images of a 50:50 blend of **15e** and **16f** taken at RT (a) before (film's edge) and (b) after thermal annealing. Maximum temperature: 150 °C, heating and cooling rate: 10 °C.min⁻¹.



Figure 4.12: Tapping mode AFM images of a 50:50 blend of **15e** and **16f** recorded at RT (a) before and (b) after thermal annealing. Colour scale: 0 - 50 nm. Maximum temperature: $150 \,^{\circ}$ C, heating and cooling rate: $10 \,^{\circ}$ C.min⁻¹.

Under CPM, all the pristine films appear non-birefringent. The micro-domains obtained during the spin-coating process might be to small to give rise to birefringence. After thermal annealing, a texture is observed. The too small film thickness, and the absence of top glass slide, made us unable to test the fluidity of the phase. Nevertheless, the drop-like shape of the micro-domains are consistent with a LC phase.

AFM has been used to probe possible changes in film morphology due to phase mixing. Before annealing, micro-domains are visible on the top of the film. As they are also visible in the phase images, they might be different in chemical composition than the background. After thermal annealing, the AFM image is significantly different. The aggregates are less visible, showing that a melting occurred during the annealing. The film surface is also smoother.

In the two pure materials, only HATNA **16f** is slightly fluorescent in the solid-state. The solution fluorescence of the Pcs is completely quenched in the condensed state. In the pristine blends, no fluorescence is observed. The thermally induced molecular mixing has for consequence to make a fluorescence visible. The peak maximum (509 nm) does



Figure 4.13: Fluorescence spectrum of a 50:50 HATNA/Pc blend (excitation at 411 nm). The solid-state absorption spectra of **15e** and **16f**, and the solid-state emission spectrum of **16f** are also given.

not correspond to the pure HATNA fluorescence (maximum at 565 nm). However, the fluorescence in the blend can be attributed to the HATNA, the difference in wavelength being due to the absorption of a part of the emitted light by the Pc present in the blend (Figure 4.13. This conclusion is reinforced by the excitation spectrum of the blend's fluorescence, which corresponds to the pure HATNA solid-state absorption spectrum. The formation of this solid solution" of Pc **15e** does not give to the material a solution-like fluorescence.

In conclusion the presence of fluorescence in the blends vouches for an absence of charge or energy transfer between these two materials.

4.2.2 Photovoltaic properties

The best way to study the photovoltaic properties of a specific blend of materials is to fabricate PVCs based on it. Experimental solar cells based on the blend of $H_2Pc(14,10)_4$ **15e** and HATNA-OC₁₆ **16f** as active layer have then been made. Seven batches of six to nine devices, with three different blend compositions (each time) have been done. The first devices (30:70, 50:50, and 70:30 blends) were made with standard conditions, using a solution concentration of 15 g.L⁻¹. Only short-circuited SC pixels were observed. The film thickness has then been increased by spin-casting from a more concentrated solution (20 g.L⁻¹). No change was observed. In order to make sure the SC was not due to a to large amplitude of film roughness, AFM topology images of the blend have been recorded (Figure 4.14). They all show a flat surface, with a maximum roughness amplitude of about 5 nm, when the film thickness is about 120 nm. No direct contact between the two electrodes can then be attributed to a too thin or too rough film. It is not the origin of the problem.



Figure 4.14: Tapping mode AFM image of a 50:50 blend of **15e** and **16f**. Topology (left image), scratch image (up right image) and its section analysis (down right image).

An other explanation was that, due to their high temperature during the deposition process, the aluminium atoms might diffuse through the film, short-circuiting the pixels. In order to investigate this, a thin protecting layer of lithium fluoride LiF (1 nm) has been evaporated between the semiconducting layer and the Al top electrode. The addition of a thin layer of the crystalline LiF has also been shown to increase the device lifetime [195] and to enhance charge transfer between the n-type material and the cathode.[196, 197] In this case, no SC pixels were observed. Unfortunately, no photocurrent was produced.



Figure 4.15: I-V characteristic and EQE action spectrum of a 50:50 HATNA-OC₁₆: $H_2Pc(14,10)_4$ film, thermally annealed after Al evaporation.

The photo-physical investigations performed on blends of 15e and 16f, have shown a huge influence of the thermal history on molecular organisation in the films. We have then tried to thermally anneal the devices (before or after Al evaporation, for a 50:50 blend, spin-coated from 20 g.L⁻¹ solution). When the films are left at 100 °C for 1 hour (in a glovebox) before Al evaporation, the resulting devices are still SC. But, when the devices are annealed under the same conditions after the top electrode deposition, no SC is measured any more. The current-voltage (I-V) characteristics in the dark (Figure 4.15) correspond to what is expected for a working PVC, but no significant change was observed under illumination at 720 nm, meaning a $V_{OC} = 0$ V (under the detection limits) and a FF of 0.00. The EQE action spectrum nicely follows the absorption spectrum recorded at RT on a thermally annealed 50:50 blend of 15e and 16f (Figure 4.15), especially in the Pc absorption region (500-750 nm). The maximum EQE is very low (1.2 ppm (= 1.2 x 10^{-4} %!) at 715 nm, in the Pc absorption region), at the detection limits of the setup. We have to be cautious about the peaks observed at short wavelength: the very low incident light intensity in that region makes the error very high. Only the baseline is affected when a bias voltage is applied; all the spectrum being shifted to higher current. The null value of V_{OC} and the very low EQE signify that the device is not working well.

The large number of SC devices can be explained by the RT liquid crystallinity of the



Figure 4.16: a) Sketch showing a possible explanation of the pixels short-circuiting. b) Frontier orbitals energy levels of **15e** and **16f** estimated by cyclovoltametry (see Sections 2.6 and 3.7).

blends, observed by CPM. During the top electrode deposition, the hot aluminum particles locally heat the film, increasing its fluidity. This decrease in viscosity allows the Al atoms to diffuse through the film, short-circuiting the pixels (Figure 4.16a). For the two non-SC batches (with the protecting layer and thermally annealed after Al deposition), the very low photocurrents observed (so low that we didn't find them in the former) can be explained by the absence of charge transfer between the two semiconductors. Figure 4.16b shows the results of cyclovoltametry measurements performed on **15e** and **16f**². Even if these results can only be seen as rough estimations of the frontier orbitals energy levels, they show that no charge transfer can occur in this system. The photocurrent observed (Figure 4.15) could be due to an inefficient exciton self-dissociation into free charges.

Even if 15e and 16f are not energetically compatible with one another, they can still be used with other discotic semiconductors. Up to date, the best result in small molecules PVCs has been obtained by Schmidt-Mende *et al.*, with a blend of a crystalline derivative of perylene (the Bis(1-ethylpropyl)-perylene-bis(dicarboximide) PTCDI 47a as n-type semiconductor and the liquid crystalline hexaphenyl-substituted hexabenzocoronene HBC-PhC₁₂ 63 as hole conducting material (Figure 4.8).[40] An EQE of > 34 % was reported with a 60 % PTCDI blend.

We have mixed these two materials with **15e** and **16f** in order to proof that the blend of these two materials together is responsible for the negative results obtained, and not the materials themselves.

²note: the energy levels can not be compared with the ones shown in Figure 4.8, since two different methods have been used.



4.3 Photovoltaic properties of PTCDI – Pc blends

Figure 4.17: A) EQE action spectra for different blend ratios (PTCDI 47a/Pc 15e). B) comparison of the best blend EQE action spectrum with the blend and the pure products absorption spectra. C) I-V characteristic of the best blend ratio. '1' and '2' refer to the film spun from 20 g.L⁻¹ and 15 g.L⁻¹ solutions, respectively.

Blends of Pc and perylene derivatives have already been used in photovoltaic devices.[39] Moreover, blends of the specific materials **47a** and **15e** were studied during Lukas Schmidt-Mende's PhD thesis (but only spin-coated from 20 g.L⁻¹ solutions), giving maximum EQE of > 1 % for a 50:50 blend.[42]

The results, obtained with different blend ratios and two different solution concentrations, are summarised in Figure 4.17. A maximum EQE of 1.15 % has been achieved at 470 nm for a 70:30 blend³ spin-coated from a 20 g.L⁻¹ solution. The thinner films are less efficient. When the active layer is obtained by spin-coating from 15 g.L⁻¹ solution, a maximum efficiency of 0.75 % is recorded for a 40 % Pc blend. This difference can be explained by the compromise that has to be found between the light absorption (better in thick films) and the number of charges that can reach the electrodes before being trapped (better in thin films). In the present case, the increase in film thickness has a positive effect on cells efficiency. The larger number of exciton created by illuminating the thick films is not counterbalanced by an increase in charge and/or exciton trapping. Charge migration and energy diffusion seems to be quite efficient over long distances, meaning that large domains are created in the blend. This conclusion has been confirmed by AFM (Figure 4.18), where micro-crystals of perylene are observed. Indeed, the AFM images recorded for pure PTCDI and the blends show similar crystal structure, but with a roughness amplitude of about one order of magnitude lower in presence of Pc. The same images have been recorded for all the PTCDI/Pc blends.



Figure 4.18: Tapping mode AFM image of pure PTCDI (A), and 70:30 PTCDI/Pc blend (B).

³All the ratios are given with the material used as electron acceptor ':' hole acceptor.



4.4 Photovoltaic properties of HATNA-OR – HBC blends

Figure 4.19: A) comparison of the working blend ratio EQE action spectrum (HATNA $16f/HBC-PhC_{12}$ 63) with the blend and the pure products absorption spectra. B) I-V characteristic of the best blend ratio. '1' and '2' refer to the film spun from 20 g.L⁻¹ and 15 g.L⁻¹ solutions, respectively.

In the other hand, the electron conductor HATNA-OC₁₆ **16f** has been blended with the p-type HBC-PhC₁₂ **63**. Different blend ratios and two different solution concentrations have been tested. The results obtained for the only non short-circuit devices are given in Figure 4.19. The efficiencies are lower than the ones obtained with the previous blend. EQE of only 0.031 % at 380 nm has been achieved for a 40:60 HATNA/HBC blend spin-coated from 20 g.L⁻¹ solution. As observed with the previous blend, charge photogeneration drops in the thinner film. Only 0.012 % of EQE is measured for a 30:70 blend, spin-coated from 15 g.L⁻¹ solution. The AFM images of HBC-PhC₁₂ (Figure 4.20A) shows regular and smooth topology, as expected from this RT liquid crystalline material. The AFM images recorded for the blends (Figure 4.20B) also shows a very smooth surface, but they might be an artefact.



The reasons of the low efficiency obtained with this blend have not been elucidated.

Figure 4.20: Tapping mode AFM image of pure HBC-PhC₁₂ (A) and of 30:70 HATNA/HBC-PhC₁₂ blend (B).



4.5 Photovoltaic properties of PTCDI – HATNA-OR blends

Figure 4.21: A) EQE action spectra for different blend ratios (HATNA 16f : PTCDI 47a). B) comparison of the best blend EQE action spectrum with the blend and the pure products absorption spectra. C) I-V characteristic of the best blend ratio. '1' and '2' refer to the film spun from 20 g.L⁻¹ and 15 g.L⁻¹ solutions, respectively.

HATNA-OC₁₆ 16f was designed to be a good electron accepting material. But, if we blend it with an other electron acceptor (like a perylene derivative), HATNA could be used as p-type material (be oxidised during the charge transfer reaction), depending on their relative redox potentials. This is the idea followed in this section. As for the previous blends, different compositions, and two thicknesses have been studied. The results are summarised in Figure 4.21. As for the other blends, a drop in EQE is observed in the thinner film. A maximum EQE of 1.07 % at 525 nm has been achieved by using **16f** as hole acceptor, for a 70:30 blend spin-coated from 20 g.L⁻¹ solution. Interestingly, a shoulder at 580 nm that does not correspond to any absorption band in the pure products spectra, is observed either in the action spectra and in the blend spectra. The same observation has already been done by Johanna P. Schmidtke (University of Cambridge) on the PTCDI : HBC-PhC₁₂ blends.[198] It is attributed to a partial change in the molecular packing of the PTCDI in presence of a second component.[199] In the thinner films, only the 80:20 blend has led to working pixels, all the other ratio devices being SC. This fact has not been further investigated.

The AFM image recorded for a 70:30 blend is given in Figure 4.22. The film surface is composed of micro-crystals that can be attributed to the PTCDI.



Figure 4.22: Tapping mode AFM image of a 70:30 PTCDI 47a/HATNA 16f blend.

4.6 Photovoltaic properties of PTCDI – HATNA-OR – Pc blends

As we have seen in the three previous sections, the blends of Pc 15e with PTCDI 47a, and HATNA 16f with PTCDI 47a have led to working devices with maximum EQE of about 1 % in both cases. No charge or energy transfer between Pc 15e and HATNA 16f has been observed. If we blend together the three components PTCDI 47a : Pc 15e : HATNA 16f, we can anticipate that PTCDI will act as electron accepting material, when Pc and HATNA will independently conduct holes. The particularity of the three components of this tertiary blend is their complementarity in light absorption (Figure 4.23).



Figure 4.23: Solid-state absorption spectra of the three constituents of the tertiary blends.

As for the other blends, different blend ratios (1:1:1, 2:1:1, 2:1:2) and two film thicknesses have been studied. The results obtained are summarised in Figure 4.24.

As expected, a photo-current is produced by illumination at any wavelength from 350 to 730 nm. Unfortunately, the efficiencies are not the sum of the binary blends ones, the maximum EQE recorded being 0.41 % at 530 nm for a 2:1:1 blend spin-coated from 15 g.L⁻¹ solution. For the first time, the thinner films are more efficient than the thicker ones, it suggests that transport processes limit the device efficiency. The two peaks at 680 and 715 nm, observed only in the action spectra, are attributed to isolated Pc molecules. Using the same explanation as for the photo-physical properties characterisations of HATNA/Pc blends (Section 4.2.1), we can conclude that the Pc molecules are partially mixed, in a



Figure 4.24: A) EQE action spectra for different blend ratios (Pc 15e : HATNA 16f : PTCDI 47a). B) comparison of the best blend EQE action spectrum with the blend and the pure products absorption spectra. C) I-V characteristic of the best blend ratio. '1' and '2' refer to the film spun from 20 g.L⁻¹ and 15 g.L⁻¹ solutions, respectively.

molecular scale, with the other materials. The different molecular organisation obtained in the binary and the tertiary blends is certainly the origin of the non-additive device efficiencies. Indeed, the presence of Pc molecules, inserted in the other materials, might create traps for charges in the active layer.

This result constitutes the first example of organic photovoltaic cell comprising three disk-shaped semiconducting materials.

4.7 Conclusions

The last part of this work has been devoted to the study of the photo-physical and the photovoltaic properties of blends of discotic materials.

The photo-physical behaviour of thin films of $H_2Pc(14,10)_4$ **15e**/HATNA-OC₁₆ **16f** blends has been investigated in function of temperature. All the blend ratios show the same behaviour. The pristine films absorption spectra are close to the sum of the once of the pure products, showing that the materials mainly interact with molecules of the same chemical nature. When the films are heated, an optical transition is observed between RT and 50 °C. The appearance of an absorption pattern characteristic for the phthalocyanine in dilute solution reveals a molecular-scale mixing of the two components. After cooling at 10 °C.min⁻¹, the initial absorption spectrum is not recovered. Two weeks at RT or one night of toluene vapour annealing are needed to erase the effects of the thermal annealing. The solid-state fluorescence of **16f** is quenched when it is blended with **15e**. When the mixed phase is present (at RT after thermal annealing), the pure HATNA fluorescence spectrum is recorded in the blends, with an excitation spectrum corresponding the pure HATNA absorption spectrum. Neither charge nor energy transfer are observed in these blends.

In order to study the photovoltaic properties of the materials studied in this work, solar cells based on $H_2Pc(14,10)_4$ **15e** and HATNA-OC₁₆ **16f**, blended together or with other discotic materials, have been made. The best results are given in Table 5.2



Figure 4.25: Picture of some experimental photovoltaic devices made in this work. The active layer consists in a 50:50 blend of, from left to right, HATNA-OR/Pc, PTCDI/Pc, HBC-PhC₁₂/HATNA-OR, PTCDI/HATNA-OR, and PTCDI/HATNA-OR/Pc, respectively.
| blend | best ratio | solution concentration | EQE % $(\lambda \text{ nm})$ |
|---|------------|---------------------------|--------------------------------|
| HATNA-OR ${\bf 16f} \ / \ {\rm Pc} \ {\bf 15e}$ | 50:50 | 20 g.L^{-1a} | $1.2 \mathrm{x} 10^{-4}$ (715) |
| PTCDI 47a / Pc 15e | 70:30 | $20~{\rm g.L^{-1}}$ | 1.15 (470) |
| HATNA-OR $16f$ / HBC-PhC ₁₂ 63 | 40:60 | 20 g.L^{-1} | 0.031 (380) |
| PTCDI 47a / HATNA-OR 16f | 70:30 | 20 g.L^{-1} | 1.07(525) |
| PTCDI 47a / HATNA-OR 16f / Pc $15e$ | 2:1:1 | 15 g.L^{-1} | 0.41(530) |
| PTCDI 47a / HBC-PhC ₁₂ 63 | 60:40 | 15 g.L^{-1} | 34 (490) |

a result obtained after thermal annealing.

Table 4.1: Summary of the best PVC obtained with the different blends of discotic materials. The PTCDI 47a / HBC-PhC₁₂ 63 blend has been added for comparison.[40]

Unfortunately, despite seven batches of six to nine devices, with three different blend compositions (each time), no working device has been obtained. Nearly all the devices made with these two materials were short-circuited SC. This negative result is attributed to the high fluidity of the blends, under manufacturing conditions. No significant photo-current (maximum 1.2×10^{-4} %!) has been obtained for the only few not SC devices. This negative result has been attributed to the absence of charge transfer between **15e** and **16f**, as evidenced by the optoelectronic properties investigation.

These two materials have been blended separately with other discotic semiconductors. The goal of this experiment was to show that 15e and 16f can be used as semiconductors in PVCs, when they are mixed with well-matched materials. The perylene derivative PTCDI 47a and the hexabenzocoronene derivative HBC-PhC₁₂ 63 were chosen for their known capacity to photo-generate charges. They are indeed the two components of the most efficient discotic materials containing PVC published up to date.[40]

The phthalocyanine **15e** has been mixed with PTCDI **47a**, giving maximum efficiency of 1.1 %. Even if this result is far lower than the record EQE, it can be seen as quite good in comparison with the other published devices.[41] It also proves that the Pc derivative **15e** can act as p-type semiconductor when blended with an appropriate n-type material.

When HATNA **16f** is blended together with HBC-PhC₁₂ **63**, no efficient cell is obtained (maximum EQE = 0.03 %). The reasons of this low efficiency have not been elucidated.

The n- or p-type character of a semiconductor is a relative distinction. When two

electron acceptors are blended together, one of them might act as p-type material. We have then tried to blend the potentially n-type HATNA 16f with PTCDI 47a. Unexpectedly, an efficiency of 1 % has been achieved in the best case. Such an efficiency means that charge transfer occurs between the two materials, and that both conduct their respective charges to the electrodes. This result proves that the HATNA-OR derivative 16f is a good semiconducting material and is not responsible for the negative results obtained with the other blends.

The last system studied has consisted in a tertiary blend, comprising **15e**, **16f** and **47a**. The idea was to use PTCDI as electron accepting material, when both Pc and HATNA act, independently, as p-type semiconductors. Moreover, the absorption spectra of the three components are complementary, giving a device that absorbs light over the entire visible. As expected, the devices obtained by blending these three materials give a photo-current under illumination from 350 to 750 nm. In the best case, an efficiency of 0.41 % has been measured. The no-additivity of the EQE in comparison with the corresponding binary blend devices has been attributed to a change in molecular organisation in comparison to the binary blends.

In conclusion, we have shown that the two tailor-made materials obtained in this work can act as organic semiconductors in photovoltaic device applications. Nevertheless, we have also demonstrated the importance of the choice of the second material. Indeed, even if each material is a good semiconductor, they have to be well-matched otherwise no high efficiency device can be expected.

4.8 Experimental part

The study of the blends photo-physical properties were performed on relatively thick film (around 300 nm), obtained by spin-coating (1500 rpm, 30 sec.) from chloroform solution (50 g.L^{-1}) of known composition. The solid-state absorption spectra were recorded with a Perkin-Elmer Lambda 5 spectrophotometre equipped with a Mettler PF hot stage. The emission measurements were carried out with a SLM-Aminco 3000 diode array spectrophotometre.

The photovoltaic characteristics were carried out on devices fabricated according to the procedure developed in Section 4.1.2. The devices were illuminated from the ITO side at intensities of the order of 0.1 mW.cm^{-2} using a Bentham quartz tungsten halogen lamp, dispersed by a Czerny-Turner Bentham M300 single-grating monochromator using a 1200 lines.mm⁻¹ grating. The sample holder allowed automatic contacting of the 8 pixels + the ITO contact using spring contacts made of berylium-copper. The holder was closed to apply a vacuum and was still optically accessible through quartz windows. A 580 nm filter was used for the range from 600- 1200 nm to block the higher orders of the monochromator grating. Quantum efficiencies were determined by normalisation with a calibrated silicon photodiode (HAMAMATSU S5106). Electrical data were taken and bias was applied using a Keithley 237 source-measure unit.

Solid-state absorption spectra were measured with a Hewlett-Packard 8453 UV-Vis spectrophotometer. The films morphology was investigated by means of a Nanoscope III atomic force microscope AFM used in the tapping mode. The AFM study was carried out on the actual devices for which the spectral response had been measured beforehand.Thermal treatments were performed on a high precision hot stage, under nitrogen filled glovebox. The devices were kept under nitrogen atmosphere during the entire treatment.



Chapter 5

General conclusions and perspectives

5.1 Conclusions

The initial goal of this work was to obtain tailor-made mesogenic materials, specially designed for photovoltaic device applications. For this purpose, two families of materials have been developed. Indeed, both p- and n-type semiconductors are necessary for the manufacturing of efficient photovoltaic devices.





Their chemical structures were designed in order to obtain materials that show a specific set of properties, chosen for to optimise the different key parameters of the charge photo-generation process. These properties are the following: a strong light absorption in the visible, a strong n- or p-type character, a non-crystalline phase at RT, a columnar LC phase, an isotropic phase present below 200 °C. Moreover, the materials have to be accessible with a high degree of purity, in a minimum number of efficient synthetic steps. They also have to be highly soluble in common organic solvents.

Both families of materials have been carefully designed according to the known properties of similar compounds.

In the search of a potentially p-type semiconductor or hole accepting material, we have chosen to develop a new series of phthalocyanine derivatives 15.

For the potentially n-type semiconductors or electron accepting materials, we have decided to study a new series of hexaazatrinaphthylene derivatives **16**.

| properties | requirements | 15e | 16f |
|---|--------------------------|---------------------------|-----------------------------|
| Number of synthetic steps | minimum | 2 | 4 |
| Average global yield | maximum | 18 to $25~%$ | 17 to $32~%$ |
| Purity of the final product | > 99 % | 99.8 % | > 99~% |
| Solubility | maximum | high | high |
| Clearing temperature | $<200^{\circ}\mathrm{C}$ | 177 °C | $168-182^{\circ}\mathrm{C}$ |
| Mesophases | any Col | Colrd and Colho | Col_{hd} |
| State at RT | not K | Col_{rd} | amorphous or L $^{\rm a}$ |
| Absorption coefficient in solution | maximum | 140000 (707 nm) | 98000 (427 nm) |
| (λ) in toluene, in L.mol ⁻¹ .cm ⁻¹ | | | |
| Absorption coefficient in thin film | maximum | 32000 (615 nm) | 77000 (300 nm) |
| (λ) in dm ³ .mol ⁻¹ .cm ⁻¹ | | | |
| EA (in eV) | - | ≈ 4.0 | ≈ 3.5 |
| IP (in eV) | - | ≈ 5.7 | ≈ 6.0 |

^a At the present time, we are unable to give a confident characterisation of this phase. This point is still under investigation.

Table 5.1: Comparison between the required properties and the results.

For each family, a complete series of potentially mesogenic materials have been synthesised. After a comprehensive study of the thermotropic behaviour of each material, the most promising compounds, **15e** and **16f**, have been more extensively investigated. A study of their optoelectronic properties in solution and in the solid-state has been performed, giving important information on the potential of these materials in future photovoltaic applications. Their electrochemical properties have also been investigated in order to probe the p- or n-type character or each family.

A comparison between the physical and chemical requirements and the results obtained with the most promising materials is given in Table 5.1.

All the requirements have been fulfilled for one material of each family. All the eleven potentially mesogenic products can be obtained *via* a relatively efficient two or foursteps synthetic routes, with a high degree of chemical purity. They all strongly absorb light in the visible and show at least one columnar LC phase in their thermotropic behaviour. But only $H_2Pc(14,10)_4$ **15e** and HATNA-OC₁₆ **16f** have, in addition to these last properties, a clearing point below 200 °C and a non-crystalline phase at RT (upon cooling at 10 °C.min⁻¹ from their isotropic phase). Moreover, $H_2Pc(14,10)_4$ **15e** has shown a high tendency to form homeotropic alignments between two glass slides, which remains down to RT. This columnar orientation is certainly the most promising structure for efficient bilayer solar cells. For all these reasons, these two materials have been more extensively studied in this work.

To go further in the understanding of these two materials, the optoelectronic properties of their blends have been investigated. The study of blends of discotic materials is still rare and most of the time difficult to analyse confidently. In this case, the results, however surprising, clearly suggest that the materials are separated in the pristine film. They mainly interact with molecules of the same nature. Upon heating, an optical transition is observed between 27 and 50 °C for all the blends. The resulting absorption pattern indicates the presence of a "solid solution" of phthalocyanines. Such an effect suggest a molecular-scale phase mixing between the two materials. After cooling to RT, this "mixed" phase is partially kept. Two weeks at RT or one night of solvent annealing are necessary to recover the initial pristine absorption spectra. The importance of thermic history is then enhanced.

In order to test the photovoltaic abilities of these two materials, solar cells have been made with **15e** and **16f**, blended together or separately with other discotic materials. The best results obtained for the different device compositions are summarised in Table 5.2.

Unfortunately, none of the solar cells based on the blend of the two most promising

materials synthesised in this work (15e and 16f) has given efficient devices. Despite many attempts, changing the film thickness or coating an additional protecting layer, the best EQE achieved with this system has only been of 1.2×10^{-4} %. This negative result has been explained by the absence of charge transfer between the two materials. The large number of short-circuited devices has been input to the high fluidity of the blend under manufacturing conditions, that might give rise to the diffusion of aluminium atoms through the active organic layer.

| blend | best ratio | solution | EQE % |
|--------------------------------------|------------|------------------------|----------------------------|
| | | concentration | (A nm) |
| HATNA-OR 16f / Pc 15e | 50:50 | 20 g.L^{-1a} | 1.2×10^{-4} (715) |
| PTCDI 47a / Pc $15e$ | 70:30 | 20 g.L^{-1} | 1.15(470) |
| HATNA-OR $16f$ / HBC-PhC_{12} 63 | 40:60 | 20 g.L^{-1} | 0.031 (380) |
| PTCDI 47a / HATNA-OR 16f | 70:30 | 20 g.L^{-1} | 1.07(525) |
| PTCDI 47a / HATNA-OR 16f / Pc $15e$ | 2:1:1 | 15 g.L^{-1} | 0.41(530) |
| PTCDI 47a / HBC-PhC ₁₂ 63 | 60:40 | 15 g.L^{-1} | 34 (490) |

a result obtained after thermal annealing.

Table 5.2: Summary of the best PVC obtained with the different blends of discotic materials. The PTCDI $47a / \text{HBC-PhC}_{12}$ 63 blend has been added for comparison.[40]

The two materials have then been blended separately with the discotic compounds, PTCDI **47a** and HBC-PhC₁₂ **63**, that have given the highest EQE obtained for a discotic materials containing solar cell. When HATNA-OC₁₆ is used as n-type materials, in blend with HBC-PhC₁₂ the resulting devices are less efficient. No reliable explanation of this result has been found. In the other hand, when PTCDI **47a** is used as n-type semiconductor with both **15e** and **16f**, maximum EQE of > 1 % have been achieved.

Finally, tertiary devices, consisting in blends of PTCDI 47a, HATNA-OC₁₆ 16f, and $H_2Pc(14,10)_4$ 15e have been made. It was expected that the complementarity of these three materials in absorption spectra would lead to charge photo-generation for any excitation wavelength in the visible. And indeed, charges are produced by shining the device from 350 to 750 nm, with, in the best case, a maximum EQE of 0.4 % has been obtained. This is the first example of three-components discotic materials-containing solar cells.

The two tailor-made materials obtained in this work can then act as organic semi-

conductors in solar cells. Nevertheless, the results obtained in this work demonstrate the importance of the choice of a pair of materials. Indeed, even if each material is a good semiconductor, they have to be well-matched otherwise no high efficiency device can be expected.

Even if the device efficiencies achieved in this work (> 1 %) are far lower than the best result reported with discotic materials (34 % [40]), they are of the same order than the most commonly reported values. [41]

The results of this work contribute to reinforce the potential of discotic mesogens as semiconductors in photovoltaic device applications. Nevertheless, many perspectives can be envisaged. Some of them are developed in the next section.

5.2 Perspectives

Regarde plus loin, la solution s'y trouve sûrement ...

In addition to some additional investigations that have to be done to better understand the properties of the materials obtained in this work (nature of the "black" phase, more accurate frontier orbital energy determination, ...), and of their blend (better understanding of the influence of film morphology of device efficiency, ...), some small changes in the molecular design can be envisaged.



Figure 5.2: Suggested chemical structures of high potential future discotic materials for photovoltaic device applications. R = alkyl chain, X = halogen atom.

In order to improve the charge mobility and the exciton diffusion length in the phthalocyanine derivative 15, one can envisage the synthesis of the corresponding platinum (II) derivatives **64**. Indeed, introduction of a platinum atom in the cavity of the Pc ring has been shown to reduce the distance between the disks in the columnar packing (from \approx 3.5 Åfor H₂Pc to < 3.3 Åfor PtPc).[200] This closer packing is expected to dramatically improve the performances of the final material.

In the other hand, we have seen that the HATNA-OR derivatives 16f have not been efficient as n-type material, when blended with HBC-PhC₁₂. In order to increase the electron affinity of 16, one can envisage the introduction of halogen atoms in the aromatic HATNA system to form 65 (with three or six halogen atoms). Indeed, theoretical investigations performed in Mons by Vincent Lemaur, have shown that the charge mobility would not been much affected by the presence of halogen atoms, but the they are expected to increase the material's electron affinity.[156]

Finally, the conditions of PVC's manufacturing can be modified (solvent, temperature

of aluminum evaporation, nature of the cathode, addition of a thin polymer layer (e.g. PEDOT-PSS), ...) in order to change the film morphology or to improve charge transfer to the electrodes. The use of other blends can also be envisaged: with other discotic materials, soluble C60 derivatives, inorganic semiconductors such as cadmium selenide CdSe, or conjugated polymers.

The field of organic electronics is still at its beginning. No discovery can be made without research ...

Science may set limits to knowledge, but should not set limits to imagination. Bertrand Russell (1872 - 1970)



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