Thermal Properties, Molecular Structure, and Thin-Film Organic Semiconductor Crystallization

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INTRODUCTION

Organic semiconductors hold the promise of further deployment in low-cost, lightweight, flexible electronic devices. Examples of their success include organic light-emitting diodes (OLEDs), which have achieved considerable commercial success, and organic photovoltaics (OPVs), which are experiencing steadily increasing power conversion efficiencies and now exceed 17%. However, these materials are currently made of highly disordered, amorphous layers despite the demonstration of superior charge carrier mobility and exciton diffusion length in crystalline frameworks. For devices such as OPVs and certain lighting applications where a large active area is required, attaining coverage of a crystalline film can prove difficult but has been shown to have considerable benefits with regard to the exciton diffusion length and energy loss. Furthermore, grain boundaries need to be minimized as they can be sources of recombination and are detrimental to device performance. Toward both of these goals, progress has been made using methods such as abrupt thermal annealing, growth on self-assembled monolayers, or inert substrates, organic vapor phase deposition, organic epitaxy, structural templating, and substrate-induced phases.  

To achieve large-area crystalline domains with complete film coverage, we build upon a technique that involves thermally annealing an amorphous thin film resulting in single-crystal grains, or platelets, with dimensions of hundreds of microns. This method takes advantage of uniform film formation in the initially deposited amorphous film, with the development of long-range crystallization only occurring in a subsequent step. However, our understanding of the role that structural and thermal properties play in this transformation requires further development. For instance, it is unclear if the molecular flexibility arising from a given material’s number of conformers enhances or inhibits nucleation. Here, we expand not only the number of materials that are capable of crystallizing as platelets but also begin to develop indicators that might allow prediction of an untested molecule to crystallize into these long-range, platelet morphologies.  

Since this process requires the initial film to be amorphous, materials need the ability to make a glassy film as well as be able to crystallize. Therefore, candidate materials require a balance of properties that allow for glass formation and crystallization. Many works have been devoted to understanding what makes a good glass-forming material, such as nonplanar molecular structures, the existence of different conformers, large molecular sizes, the presence of bulky side groups, the presence of a spiro junction, and a sufficient number of bonds with rotational degrees of freedom. On the other hand, molecules cannot possess too many of these characteristics,21 the presence of a spiro junction,22 and a sufficient number of bonds with rotational degrees of freedom.17 On the other hand, molecules cannot possess too many of these characteristics, which can help determine which organic molecules have a greater likelihood of growing into large-scale crystalline frameworks, a key step for improving the charge carrier mobility and exciton diffusion length in organic semiconductors.

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help determine whether a material is able to (a) crystallize in a thin film and, if so, (b) crystallize as a platelet. These trends are based on the molecular structure and thermal properties of the molecule, both of which are readily accessible. To investigate this topic the crystallization and thermal properties of a series of organic semiconducting molecules with slightly different molecular structures are studied. Since crystal nucleation and growth are highly dependent on temperature, the molecular structure will have a coupled effect on both the thermal properties and whether a material will crystallize. To determine the crystallizability of these materials, they are deposited as amorphous thin films, annealed, and then analyzed under a polarized optical microscope (POM). Thermal properties are determined by differential scanning calorimetry (DSC). Using DSC, we compare how subtle molecular structure alterations impact thermal properties and thus crystallizability.

We present a metric based on thermal properties that illustrates trends distinguishing materials that can crystallize into a platelet morphology, spherulite morphology, or those that resist crystallization altogether. We find that the crystallization driving forces at the crystallization temperature ($\Delta G_c$) and the melting point ($T_m$) are able to explain not only the crystallizability of materials but also show trends involving platelet formation versus spherulite formation. These results, along with the molecular structure of the molecules investigated, allow for observations involving the effects of various side groups and attachment locations on crystallization.

### METHODS

#### Materials

Materials were purchased from commercial vendors:

**Lumtec:** N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB), N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-2,2'-dimethylbenzidine ($\alpha$-NPB), N,N'-bis(naphthalen-2-yl)-N,N'-bis(phenyl)-benzidine ($\beta$-NPB), N,N,N',N'-tetra-naphthalenyl-benzidine ($\alpha$-TNB), N,N,N',N'-tetra-naphthalenyl-2-yl-benzidine ($\beta$-TNB), 4,4',4''-tris(N-(naphthalen-1-yl)-N-phenyl-amino)triphenylamine (1T-NATA), 1,3,5-tris(carbazol-9-yl)-benzene (TCP), tris(4-(5-phenylthiophen-2-yl)phenyl)amine (TPTPA), 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi), 4,7-diphenyl-1,10-phenanthroline (Bphen), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), 4,4'-bis(carbazol-9-yl)biphenyl (CBP), N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)-benzidine (TPD), di-[4-(N,N-di-p-tolyl-amino)-phenyl]cyclohexane (TAPC), N,N,N'-bis(9,9-dimethyl-9H-fluoren-2-yl)-N,N,N'-triphenyl-biphenyl-4,4' diamine (BFDPB), 5,10,15,20-tetraphenyldibenzeno[1,2,3-cd:1',2',3'-lm]perylene (DBP), 9,9-bis(4-carbazol-9-yl)-phenyl]fluorene (FL-2CBP), and boron subphthalocyanine chloride (SubPc).

**Nichem:** rubrene and 4,4',4''-tris(carbazol-9-yl)-9H-fluorine (TCTA).

**Sigma-Aldrich:** N,N,N',N'-tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD), 4,4',4''-tris(N-3-methylphenyl-N-phenyl-amino)triphenylamine (m-MTDATA), and 6,13-diphenyl-pentacene (DPP).

**TCI America:** N,N,N',N'-tetraphenylbenzidine (TPB).

![Figure 1. Polarized optical microscopy (POM) images and molecular structures of the materials considered in this work. Each image is the result of an optimization that focused on producing plateletlike crystal domains, testing various film thicknesses, annealing temperatures, and underlayers. The materials have been categorized into three groups depending on the crystal morphology: platelet-forming, spherulite-forming, and those that resist crystallization. Materials that resist crystallization showed little to no crystal growth and therefore have no associated POM images.](image-url)
Ossila: 2,4,5,6-tetra(9H-carbazol-9-yl) isophthalonitrile (4CzIPN).

All materials were purchased and used as received except rubrene, NPB, BCP, TCTA, DPP, and DBP, which were first purified via thermal gradient sublimation. Furthermore, 6,13-bis(2-thienyl)pentacene (DTP) was synthesized by Prof. John Anthony for this project. The material 2,2′-bis(4′-(carbazol-9-yl)phenyl)-biphenyl (BCBP) could not be found commercially so the data for BCBP was determined from literature\textsuperscript{11} (see Acknowledgments).

**Fabrication.** All substrates were cleaned successively by sonication in deionized water with Extrax soap in a 6:1 ratio, deionized water, acetone, and isopropanol followed by an oxygen plasma treatment. Samples were deposited using thermal evaporation with a base pressure of $\sim 10^{-7}$ Torr. The annealing step was completed by placing the samples directly on a preheated hotplate in a nitrogen-filled glovebox.

**Characterization.** Images of the annealed samples were taken with a polarized optical microscope (Olympus BX60FS). Ellipsometry measurements were done with a J.A. Woollam M-2000 variable angle spectroscopic ellipsometer along with CompleteEASE software. Differential scanning calorimetry measurements were performed with a TA Instruments Differential Scanning Calorimeter Q2000 equipped with an RCS90 cooler under nitrogen flow. The pans used in the DSC measurements were Tzero Aluminum Hermetic pans and lids and were filled with approximately 5–10 mg of material and hermetically sealed. The DSC is calibrated frequently according to standard procedures (using indium and sapphire). To observe a crystallization peak, some materials required a seed crystal either from the as-received material or a crystal we grew via thermal gradient sublimation. For these experiments, a hole was made in the top of the sealed pan, where the seed crystal was added after melting and quenching steps. A hole was also made in the reference pan. The X-ray diffraction (XRD) characterization was completed with a Bruker D8 Discover X-ray diffractometer with a copper source and a wavelength of 1.54 Å.

**RESULTS AND DISCUSSION**

A series of molecules were chosen with similar molecular structures, as shown in Figure 1. Of particular note are families of molecules that differ only slightly. For instance, $\alpha$-NPD (Figure 1q) and $\beta$-NPD (Figure 1r) differ from NPB (Figure 1c) by the addition of two methyl groups and the attachment location of the naphthalene groups, respectively. Another example is the molecules MeO-TPD (Figure 1h) and TPD (Figure 1s), which are both based on the core of TPB (Figure 1g) but with the addition of methoxy groups and methyl groups, respectively. Although not listed here, one can recognize other subsets of molecules with shared cores but differing end groups by examining the molecular structures in Figure 1. The other materials shown here include rubrene (Figure 1a), TPBi (Figure 1b), TCTA (Figure 1d), BCBP (Figure 1e), 4CzIPN (Figure 1f), BPhen (Figure 1i), BCP (Figure 1j), TTPTPA (Figure 1k), CBP (Figure 1l), $\alpha$-TNB (Figure 1m), TCP (Figure 1n), BF-DPB (Figure 1o), 1T-NATA (Figure 1p), $\beta$-TNB (Figure 1t), m-MTDATA (Figure 1u), and TAPC (Figure 1v).

Each of these materials is deposited on a glass/indium tin oxide (ITO) substrate via thermal evaporation with thicknesses ranging from 20 to 80 nm. Subsequently, the films are annealed on a preheated hotplate in a nitrogen-filled glovebox, as described elsewhere.\textsuperscript{9,10} A series of annealing temperatures are tested for each film thickness beginning just above the material’s glass transition temperature ($T_g$) and increasing in 40 °C steps. The films are annealed for 5–10 min depending on the material. All films are then examined with a POM to determine if the film crystallized. For any promising materials, as indicated by large-area crystals with few branching arms, the above process is repeated with smaller step sizes in thickness and temperature focused around the parameters that yielded the best sample from the initial experiment. Another parameter we use to tune these materials to grow as platelets is the use of a thin underlayer (approximately 5 nm thick) between the ITO substrate and the material under study. This underlayer is chosen based on the relationship between its $T_g$ and the temperature at which crystal growth begins for the material being studied. The use of an underlayer has shown to help organic materials crystallize more reliably and in larger domains.\textsuperscript{10}

The results of these experiments are shown in Figure 1, where each image represents the most plateletlike crystal we could grow, characterized by single-crystal domains, low density of branching, or thick rays. Therefore, each has different growth conditions such as annealing temperature, annealing time, film thickness, and underlayer as described in Table S1. The film thickness was verified by ellipsometry to within a couple of percent of the reported thickness. Based on the POM images, each material is categorized as platelet-forming, spherulite-forming, or those that resist crystallization. Platelets are characterized by crystals that appear under a POM as large single-hued domains, which indicate that each domain is a single crystal, as confirmed previously for the case of rubrene.\textsuperscript{10} The other platelet-forming materials identified here include TPBi, NPB, TCTA, BCBP, and 4CzIPN and have been shown to grow in this morphology elsewhere.\textsuperscript{11,23} Spherulites can exhibit morphologies ranging from circular, needlelike structures to smooth gradients reminiscent of a Maltese cross.\textsuperscript{24} As further evidence of the crystallinity of these films, XRD measurements were taken of each film with the results shown in Figure S1. Materials with known crystal structures have their simulated powder XRD pattern included in these plots, illustrating that the thin-film structures match that of the bulk crystal structures. Materials that resist crystallization as a thin film show no contrast under the POM, implying that the film remained amorphous. Some materials in this category, like TPD and $\alpha$-NPD, can exhibit a small degree of crystallization when annealed for several hours (see Figure S2). However, these crystals are spindlelike and do not completely cover the substrate, unlike the platelet and spherulite-forming materials. Therefore, these materials are better grouped in the resist crystallization category since their crystal growth behavior is distinct from the other groups.

It should also be noted that all of the materials in the platelet-forming category, except BCBP, can form both platelets and spherulites depending upon the annealing temperature, the thickness of the film, or the underlayer. Annealing conditions and POM images of these materials grown as spherulites can be found in Table S2 and Figure S3. It is likely that BCBP can also grow spherulitic, but lacking access to the material, we could not test this ourselves. For the platelet-forming materials we worked with, we found that it is always possible to change the crystallization conditions (e.g., by elevating the temperature or removing the underlayer) to allow for spherulitic growth. However, the opposite is far from

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true; it is not always possible to take a spherulite-forming material and adjust parameters for platelet growth. Even annealing experiments conducted just below a material’s melting point, which has been shown to grow single crystals,25 resulted in spherulitic growth as we have demonstrated for annealing experiments conducted just below a material’s DSC thermogram, respectively. If data are missing in a row, it means that no feature was present in the DSC measurement. Materials with multiple $T_m$ or $T_c$ values exhibit polymorphism.

Following categorization of the morphology of these materials, we group them according to the number of single bonds to bulky, conjugated, side groups. Methyl groups are not included because these groups are not conjugated, cannot rotate, and do not add substantially to a material’s degrees of freedom (rotational, translational, etc.). We include the CN groups on 4CzIPN and methoxy groups in MeO-TPD in this single bond category due to the nonsigma bonding in these groups. The number of single bonds for each molecule is listed in Table 1. These data, along with the categorization of Figure 1, are plotted as histograms in Figure S5.

When considering simply whether or not a material has the propensity to crystallize starting from an amorphous thin film, Figure S5a shows that materials that tend to crystallize have fewer single bonds than materials that resist crystallization. While there is some overlap between the groups in the 7–11 single bond range, it is clear that after a point (≤6) all materials that we studied and that possess a relatively small number of single bonds crystallized. One possible explanation of this result is that a greater number of rotatable bonds has been linked to better glass-forming ability.17 Good glass-forming materials resist crystallization due in part to their flexibility, which makes it difficult for molecules to find the correct orientation that facilitates crystallization.18 More rigid molecules, which are characterized by fewer single bonds, have fewer degrees of freedom, making it easier for them to find the proper conformation that leads to crystallization.

We can further break down the group of molecules that readily crystallize into those that form platelet or spherulite morphologies, as visualized in Figure S5b. In this case, there appears to be an optimal range of single bonds, between 4 and 7, where platelets are able to grow. However, since there are spherulite-forming materials in this range as well the single bond metric is limited in its ability to distinguish between the crystallizing groups. Figure 2b, though, illustrates the point that platelet morphology is likely to exist only in a certain range of single bonds. Too many single bonds, as discussed above, inhibit crystal growth. In the other extreme case of zero single bonds, there are well-known materials that cannot even form an amorphous film from thermal evaporation because they crystallize upon deposition, such as polycyanes like tetracene or pentacene26 or C60.27 Such materials are not included in this study because they tend to form small crystalline domains and therefore have many grain boundaries. All in all, while this

| molecule | $T_m$ (°C) | $T_c$ (°C) | $T_\beta$ (°C) | $\Delta H_m$ (J/g) | number of single bonds | source
|----------|------------|------------|---------------|-------------------|------------------------|------|
| a rubrene | 293        | 135        | 173           | 102.7             | 4                      | tw
| b TPBi   | 275        | 120        | 151           | 79.0              | 6                      | tw
| c NPB    | 274        | 96         | 175           | 101.3             | 7                      | tw
| d TCTA   | 268        | 151        | 213           | 41.6              | 6                      | tw
| e BCBP   | 277        | 120        | 170           | 5                 | 11                     |      |
| f 4CzIPN | 378 ± 1    | 106        |               |                   |                        |      |
| g TPB    | 231        | 73         | 109, 153      | 103.2             | 7                      | tw
| h MeO-TPD| 187        | 54         | 132           | 71.9              | 11                     | tw
| i BPhen  | 220        | 62         | 95            | 120.1             | 2                      | tw
| j BCP    | 287        | 189 ± 7    |               | 121.7             | 2                      | tw
| k TPTPA  | 208        | 86         | 113           | 52.8              | 9                      | tw
| l CBP    | 281        | 92         |               | 75.4              | 3                      | tw
| m α-TNB  | 395 ± 10   | 157        | 198           | 7                 | 40                     |      |
| n TCP    | 274        | 124        | 168           | 58.8              | 3                      | tw
| o BF-DPB | 262        | 112        | 187 ± 5       | 84.8              | 7                      | tw
| p IT-NATA| 119        |            |               | 12                | 7                      | tw
| q α-NPD  | 252        | 95         | 187           | 90.6              | 7                      | tw
| r β-NPB  | 96         |            |               | 7                 | 7                      | tw
| s TPD    | 168        | 65         | 89            | 77.4              | 7                      | tw
| t β-TNB  | 233        | 132        | 170           | 55.6              | 7                      | tw
| u m-MTDATA| 203       | 75         | 160           | 50.7              | 12                     |      |
| v TAPC   | 184        | 81         | 147           | 73.3              | 8                      | tw

*tw—this work; otherwise, reference is provided. *Determined from DSC conducted in this work. *Out of DSC range so determined by melting on a hotplate in a nitrogen-filled glovebox. *The $T_m$, $T_\beta$ and $T_c$ values were determined using the onset, midpoint, and onset values of each feature in a material’s DSC thermogram, respectively. When considering simply whether or not a material has the propensity to crystallize starting from an amorphous thin film, Figure S5a shows that materials that tend to crystallize have fewer single bonds than materials that resist crystallization. While there is some overlap between the groups in the 7–11 single bond range, it is clear that after a point (≤6) all materials that we studied and that possess a relatively small number of single bonds crystallized. One possible explanation of this result is that a greater number of rotatable bonds has been linked to better glass-forming ability.17 Good glass-forming materials resist crystallization due in part to their flexibility, which makes it difficult for molecules to find the correct orientation that facilitates crystallization.18 More rigid molecules, which are characterized by fewer single bonds, have fewer degrees of freedom, making it easier for them to find the proper conformation that leads to crystallization.

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simplistic model of single bonds cannot pinpoint which materials will form plateletlike crystals, it can serve as an easy sorting tool to find promising materials to investigate further.

To deepen our understanding of what allows some materials to crystallize while others do not, we consider three materials: NPB, α-NPD, and β-NPB. We compare this subset of materials because, despite similar molecular structures, only NPB crystallizes readily into plateletlike morphology. Structurally, they differ by the addition of methyl groups in the case of α-NPD or the attachment locations of the naphthalene groups in β-NPB’s case. Therefore, these materials represent a useful case study into how small changes in molecular structure can affect crystallization in a thin film. Thermal properties from DSC are shown in Figure 2. Each material was prepared by melting the material in the DSC pan and subsequently cooled at a rate of 5 °C/min to below its Tg. No crystallization peak was observed upon cooling meaning each material began amorphous, mimicking the as-deposited amorphous thin films before the annealing step. A heating rate of 1 °C/min was used to produce the thermograms in Figure 2.

From these measurements, we are able to extract Tg, Tm, and ΔHm, the enthalpy of melting (ΔHm), and the crystallization temperature (Tc) if it exists. These values are included in Table 1. Figure 2 shows that NPB crystallizes upon heating while neither α-NPD nor β-NPB does, consistent with our observations upon thin-film annealing (cf. Figure 1). The Tc values are also consistent with the literature.28 While α-NPD did not crystallize upon heating, as shown in Figure 2, it did crystallize during its first DSC scan (not shown) because the material started partially crystalline as received from the vendor. The first heating of α-NPD completed the crystallization, and therefore, we were able to obtain Tg, Tm, and ΔHm for α-NPD. This was not the case for β-NPB, which was received amorphous and did not crystallize through DSC. In general, however, materials classified here as resistant to thin-film crystallization does not imply that they cannot crystallize in the bulk or through other methods. In fact, most materials in this category did crystallize during DSC measurements, albeit slowly, which allow us to access relevant thermal properties, such as Tg, Tm, and ΔHm.

These thermal properties also allow us to determine crystallization driving force (ΔG) from the classical nucleation theory using eq 1, assuming that the change in heat capacity is negligible.49

\[
\Delta G = -\frac{\Delta H_m}{T_m}(T_m - T)
\]

(1)

where T is the temperature of the material. To be able to compare ΔG between materials, we evaluate it at the onset temperature of the exothermic feature in the DSC scan of each material, or at T = Tc. We denote this value ΔGc.

Using eq 1 and the Tc for NPB and α-NPD, we find that ΔGc is −10.8 and −6.9 kJ/mol for NPB and α-NPD, respectively. Since ΔGc is greater in magnitude for NPB and we observe that NPB crystallizes as a thin film, whereas α-NPD does not and has a ΔGc smaller in magnitude, we believe ΔGc is to be a good metric to determine whether a material will readily crystallize or resist crystallization as a thin film. Additionally, the melting points of NPB, α-NPD, and β-NPB vary by more than 100 °C with NPB having the highest melting point. Therefore, of the thermal properties that may be useful predictors of good crystal formation, Tm and ΔGc appear promising. In fact, it has been demonstrated that organic materials that tend to crystallize have on average higher Tm and ΔHm and therefore larger ΔG.17 This is not to say that thermal properties, such as these, are the only method to be used to predict crystal growth. Molecular diffusion coefficients, as discussed later, certainly play a role. In fact, the variety of molecular sizes, which diffusion coefficients inversely depend on, and molecular weights of the materials considered here guarantee different degrees of molecular mobility. Thermal properties, however, we deemed as more accessible than diffusion coefficients, so we focus on them here.

To expand the scope of the work, thermal properties were determined for the other materials we attempted to crystallize either via DSC measurements (see Figure S6) or from the literature. The results are listed in Table 1. We note, however, this study was not limited to the materials listed here. Other materials were found to grow spherulitic; however, since certain thermal properties could not be determined, they are excluded from Table 1 and the following thermal property analysis but are included in the histograms in Figure S5. Information and POM images of these materials can be found in Figure S7.

Since we present data related to thin-film crystallization and bulk thermal properties, we note that a material’s bulk Tm and Tc values can differ from their thin-film values. As the film thickness is reduced, these quantities decrease.12 The motivation for using the bulk thermal properties is twofold. First, the bulk thermal properties are easier to determine than thin-film values because bulk properties do not depend on the thickness and do not require advanced measurement techniques like ellipsometry35 or flash DSC.33,34 With our aim of providing an accessible way to distinguish between materials that crystallize and those that do not crystallize as a thin film, we avoided relying on these uncommon techniques. The second reason for using bulk thermal properties is that the thin-film effect on Tm and Tc is minimal until approximately 20 nm and most of the films studied here are thicker than 20 nm.

It should be noted that some of the materials exhibit polymorphism, namely, rubrene, TCTA, TCP, TPTPA,42 and TPB. In this work, we focus on the orthorhombic phase of rubrene because this is the phase of the platelets in Figure 1a, confirmed via grazing-incidence X-ray diffraction (GIXD).6 The crystal phase of rubrene that grows in DSC is also orthorhombic because the measured Tm is consistent with that of orthorhombic rubrene.43 For TCP, there are two melting
peaks, one with an onset temperature of 274 °C and another at 328 °C. The higher \( T_m \) was only observed on the first heating in the DSC, implying that the crystal phase of the as-received TCP differs from the phase that occurs on subsequent heatings. The lower-\( T_m \) crystal has a \( T_c \) of 168 °C, which is consistent with the annealing temperature used in the thin-film experiments. Therefore, we assign the lower \( T_m \) value with the observed thin-film crystal. The polymorphism of TCTA is exhibited by two crystallization peaks beginning at 190 and 213 °C. The platelet crystals we observe in the thin film begin forming at 190 °C, so we assign the platelet crystal phase to this \( T_c \) and its associated melting peak, \( T_m = 296 \) °C. The lower crystallization temperatures for TPTPA and TPB, 113 and 109 °C, respectively, are consistent with the temperature at which crystals begin to appear in thin films of these materials. Therefore, these \( T_c \) values are used to calculate each material’s \( \Delta G_c \).

With these thermal properties measured, we plot \( \Delta G_c \) against \( T_m \) in Figure 3 since these were the two properties imply a high \( \Delta H_m \), \( T_m \) and \( T_m - T_c \). Large \( \Delta H_m \) means there is a substantial energy difference between the crystalline phase and the amorphous phase of a given material, where the crystalline phase is more energetically favorable. Materials with high \( T_m \) require more energy to break down the crystalline lattice, implying they have a more stable crystal compared to low \( T_m \) materials. This stability makes it more energetically favorable for high \( T_m \) materials to form nuclei in an amorphous film and grow crystalline. As a result, a material with a large \( \Delta G_c \) due to large \( \Delta H_m \) and \( T_m \) is a material that has a strong propensity to crystallize. Alternatively, small-\( \Delta G_c \) materials, like the ones that resist crystallization, have a weak propensity to crystallize.

Another way to illustrate this is by considering energy barrier to homogeneous nucleation (\( \Delta G^* \)) derived by the classical nucleation theory as expressed in eq 2

\[
\Delta G^* = \frac{16\gamma_d^3}{3} \frac{1}{\Delta G^2}
\]

(2)

where \( \gamma_d \) is the interfacial energy between the nucleus and amorphous material. Therefore, we expect materials with high \( \Delta G_c \) to have a small \( \Delta G^* \), or a low barrier to nucleation, making crystallization easier. Materials that resist crystallization, which have a small \( \Delta G_c \), are expected to have a relatively large energy barrier to nucleation, effectively inhibiting crystallization.

Since eq 2 is derived for three dimensions, it is worth noting that the heterogeneous energy barrier for nucleation on a substrate is \( \Delta G^* \) \( f(\theta) \), where \( f(\theta) \) is

\[
f(\theta) = \frac{2 - 3 \cos(\theta) + \cos^3(\theta)}{4}
\]

(3)

and \( \theta \) is the contact angle between the nucleus and the substrate. Within our experiments, crystallization was monitored on both glass and ITO, which have different surface energies and therefore different \( \theta \). In nearly every case, we found that a material’s crystal category (platelet, spherulite, or resists crystallization) does not depend on whether the material was grown on ITO or glass meaning that \( f(\theta) \) has a minimal effect on the category each material is placed. Another modification to classical nucleation theory we consider is that confining a material to two dimensions can lower the energy barrier to nucleation. However, since all materials were crystallized as nearly 2D films they all benefit similarly. It therefore suffices to simply consider \( \Delta G^* \) and therefore \( \Delta G_c \) because it is the only significant differentiating factor between the materials.

The other trend we can extract from Figure 3 is that platelet-forming materials have high \( T_m \) and large \( \Delta G_c \) separating them from spherulite-forming materials. This result is interesting given that spherulitic growth requires a high driving force whether it be large undercooling \((T - T_m)\) when crystallizing from a melt or large supersaturation when crystallizing from a solution. However, the conditions in which our materials are crystallized differ from these more commonly treated conditions. Namely, our materials are confined to nearly two dimensions where the thickest films we tested were only 80 nm. Additionally, the amorphous films we studied are prepared via thermal evaporation and therefore have a different thermal history than materials that are crystallized from a melt, the situation for most of the materials considered in ref 25. While we acknowledge these differences, it does not fully explain why

![Figure 3](https://dx.doi.org/10.1021/acs.jpcc.0c09408)

Figure 3. Crystallization driving force at \( T_c \) as a function of \( T_m \) for the materials for which \( \Delta G_c \) could be determined. The center of each shaded box is the average \( \Delta G_c \) and \( T_m \) for the corresponding category. The distance from the center to the edge of each box is one standard deviation.

that NPB and \( \alpha \)-NPD differed by significantly. The three crystal growth categories are separated by \( \Delta G_c \) and \( T_m \) as indicated by the shaded boxes included in Figure 3. The center of each box indicates the average \( \Delta G_c \) and \( T_m \) values, and the distance from the center to the edge is one standard deviation of the data for the corresponding category. We note that all of the materials that resist crystallization as a thin film have a smaller driving force of crystallization than the spherulite and platelet-forming materials. Plateletlike materials tend to have high \( T_m \) and large \( \Delta G_c \), while spherulite-forming materials tend to fall between these extremes. Not all of the materials considered in this study are plotted in Figure 3 because either \( \Delta H_m \) or \( T_c \) values could not be determined.

It is worth noting here that we also investigated the role entropy has to play since the entropy of melting is readily calculated from \( \Delta H_m \) and \( T_m \) (\( \Delta S_m = \Delta H_m/T_m \)). Furthermore, entropy is a relevant factor for this work since configurational changes that may arise from the number of rotatable bonds contributes to its value. However, as Figure S8 shows, \( \Delta S_m \) does not explain the differences between the three proposed categories so we return to the trends observed with \( \Delta G_c \) in Figure 3.

To understand why low-\( \Delta G_c \) materials resist crystallization, we note that organic materials with large (in magnitude) \( \Delta G_c \)
materials with large $\Delta G_c$ and high $T_m$ seem to prefer to grow as platelets rather than the more common spherulitic growth. We propose the most likely origin of the spherulitic growth stems from the role molecular mobility plays. At large undercooling values, the rotational diffusion coefficient ($D_\beta$) decreases faster than the translational diffusion coefficient ($D_\alpha$), effectively decoupling the two parameters. This leads to a situation where molecules cannot rotate fast enough to join the crystal growth front, resulting in noncrystallographic branching and spherulites. To connect this with the large $\Delta G_c$ and $T_m$ of platelet-forming materials, we note that a high $T_m$ also provides for, on average, high $T_c$. In our experiments, we find $T_{c,avg} = 172 \pm 11 \degree C$ for platelet-forming materials and $T_{c,avg} = 143 \pm 41 \degree C$ for spherulite-forming materials, where the error is one standard deviation. Therefore, platelet-forming materials tend to grow in higher energy environments than spherulite-forming materials, which may allow their diffusion coefficients to remain coupled. Sufficient molecular mobility paired with high $\Delta G_c$ could explain the formation of platelets.

To show an example of how thermal properties and molecular structure play a role in crystallization, we consider again the NPB family of materials. Between NPB and $\alpha$-NPB for instance, the addition of the methyl groups can, as in this case, reduce $T_m$ and $\Delta H_m$. In the context of the trends presented here, the addition of the methyl groups lower $\alpha$-NPB’s $T_m$ and $\Delta H_m$ and therefore $\Delta G_c$ which may explain why it resists crystallization. There is also evidence that the attachment location of naphthalene groups can dramatically alter $T_m$—mirroring the difference we see between NPB and $\beta$-NPB. In this case, the naphthalene’s attachment site on $\beta$-NPB lowers its $T_m$, which we have shown to be characteristic of materials that resist crystallization. These molecular effects are not confined to the NPB family, however. The effect of the methyl group can be seen for TPB and TPD while the $\alpha$-TNB and $\beta$-TNB pair is another example of how the naphthalene attachment site impacts thermal properties and therefore crystallization. There is also evidence here that carbazole groups are beneficial for crystal formation. For instance, comparing TCTA, TPTPA, 1T-NATA, and m-MTDATA, which all share a triphenylamine core, we find that only TCTA forms platelets. The carbazole groups on TCTA give it the highest $T_m$ and $\Delta G_c$ of this subset, which may be why it crystalizes so well.

In the context of the role molecular structure plays in crystal growth, it is worth mentioning that neither molecular symmetry nor packing motif is able to explain the differences presented here (see Figure S9 for more detail). While materials that resist crystallization as a thin film seem to be slightly less symmetric, which is consistent with other results, there also exist platelet-forming and spherulite-forming materials with a similar degree of symmetry. Therefore, symmetry is not a reliable predictor of a molecule’s propensity to crystallize as a thin film.

## CONCLUSIONS

Of the organic semiconductors considered in this work, six can be annealed into large-area thin-film single-crystalline domains or platelets. Nine of the materials formed spherulitic crystals characterized by a high degree of noncrystallographic branching. The last group of materials remained mostly amorphous despite our best efforts to crystallize them through different annealing temperatures, film thicknesses, and the use of underlayers. Our thermal property analysis finds that a good indicator of platelet-forming behavior in organic small molecules is having a high $T_m$ and high $\Delta G_c$. Additionally, a distinction between materials that crystallize readily and those that do not is identified through $\Delta G_c$. We show that materials with small $\Delta G_c$, implying a low driving force to crystallize and large energy barrier to nucleation, resist crystallization as one might expect. While it remains elusive to be able to predict reliably how an organic semiconducting thin film will crystallize, we present trends utilizing accessible material properties that allow for a faster, more efficient selection of candidate materials with a good chance to crystallize into a platelet, spherulite, or not at all. With continued research, eventually, it may be possible to design crystallizable molecules for a given application.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c09408. Crystal growth conditions, XRD, extended duration annealing experiments, POM images of other materials included in this work and platelet-forming materials grown as spherulites, near-$T_m$ annealing experiments, histogram of a number of single bonds to the conjugated core, differential scanning calorimetry measurements, plots of $\Delta S_m$ and crystal structure symmetry analysis (PDF).

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