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Supporting Information

Formation of a Dinuclear Mercury(II) Complex with a Regular Bis-Strapped Porphyrin Following a Tunable Cooperative Process**

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Total energy and cartesian coordinates of the complexes optimized at the B88P86/SDD level of theory.

Experimental part

General procedures

Pyridine was distilled over potassium hydroxide, dichloromethane was distilled over CaH_2 and stored on potassium carbonate. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance instrument operating at 500 MHz and 125 MHz, respectively. UV-vis spectra were recorded on a Uvikon XL spectrometer. IR spectra were recorded on a Bruker IFS 28 spectrometer.

Synthesis of 1Hg$_2$

To a solution of **1**[1] (17 mg, 13.5 μmol) in pyridine (3 mL) was added Hg(OAc)$_2$ (13 mg, 40.5 μmol). The solution was stirred at RT for 15 min (UV-vis monitoring showed complete metal insertion) then concentrated to dryness. The green-purple solid was dissolved in neutralized dichloromethane, the insoluble mercury salts were removed by filtration on celite, and the solution was then evaporated under reduced pressure. This operation was repeated twice, yielding 18 mg of **1Hg$_2$** as a green solid (82 %). ^{1}H NMR (CDCl$_3$, 298 K, 500 MHz) : δ 9.37 (2H, d, J = 4.9 Hz, βpyr), 9.30 (s, 2H, βpyr), 9.29 (2H, d, J = 5.0 Hz, βpyr), 9.21 (2H, d, J = 8.4 Hz, H$_{Ar}$), 9.16 (2H, d, J = 8.4 Hz, H$_{Ar}$), 8.93 (2H, s, βpyr), 8.08 (2H, d, J = 7.4 Hz, H$_{Ar}$), 7.99 (2H, t, J = 7.6 Hz, H$_{Ar}$), 7.96 (2H, d, J = 5.0 Hz, H$_{Ar}$), 7.90 (2H, t, J = 7.8 Hz, H$_{Ar}$), 7.82 (2H, s, NHCO), 7.65 (2H, t, J = 7.7 Hz, H$_{Ar}$), 7.57 (2H, d, J = 7.9 Hz, H$_{Ar}$), 7.53 (2H, d, J = 7.9 Hz, H$_{Ar}$), 7.45 (2H, t, J = 7.4 Hz, H$_{Ar}$), 7.40 (2H, s, NHCO), 7.03 (2H, t, J = 7.7 Hz, H$_{Ar}$), 6.95 (2H, t, J = 7.7 Hz, H$_{Ar}$), 6.77 (2H, d, J = 7.5 Hz, H$_{Ar}$), 6.68 (2H, d, J = 7.5 Hz, H$_{Ar}$), 5.25 (2H, s, H$_{Ar}$), 4.99 (2H, s, H$_{Ar}$), 2.28 (2H, d, J = 12.6 Hz, CH$_{2benz}$), 2.13 (2H, d, J = 12.6 Hz, CH$_{2benz}$), 1.43 (2H, m, CHCOO), 1.27 (2H, m, CH$_{2benz}$), 0.95 (2H, t, J = 12.2 Hz, CH$_{2benz}$). ^{13}C NMR (CDCl$_3$, 298 K, 125 MHz): δ_C 173.3, 165.6, 165.3, 155.7, 153.5, 153.4, 152.4, 139.5, 138.8, 138.7, 138.3, 135.6, 135.5, 134.9, 134.8, 134.6, 134.3, 133.6, 132.2, 131.9, 131.7, 130.9, 130.8, 130.2, 129.1, 129.0, 127.5, 127.2, 125.0, 123.6, 123.5, 123.1, 120.9, 120.4, 119.7, 118.2, 52.4, 41.6, 39.8. UV-vis (CHCl$_3$): λ/ nm ($10^{-3}\varepsilon$, dm^3 mol^{-1} cm^{-1}): 448 (234.8), 550 (10.0), 576 (11.8). FTIR (KBr): ν = 3408, 1662, 1580, 1515, 1442 cm^{-1}. Anal. Calcd for C$_{80}$H$_{54}$N$_8$O$_8$Hg$_2$·3CDCl$_3$: C, 49.41; H, 3.00; N, 5.55. Found: C, 49.11; H, 2.95; N, 5.34. ESI-HRMS: m/z calcd for C$_{80}$H$_{54}$N$_8$O$_8$NaHg: 1479.3669 [**1**+Hg-4H+Na]$^-$; found: 1479.3689. Comment: although ESI-HRMS analysis was consistent with a mononuclear complex (namely **1Hg**), elemental analysis and spectroscopic studies (see text) suggest that this adduct is the result of a demetalation process occurring in the electrospray.

DFT calculations

Geometry optimization calculations were performed on **1Hg$_2$** with three, two or zero DMSO molecules in the vicinity of the metal atoms, employing the Gaussian09 (revision A.02) package.[2]

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[1] The bis-strapped porphyrin **1** was prepared as previously described: Z. Halime, M. Lachkar, T. Roisnel, E. Furet, J.-F. Halet, B. Boitrel, *Angew. Chem. Int. Ed.* **2007**, *46*, 5120-5124.

[2] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F.

Gradient-corrected calculations were performed using the Becke exchange[3] and Perdew correlation[4] (B88P86). Stuttgart/Dresden effective core potentials (SDD) were employed for all atoms.[5]

Total energy and cartesian coordinates of the optimized complexes are given at the end of the Supporting Information file.

Protocols for NMR titrations

Representative protocol for the titration of **1** with Hg(OAc)$_2$ in pyridine-d_5/DMSO-d_6 9:1 solution, with a fixed concentration of ligand: to 0.5 mL of a 4.76 mM solution of **1** in a 9:1 (v/v) mixture of pyridine-d_5 and DMSO-d_6 were added small amounts (4-40 μL, microsyringe) of a 9:1 (v/v) mixture of pyridine-d_5 and DMSO-d_6 containing **1** (4.76 mM) and Hg(OAc)$_2$ (60.9 mM), so that at the end approximately 4 equiv. of Hg(OAc)$_2$ were present. Equilibriums were reached instantaneously.

Analytical treatment for Ka determination and fitting methods

The binding of Hg(II) by **1** can be described by the following equilibria :

$$\textbf{1} \quad + \text{ Hg} \quad \rightleftharpoons \quad \textbf{1Hg} \tag{1}$$

$$\textbf{1Hg} + \text{ Hg} \quad \rightleftharpoons \quad \textbf{1Hg}_2 \tag{2}$$

The corresponding association constants characterizing the first and second binding processes, Ka$_1$ and Ka$_2$, can be written as:

$$Ka_1 = \frac{1}{C_{\textbf{1}}} \frac{v}{u\,(R - v - 2w)} \tag{3}$$

$$Ka_2 = \frac{1}{C_{\textbf{1}}} \frac{w}{v\,(R - v - 2w)} \tag{4}$$

where $C_{\textbf{1}}$ is the total molar concentration of **1**.

R is the number of equivalents of Hg(II) : R = $C_{Hg}/C_{\textbf{1}}$, with C_{Hg} standing for the analytical molar concentration of Hg(II).

Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

[3] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098-3100.

[4] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822-8824.

[5] a) H. Dunning Jr., P. J. Hay, in *Modern Theoretical Chemistry*, Vol. 3 (Ed. H. F. Schaefer III) Plenum, New York, **1976**, p. 1; b) G. Igel-Mann, H. Stoll, H. Preuss, *Mol. Phys.* **1988**, *65*, 1321.

u, v and w are, respectively, the mole fraction of free **1**, mononuclear complex and dinuclear complex at equilibrium : $u=[\mathbf{1}]/C_{\mathbf{1}}$; $v=[\mathbf{1Hg}]/C_{\mathbf{1}}$; $w=[\mathbf{1Hg_2}]/C_{\mathbf{1}}$

In these equations, $(R - v - 2w)$ corresponds to the number of equivalents of free Hg(II) in solution, *i.e.* $[Hg]/C_{\mathbf{1}}$. Using equation (5), equations (3) and (4) can be transformed into equations (6) and (7), respectively.

$$w = 1 - u - v \tag{5}$$

$$u^2 + \frac{R-2+v}{2}u - \frac{v}{2Ka_1C_{\mathbf{1}}} = 0 \tag{6}$$

$$v^2 + \left(R-2+2u+\frac{1}{Ka_2C_{\mathbf{1}}}\right)v - \frac{1-u}{Ka_2C_{\mathbf{1}}} = 0 \tag{7}$$

Equations (6) and (7) were solved iteratively for increasing values of R. The initial value for u was estimated as:

$$u(R+dR) = u(R)+\frac{\partial u}{\partial R}(R)\times dR+\frac{1}{2}\frac{\partial^2 u}{\partial R^2}(R)\times dR^2 \quad \text{with } u = 1 \text{ and } v = w = 0 \text{ for } R = 0 \tag{8}$$

Analytic expressions for the first and second derivatives were obtained from equations (6) and (7).

The titration of **1** by Hg(OAc)$_2$ in the pyridine-d_5/DMSO-d_6 9:1 mixture of solvents (Figure S20) shows that the first and second binding processes are respectively slow and fast on the ^{1}H NMR spectral time scale. The mole fraction of free **1**, u, and the complementary mole fraction of the 1:1 and 1:2 complexes, $v + w = 1 - u$, can thus be determined experimentally by signal integrations. Chemical shift measurements can be used to characterize the second binding process. The observed chemical shift is given by equation (9), where $\delta_{\mathbf{1Hg}}$ is the chemical shift for the monuclear complex and $\Delta\delta$ is the shift induced by the second complexation.

$$\delta_{obs} = \delta_{\mathbf{1Hg}}+\frac{w}{v+w}\Delta\delta \tag{9}$$

The mole fractions u, v, w and the ratio $w/(v+w)$ computed for $C_{\mathbf{1}} = 5\times10^{-3}$ M, $Ka_1= 10^3$, 10^4 or 10^5 M^{-1} and a ratio $0.25\times Ka_1/Ka_2 = 0.1$, which corresponds to a 10-fold positive cooperativity, are shown in Figure S1. For large Ka_1 values, the mole fraction of free **1** (u) reaches 0 at $R \approx 2$, as expected. However, a significant amount of free **1** remains after the addition of one equivalent of Hg(II) and the overall decrease of u is weaker than $u = 1 - R$. The mole fraction of the mononuclear complex **1**Hg (v) remains rather small and reaches its maximum value, about 0.25, at $R \approx 1$. As expected for positive cooperativity, the mole fraction of the dinuclear complex **1**Hg$_2$ (w) is not negligible at low R values. Consequently, the ratio $w/(v+w)$ shows a strong initial increase.
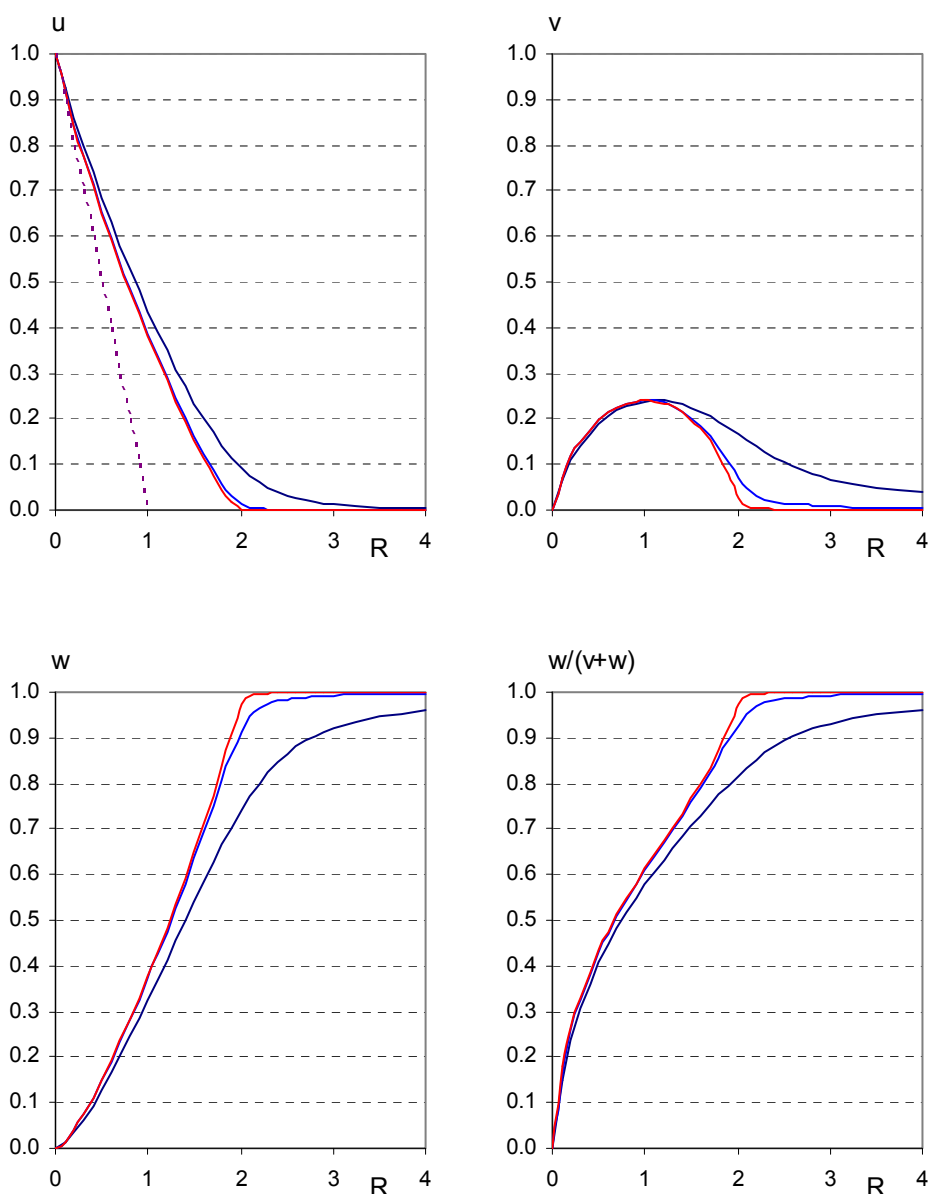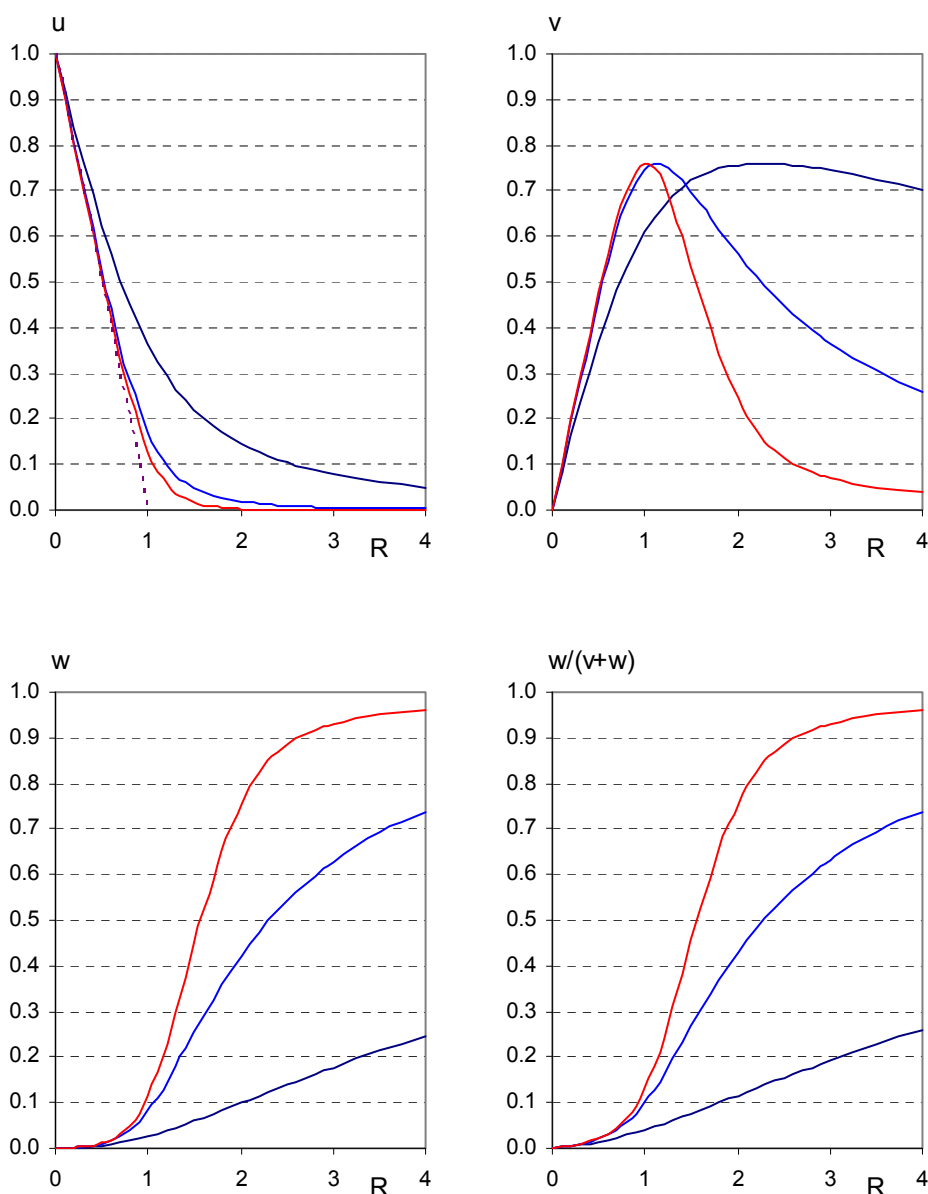
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Figure S1. Simulations in the case of a 10-fold positive cooperativity ($0.25 \times Ka_1/Ka_2 = 0.1$). $C_1 = 5 \times 10^{-3}$ M; $Ka_1 = 10^3$ M^{-1} (black), 10^4 M^{-1} (blue) or 10^5 M^{-1} (red).

The mole fractions u, v, w and the ratio w/(v+w) computed for $C_1 = 5 \times 10^{-3}$ M, $Ka_1 = 10^3$, 10^4 or 10^5 M^{-1} but now for a ratio $0.25 \times Ka_1/Ka_2 = 10$, which corresponds to a 10-fold negative cooperativity, are shown in Figure S2. For large Ka_1 values, the mole fraction of free **1** (u) also reaches 0 at $R \approx 2$ but, in contrast to the case of positive cooperativity, the amount of free **1** that remains after the addition of one equivalent of Hg(II) is low. Below one equivalent, the overall decrease of u is almost linear with a slope approaching -1 (u decreases as $1 - R$ for large Ka_1 values). The mole fraction of the mononuclear complex **1**Hg (v) is rather large and reaches its maximum value, about 0.75, at $R \approx 1$ for large Ka_1 values. As expected for negative cooperativity, the mole fraction of the dinuclear complex **1**Hg$_2$ (w) is negligible at low R values. Consequently, the ratio w/(v+w) shows a weak initial increase and a marked sigmoid-like variation for large Ka_1 values.

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Figure S2. Simulations in the case of a 10-fold negative cooperativity ($0.25 \times Ka_1/Ka_2 = 10$). $C_1 = 5 \times 10^{-3}$ M; $Ka_1 = 10^3$ M^{-1} (black), 10^4 M^{-1} (blue) or 10^5 M^{-1} (red).

The mole fraction of free **1** (u) was obtained from the integration of the ^{1}H NMR signals of H2a and H2b as determined by deconvolution of the spectrum between 4.0 and 6.3 ppm (Figure S3); the integrals of H2a and H2b signals were constrained to be identical.

Chemical shift data were obtained from spectrum deconvolution or directly from peak-picking. The chemical shift variations were normalized according to equation (10) where δ_{max} and δ_{min} are respectively the maximum and the minimum value of δ_{obs}:

$$\Delta\delta^* = \frac{\delta_{obs} - \delta_{min}}{\delta_{max} - \delta_{min}} \tag{10}$$
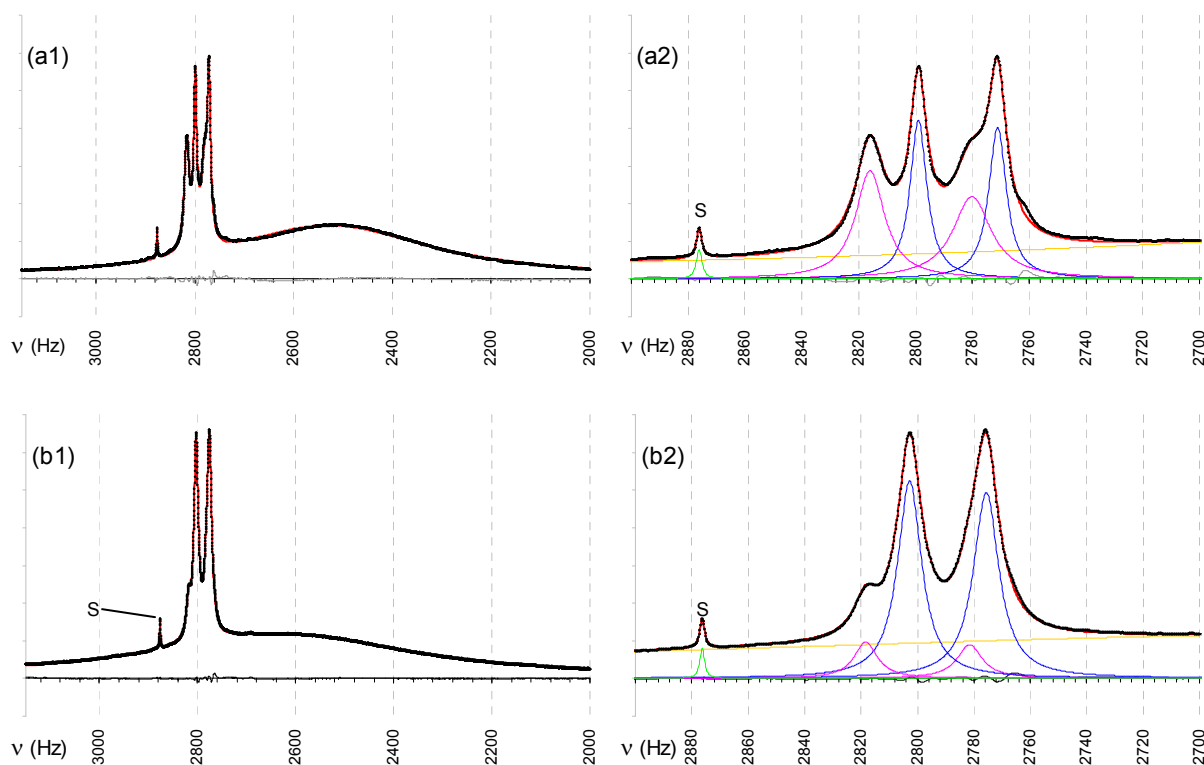
Figure S3. Deconvolution of the H2a and H2b region of the ^{1}H NMR spectrum recorded for (a) R = 0.49 and (b) R = 0.95 (1 ppm = 500 Hz). The entire deconvoluted region is shown in (a1) and (b1) where the broad signal is due to water. The experimental data points are in black and the deconvoluted spectrum in red. In the enlargements (a2) and (b2), the magenta lines correspond to the H2a and H2b signals of the free ligand **1**, the blue lines correspond to the H2a and H2b signals arising from fast exchange between the mononuclear (**1Hg**) and dinuclear (**1Hg₂**) complexes, the orange line is the signal of water and the green line is the signal of CH_2Cl_2 (S = solvent).

The mole fraction of free **1** determined experimentally (u data) and the normalized chemical shift variation observed for various ^{1}H NMR signals are shown in Figure S4 (in Figure S5, as well). These data clearly indicate that Ka_1 is (very) large and reveal strong negative cooperativity (see u and w/(v+w) variations in Figure S2). Ka_1 is probably too large for being precisely determined. The overall variation of the normalized chemical shift data is sigmoid shaped but the $\Delta\delta^*$ values at R ≈ 0.25 (first data points) and at R ≈ 3.7 (last data points) deviate from the expected variation. This suggests that an additional process, such as solvation and/or non specific interactions, somewhat affect the chemical shift. In this regard it is worth mentioning that the chemical shift and linewidth of the water signal were found to vary significantly in the course of the titration (see Figure S3, a1 and b1).

In order to estimate the association constants Ka_1 and Ka_2, the model described above was fitted to the experimental data (simultaneous fitting to u and $\Delta\delta^*$ data); the $\Delta\delta^*$ data points at R ≈ 0.25 were not considered.

First, the $\Delta\delta^*$ data were constrained to vary between 0 and 1; only two parameters (Ka_1 and Ka_2) were optimized. The results are $Ka_1 = 8.0 \times 10^5$ M^{-1}, $Ka_2 = 4.8 \times 10^3$ M^{-1}, $0.25 \times Ka_1/Ka_2 = 41.7$ (Figure S4). This fitting properly accounts for the initial variation of the $\Delta\delta^*$ data (for R > 0.25) but systematic deviations are observed for u (Ka_1 is apparently overestimated).

A second fitting analysis was completed by allowing $\Delta\delta^*$ to be different from 0 at R=0 and different from 1 for R approaching infinity. This analysis involves two additional parameters for each $\Delta\delta^*$ series of measurements, thus eight parameters in total (Figure S5). It yields $Ka_1= 2.6 \times 10^5$ M^{-1}, $Ka_2= 4.9 \times 10^3$ M^{-1}, $0.25 \times Ka_1/Ka_2 = 13.2$. This fitting properly accounts for the decrease in u; Ka_1 is somewhat smaller but remains of the same order of magnitude. Ka_2 is not significantly different from the previous estimation.
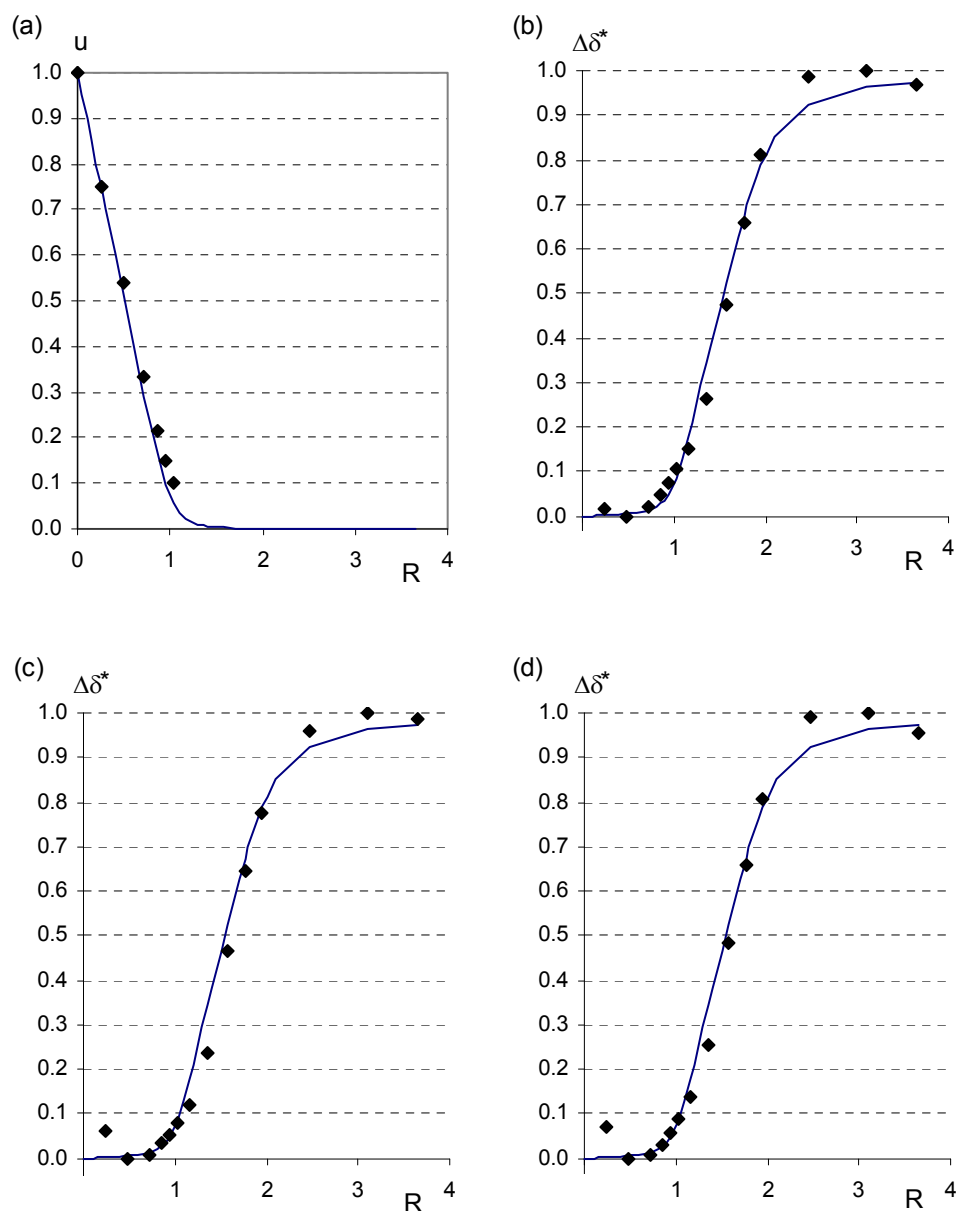
Figure S4. Experimental data (♦) and best-fit with 2 parameters. (a) mole fraction of free **1** , (b) normalized chemical shift variation for H4a/b, (c-d) normalized chemical shift variation for H2a and H2b ($C_1 = 4.8 \times 10^{-3}$ M). The experimental chemical shift variation range, $\delta_{max} - \delta_{min}$, is 0.161, 0.166 and 0.131 ppm in (b), (c) and (d), respectively. The first $\Delta\delta^*$ data points (for R ≈ 0.25) were not considered in the best-fit analysis. The fitting yields $Ka_1= 8.0 \times 10^5$ M^{-1}, $Ka_2= 4.8 \times 10^3$ M^{-1}, $0.25 \times Ka_1/Ka_2 = 41.7$.
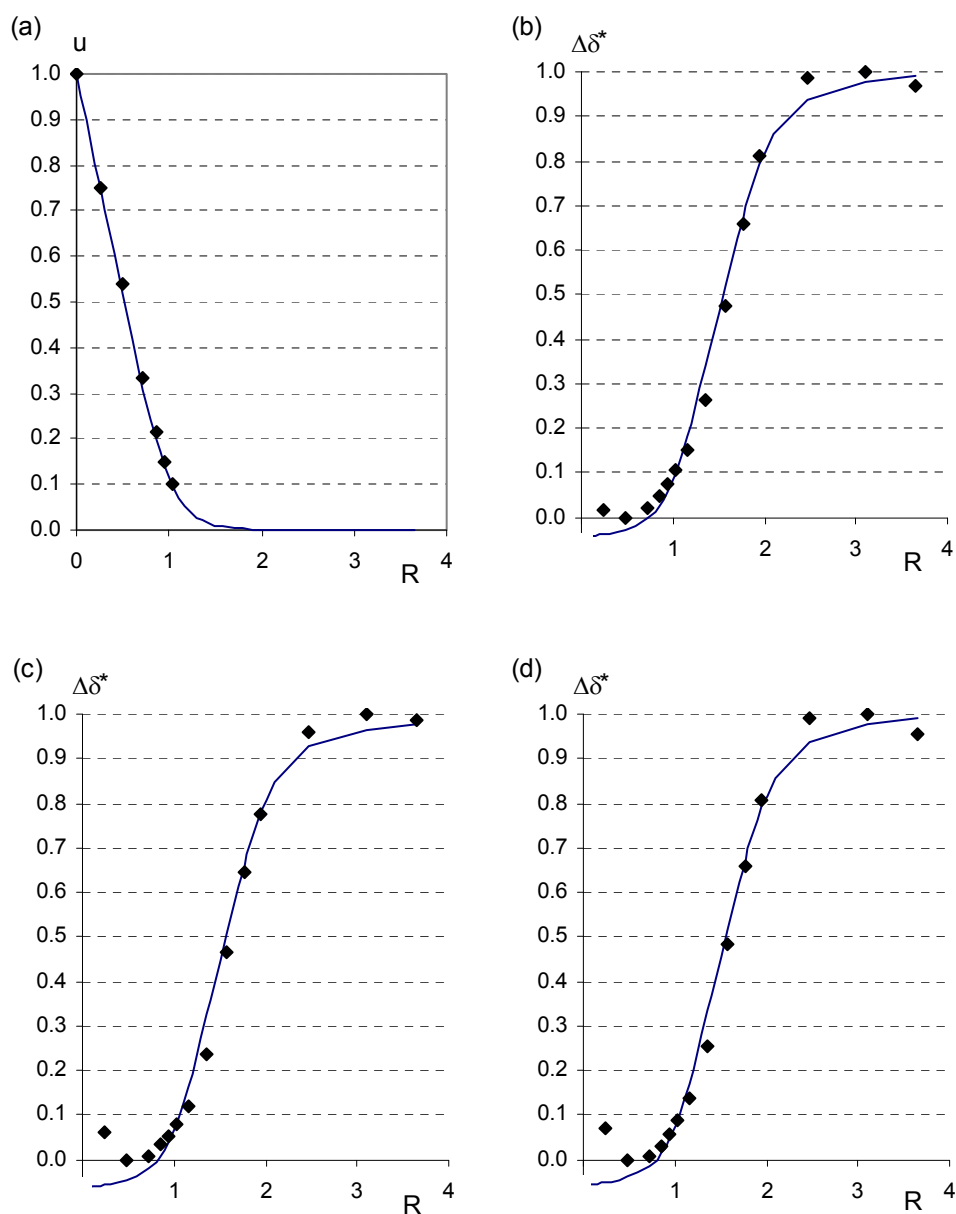
Figure S5. Experimental data (♦) and best-fit with 8 parameters. (a) mole fraction of free **1** , (b) normalized chemical shift variation for H4a/b, (c-d) normalized chemical shift variation for H2a and H2b ($C_1 = 4.8 \times 10^{-3}$ M). The experimental chemical shift variation range, $\delta_{max} - \delta_{min}$, is 0.161, 0.166 and 0.131 ppm in (b), (c) and (d), respectively. The first $\Delta\delta^*$ data points (for R ≈ 0.25) were not considered in the best-fit analysis. The fitting yields $Ka_1 = 2.6 \ 10^5 \ M^{-1}$, $Ka_2 = 4.9 \ 10^3 \ M^{-1}$, $0.25 \times Ka_1/Ka_2 = 13.2$.
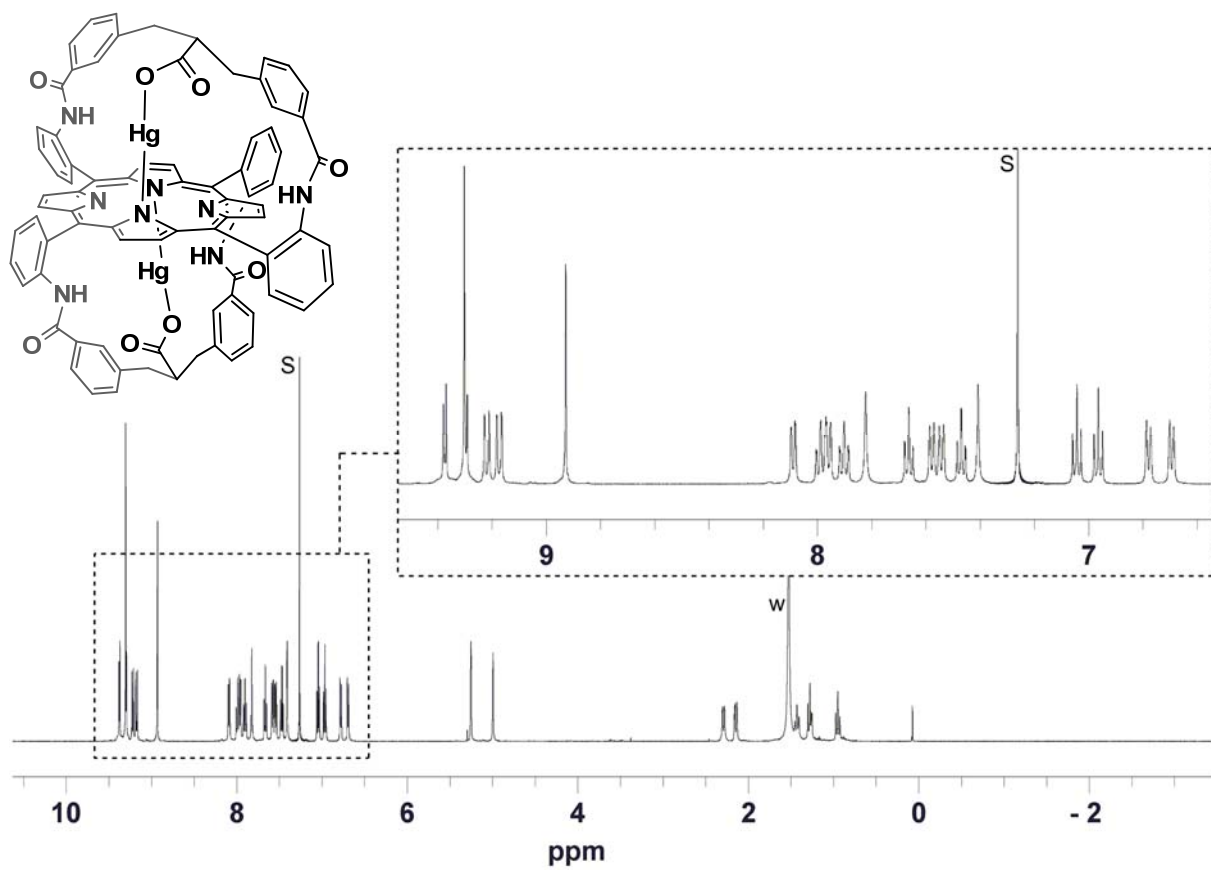
Figure S6. ^{1}H NMR spectrum (500 MHz, 298 K) of **1Hg₂** in CDCl₃. S = solvent, w = water.
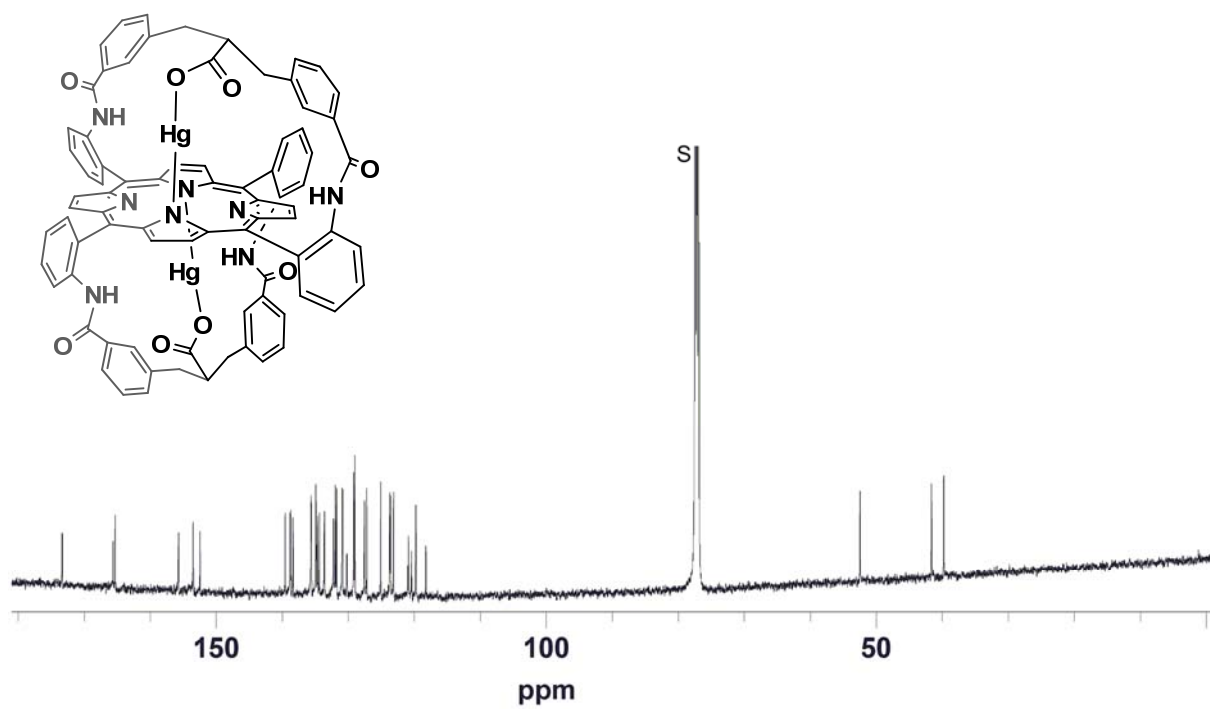
Figure S7. ^{13}C NMR spectrum (125 MHz, 298 K) of **1Hg$_2$** in CDCl$_3$. S = solvent.
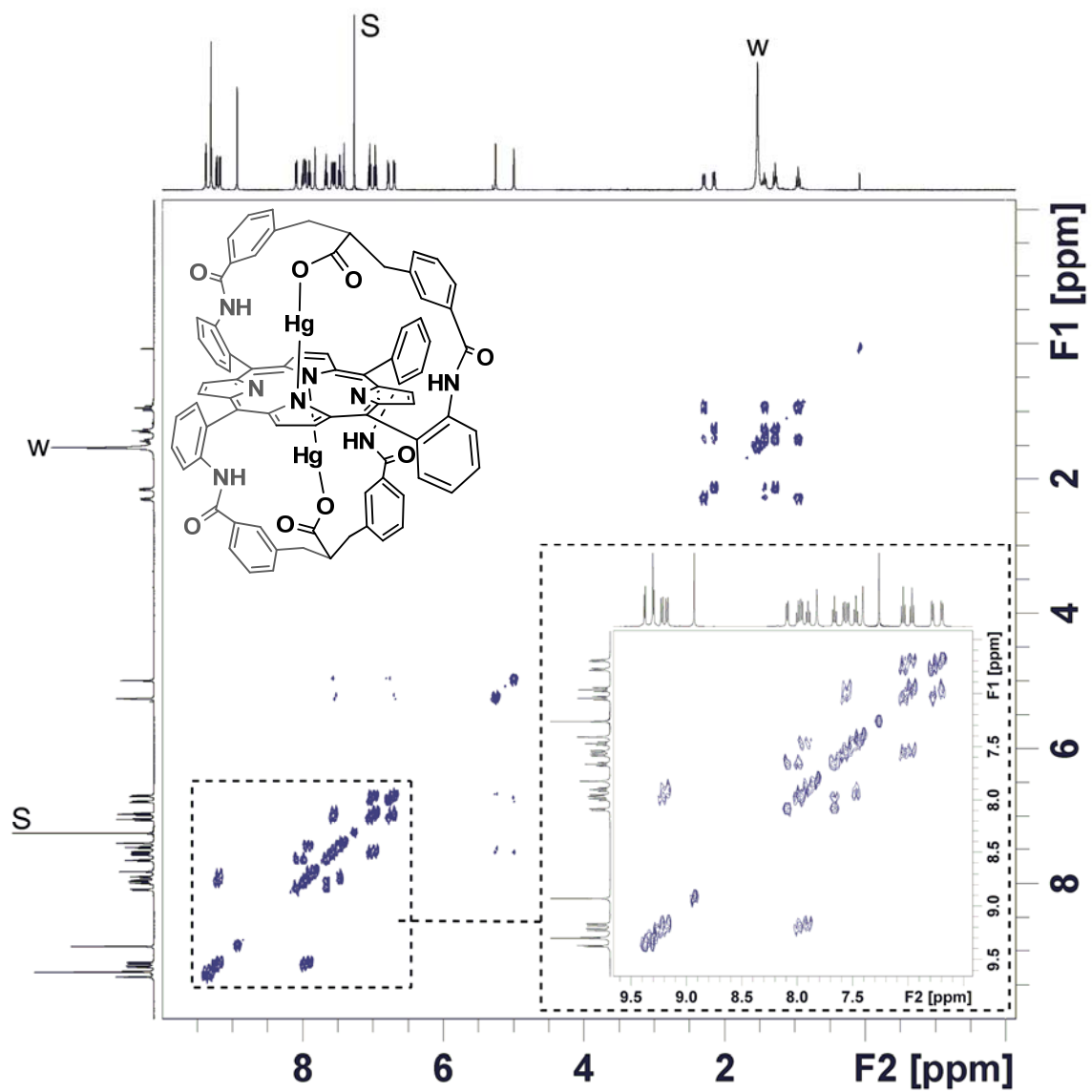
Figure S8. 2D COSY NMR spectrum (500 MHz, 298 K) of **1Hg₂** in CDCl₃. S = solvent, w = water.
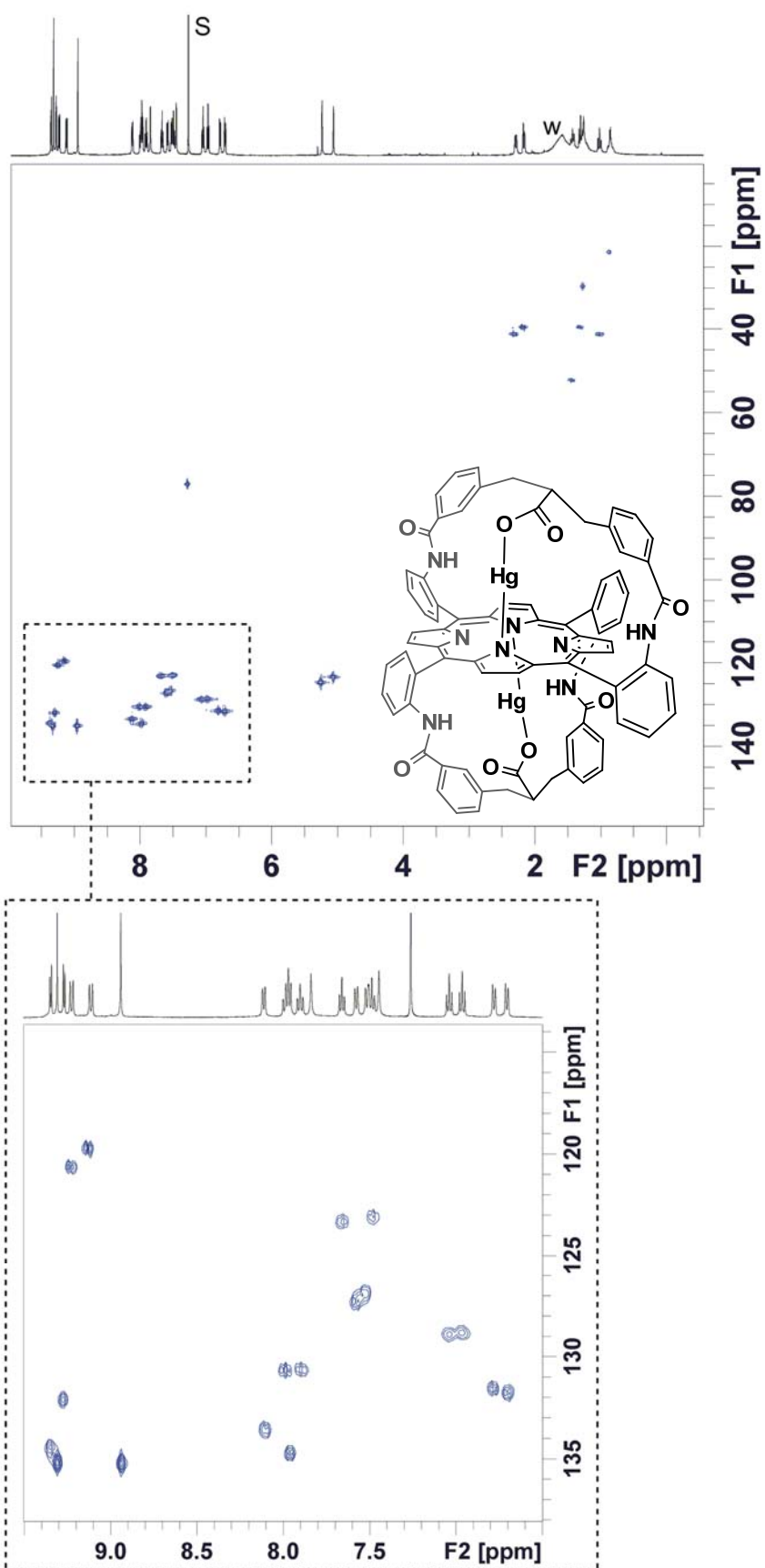
Figure S9. 2D HMQC NMR spectrum (500 MHz, 298 K) of **1Hg₂** in CDCl₃. S = solvent, w = water.
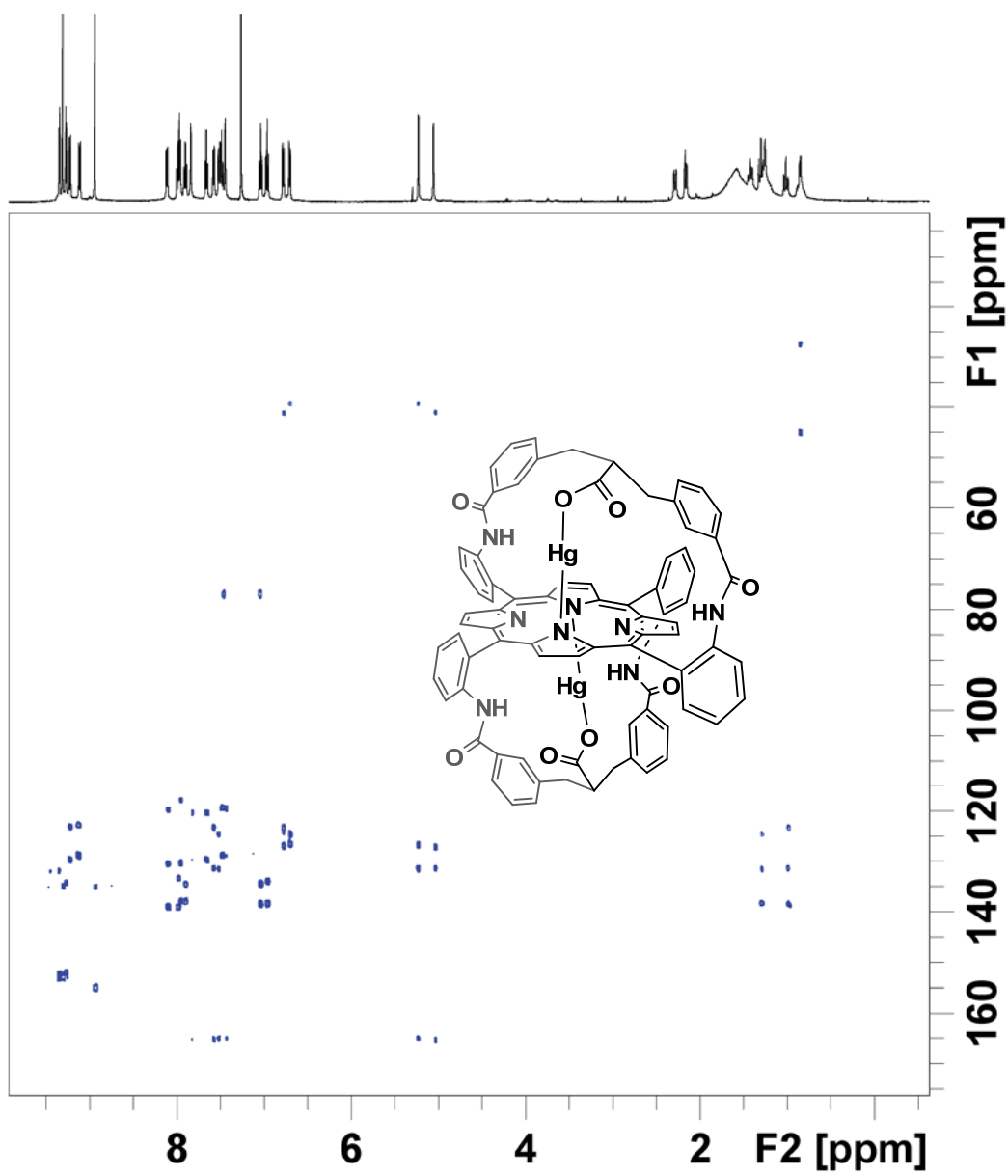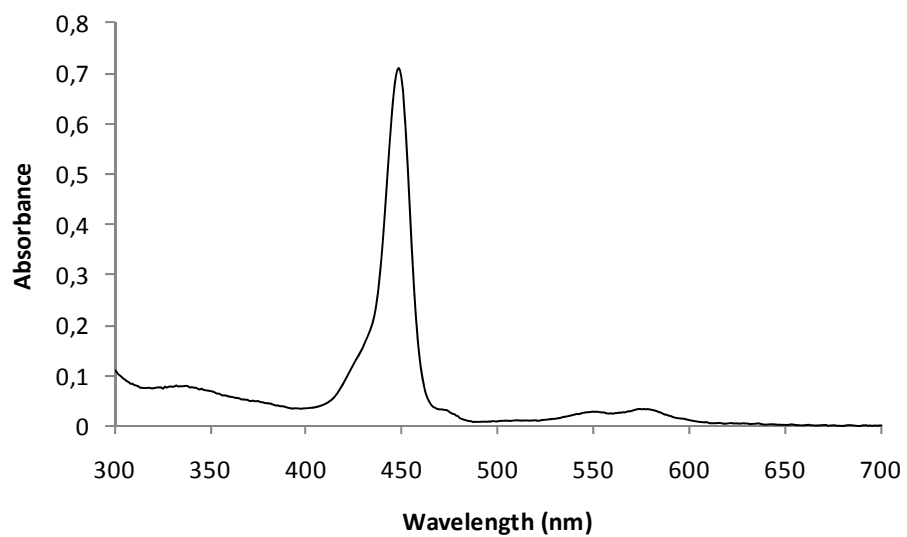
Figure S10. 2D HMBC NMR spectrum (500 MHz, 298 K) of **1Hg₂** in CDCl₃.

Figure S11. UV-visible spectrum of **1Hg₂** in CHCl₃.

Structural data of 1Hg$_2$: (2(C$_{80}$H$_{54}$Hg$_2$N$_8$O$_8$●3(C$_2$ H$_6$ O S))); M = 3781.75, Monoclinic $P2_1$/c, a = 15.9342(4), b = 42.1730(11), c = 24.2164(6) Å, β = 103.5970(10) °; V = 15817.2(7) Å^3, Z = 4, ρ_{calcd} = 1.588 gcm^{-3}; μ = 4.023 mm^{-1}, F(000) = 7520. Single crystal X-ray diffraction data has been collected at T = 150 K on a *APEXII Bruker-AXS KappaCCD* diffractometer (Mo$K\alpha$ radiation). The structure was solved by direct methods using the SIR97 program,[1] and then refined with full-matrix least-square methods based on F^2 (SHELX-97)[2] with the aid of the WINGX program.[3] The contribution of the disordered solvents to the calculated structure factors was estimated following the BYPASS algorithm,[4] implemented as the SQUEEZE option in PLATON.[5] A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 35888 unique intensities and 1984 parameters converged at ωR(F^2) = 0.1281 (R(F) = 0.0536) for 22554 observed reflections with $I > 2\sigma(I)$. Supplementary crystallographic data (CCDC 771832) for **1Hg$_2$** can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambrigde Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

[1]   A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst*. **1999**, *32*, 115-119.

[2]   G.M Sheldrick, *Acta Crystallogr*. **2008**, *A64,* 112-122.

[3]   L. J. Farrugia, *J. Appl. Cryst*. **1999**, *32*, 837-838.

[4]   *SQUEEZE* - P. v.d. Sluis, A. L. Spek, *Acta Crystallogr.* **1990**, *A46*, 194-201.

[5]   A. L. Spek, *Acta Crystallogr.* **1990**, *A46*, C34.

The crystal lattice of **1Hg$_2$** contains two isomers (namely **1Hg$_2$** and **1Hg$_2$^{iso}**) and both crystallized as a true racemic, thus two enantiomers are present for each isomer. The isomers display sligthly different structural features in terms of coordination and conformation, but both lack the C_2 symmetry. For clarity, only one isomer (**1Hg$_2$**) has been described in the text, the description of the second one (**1Hg$_2$^{iso}**) is given below.

Description of the X-ray structure of the second isomer of 1Hg$_2$, namely 1Hg$_2$^{iso}: The X-ray structure of **1Hg$_2$^{iso}** revealed a dinuclear complex with the two mercury atoms sitting on both sides of the macrocycle. In contrast to **1** but similarly to **1Hg$_2$**, isomer **1Hg$_2$^{iso}** lack the C$_2$ symmetry: the two sides of the porphyrin mainly differ by (i) the conformation of the two straps, the strap-{Hg1} being more twisted than the strap-{Hg2} (Figure S12e,f), and (ii) the *out of plane* position of Hg1 and Hg2 that are located 1.654 Å and 1.490 Å from the 24-atom mean plane, respectively (1.733 and 1.408 for **1Hg$_2$**). The two metal ions thus sit in two distinguished environment and appear to be in a triangular antiprismatic coordination polyhedron, Hg1 being six-coordinate but Hg2 being five-coordinate. For Hg1, the polyhedron is composed of three nitrogen atoms from the porphyrin (N1, N2, N4), one monohapto carboxylate group (O1) and two DMSO molecules from the solvent of crystallization (Os3 and Os4). In the case of Hg2, this polyhedron is lacking one DMSO molecule but again is described by three nitrogen atoms from the macrocycle (N1, N3, N4), one monohapto carboxylate group (O2) and one DMSO molecule (Os5) (Figure S12d). Each mercury atom clearly exhibits two short bond distances, one with a nitrogen atom of the porphyrin and one with the oxygen atom of the hanging carboxylate function (for Hg1: Hg1-N2 = 2.142 Å and Hg1-O1 = 2.079 Å; for Hg2: Hg2-N4 = 2.145 Å and Hg2-O2 2.083 Å). All the other contacts are much longer and should be considered mainly as electrostatic interactions with both the nitrogen atoms of the porphyrin and the oxygen atom of the

DMSO molecules (see depicted values in Figure S12d). Moreover, the angles O1-Hg1-N2 and O2-Hg2-N4 are close to 180° (166.00° and 162.74°, respectively). Therefore, a linear coordination (14-electron ML$_2$-type complex) is also a good description for both mercury atoms in the second isomer **1Hg$_2$^{iso}**.
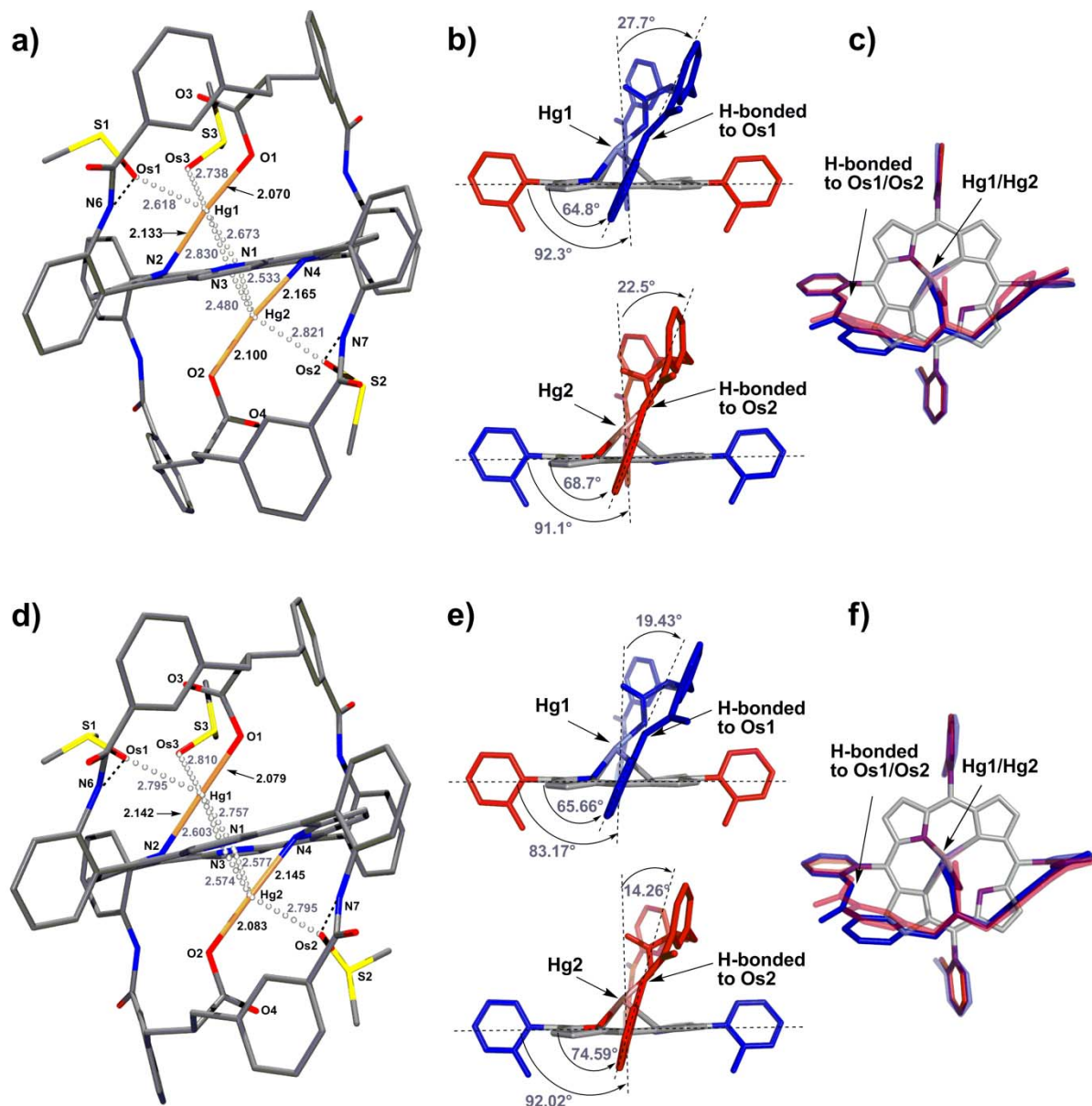

Figure S12. Comparison of the X-ray structures of **1Hg$_2$** (top) and **1Hg$_2$^{iso}** (bottom). (a) Crystal structure of **1Hg$_2$**, hydrogen atoms and non-interacting solvent molecules have been removed for clarity (distances [Å] and angles [°]: Hg1-Hg2 3.258; Hg1 to 24-atom mean plane 1.733; Hg2 to 24-atom mean plane 1.408; (N2, Hg1, O1) 166.19; (N4, Hg2, O2) 161.34). Side (b) and top (c) views of strap-{Hg1} (blue) and of strap-{Hg2} (red) upon 180° rotation around the *pseudo* two-fold axis, revealing their different conformation; bound DMSO molecules have been removed. (d) Crystal structure of **1Hg$_2$^{iso}**, hydrogen atoms and non-interacting solvent molecules have been removed for clarity (distances [Å] and angles [°]: Hg1-Hg2 3.260; Hg1 to 24-atom mean plane 1.654; Hg2 to 24-atom mean plane 1.490; (N2, Hg1, O1) 166.00; (N4, Hg2, O2) 162.74). The same side (e) and top (f) views of strap-{Hg1} and strap-{Hg2} as in (b) and (c).
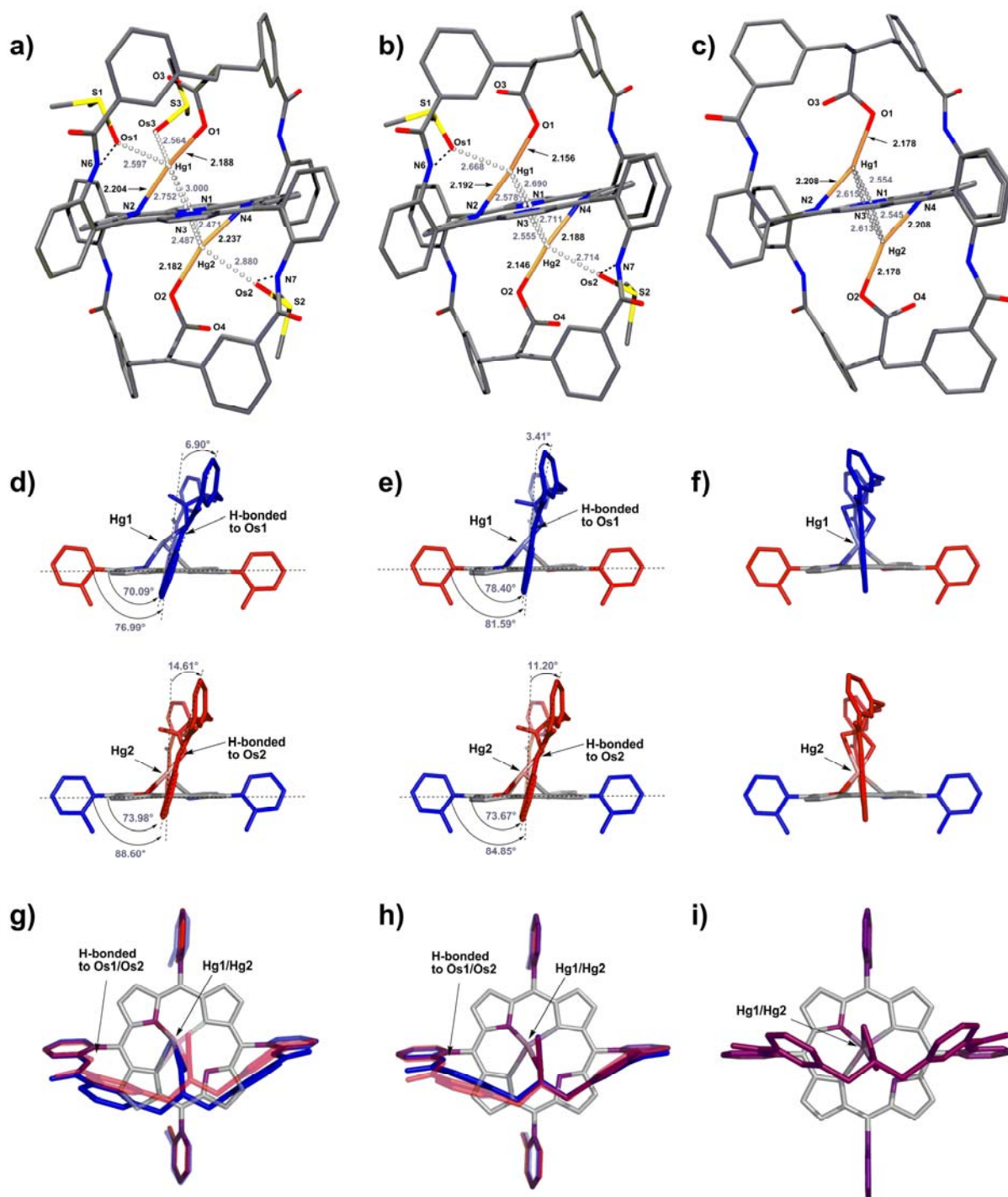
Figure S13. DFT optimized structures of (a) **1Hg₂(DMSO)₃**, (b) **1Hg₂(DMSO)₂** and (c) **1Hg₂(DMSO)₀** (hydrogen atoms have been omitted for clarity). Side (d, e, f) and top (g, h, i) views of strap-{Hg1} (blue) and -{Hg2} (red), upon 180° rotation of the latter around the *pseudo* two-fold axis; bound DMSO molecules have been removed for clarity.

Table S1. Computed distances [Å] and angles [°] for **1Hg$_2$(DMSO)$_3$, 1Hg$_2$(DMSO)$_2$** and **1Hg$_2$(DMSO)$_0$** and comparison with the crystal structure of **1Hg$_2$**. *d1*= N6-Os1; *d2* = N7-Os2.

	1Hg$_2$	1Hg$_2$(DMSO)$_3$	1Hg$_2$(DMSO)$_2$	1Hg$_2$(DMSO)$_0$
Hg1-Hg2	3.258	3.334	3.246	3.095
Hg1-*oop*	1.733	1.846	1.563	1.506
Hg2-*oop*	1.408	1.363	1.562	1.505
Hg1-N2	2.133	2.203	2.191	2.208
Hg1-O1	2.070	2.188	2.156	2.178
N2-Hg1-O1	166.19°	159.84°	167.58°	157.16°
Hg2-N4	2.165	2.337	2.187	2.208
Hg2-O2	2.100	2.182	2.146	2.178
N4-Hg2-O2	161.34°	160.31°	168.80°	157.21°
θ1	64.8°	70.09°	78.40°	87.16°
θ1'	92.3°	76.99°	81.59°	82.59°
θ1- θ1'	27.7°	6.90°	3.41°	4.81°
θ2	68.7°	73.98°	73.67°	87.27°
θ2'	91.1°	88.60°	84.85°	82.51°
θ2- θ2'	22.5°	14.61°	11.20°	4.99°
d1	2.840	2.803	2.817	-
d2	2.934	2.832	2.861	-

θ and θ' are the angles between the 6-atom mean plane of the meso aromatic units and the 24-atom mean plane of the porphyrin macrocycle (θ and θ': front and back meso aromatic units, respectively, Figure S13).
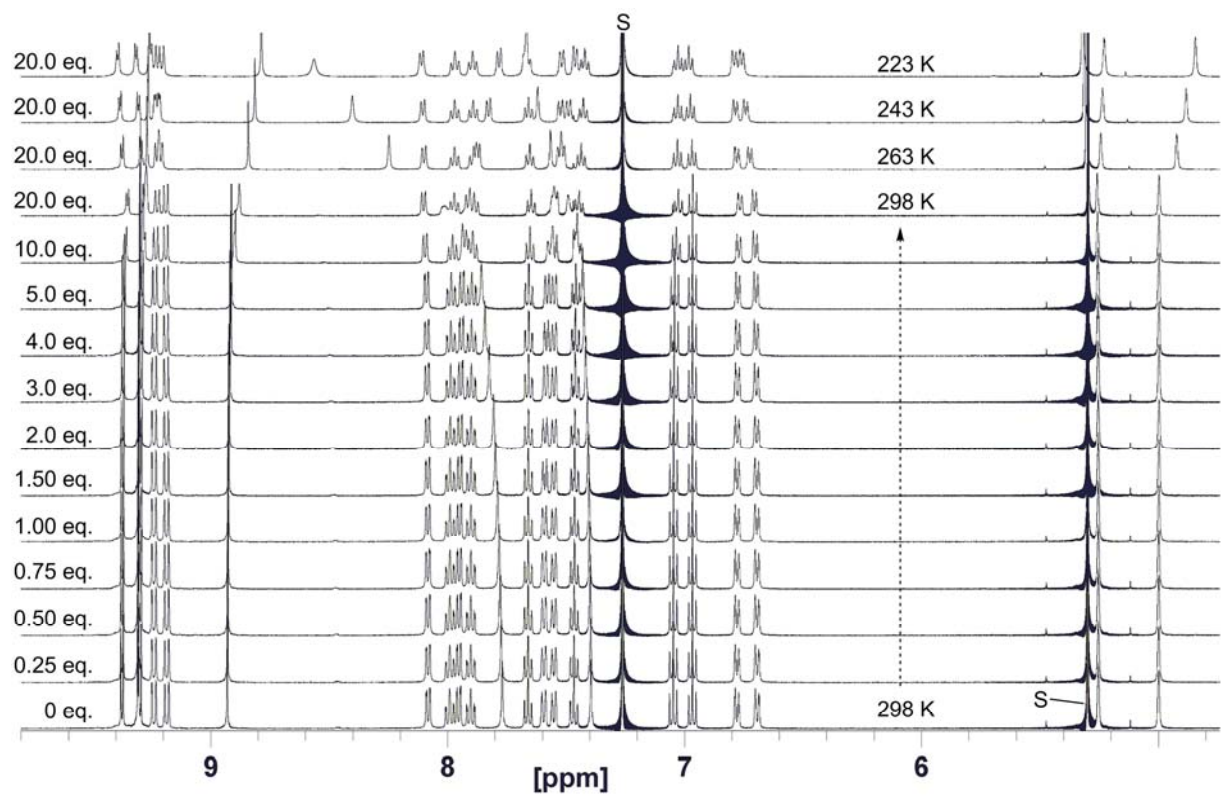
Figure S14. ^{1}H NMR titration experiment of **1Hg₂** with DMSO (500 MHz, CDCl₃, 298 K), selected area. S = solvent.
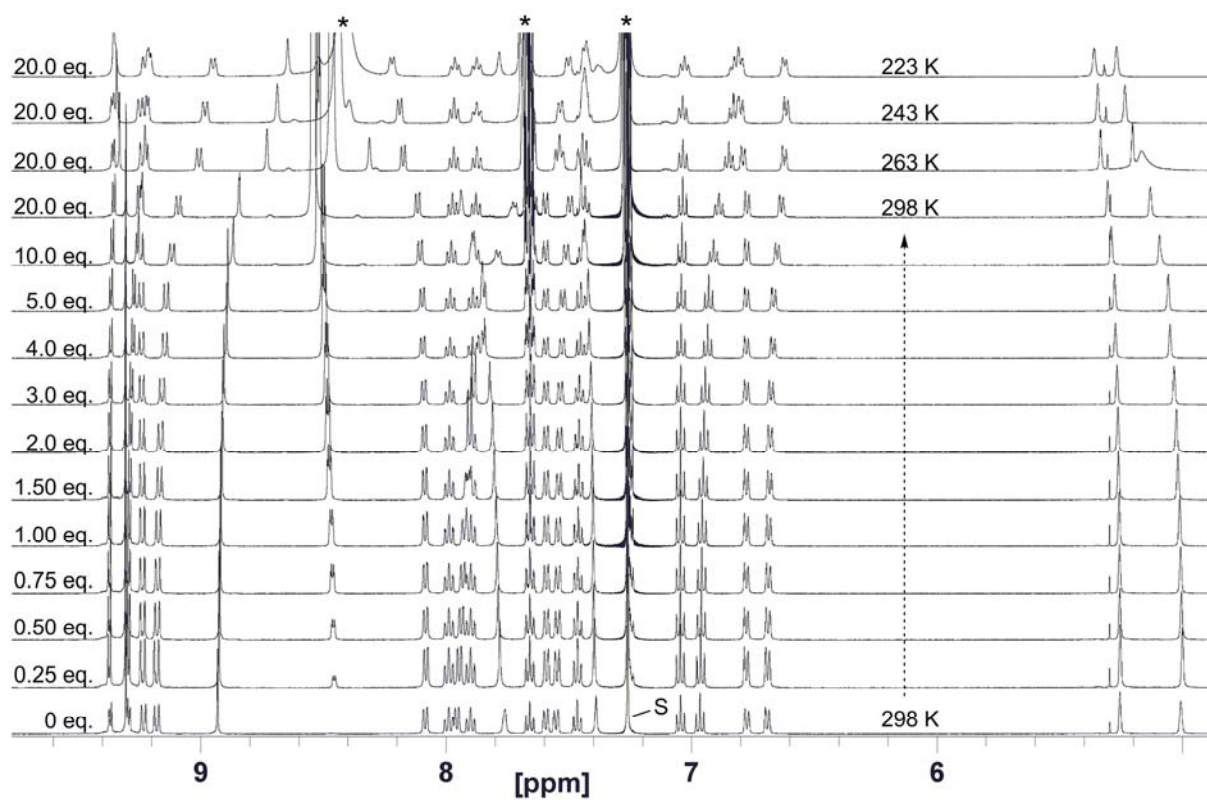
Figure S15. ^{1}H NMR titration experiment of **1Hg₂** with pyridine (500 MHz, CDCl₃, 298 K), selected area. S = solvent; * = pyridine.
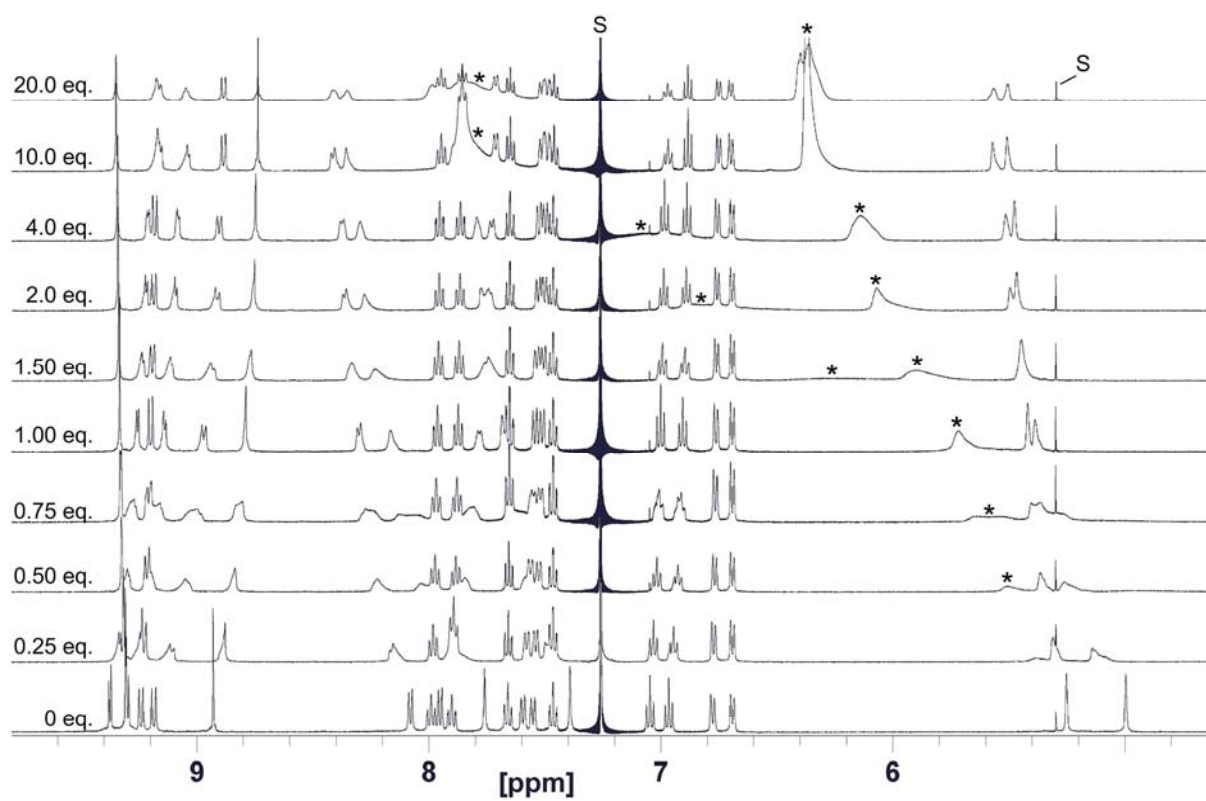
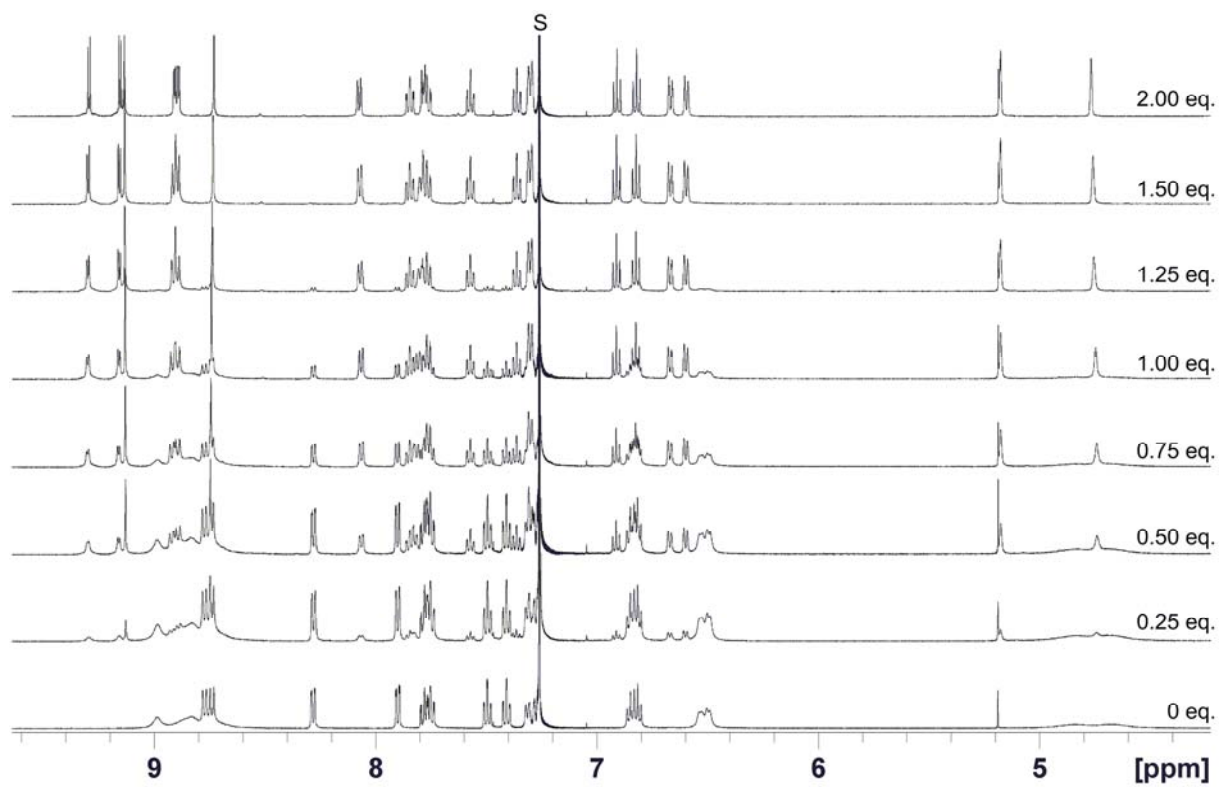**Figure S16.** ^{1}H NMR titration experiment of **1Hg$_2$** with DMAP (CDCl$_3$, 298 K), selected area. S = solvent; * = DMAP.

Figure S17. ^{1}H NMR spectra (500 MHz, 298 K) for the titration of **1** with Hg(OAc)$_2$ in CHCl$_3$/CD$_3$OD (9:1), selected area. S = solvent.
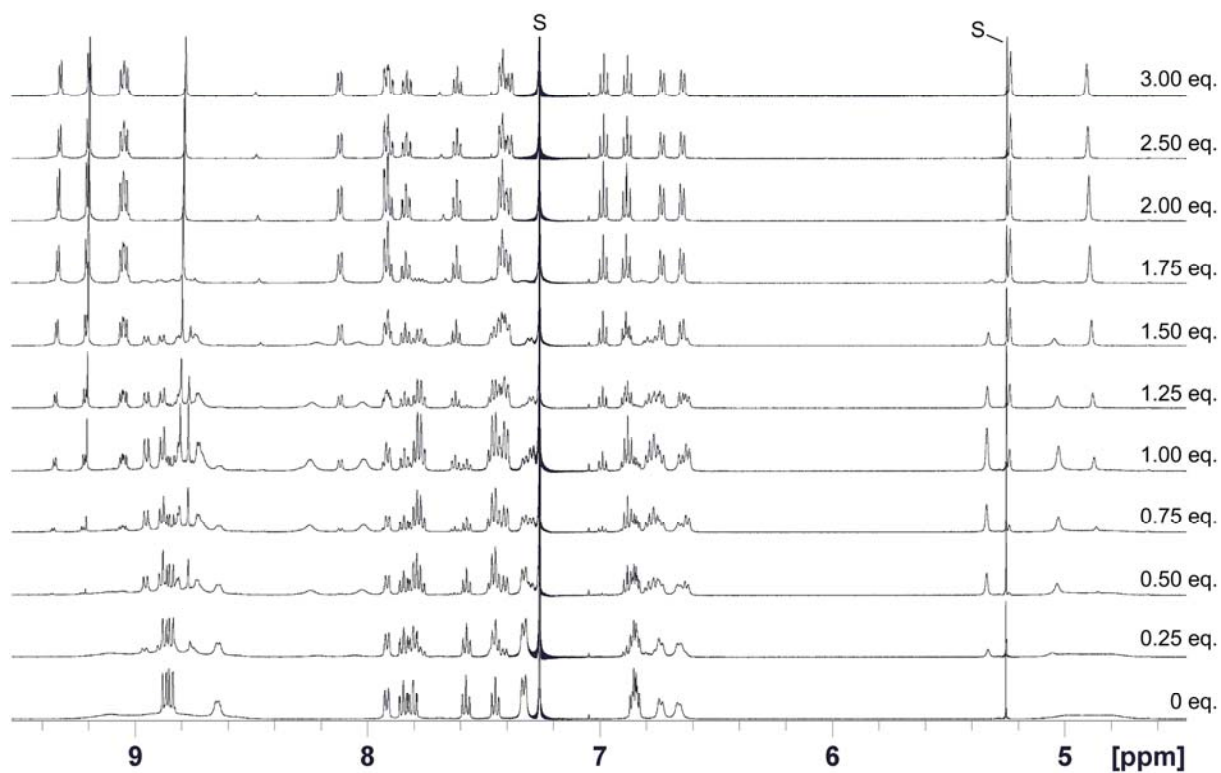
Figure S18. ^{1}H NMR spectra (500 MHz, 298 K) for the titration of **1** with Hg(OAc)$_2$ in CHCl$_3$/CD$_3$OD (9:1) with excess DIPEA (15 equiv.), selected area. S = solvent.
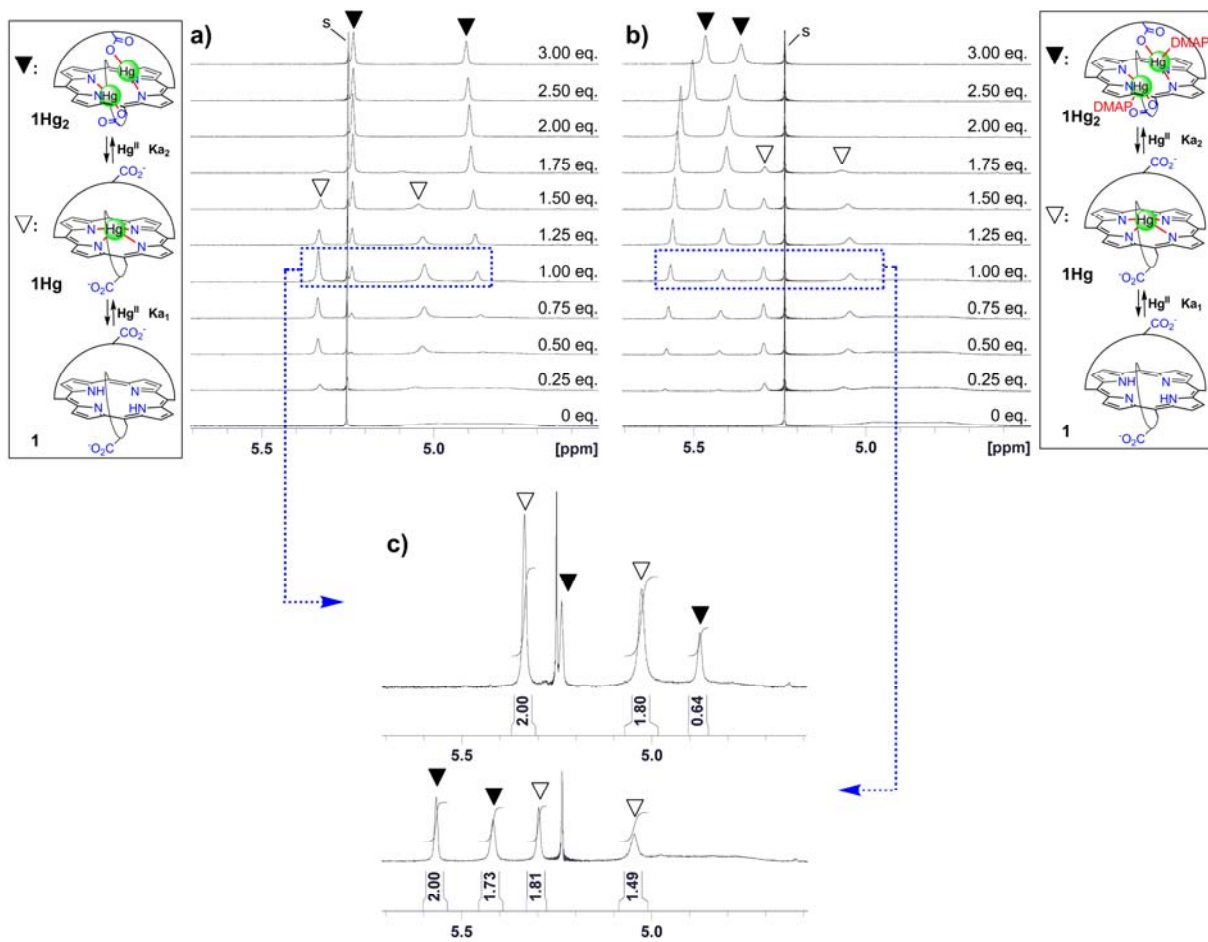
Figure S19. Influence of DMAP on the cooperativity of the metal insertion process. ^{1}H NMR spectra (500 MHz, 298 K, expended view on the signals of protons H_{2a} et H_{2b}, see text for labeling) for the titration of **1** with Hg(OAc)$_2$ (CHCl$_3$/CD$_3$OD 9:1, 15 equiv. DIPEA): a) without DMAP; b) with 4 equiv. of DMAP. c) Comparison of the **1Hg/1Hg$_2$** ratio at 1 equiv. of Hg[II] for both situations.
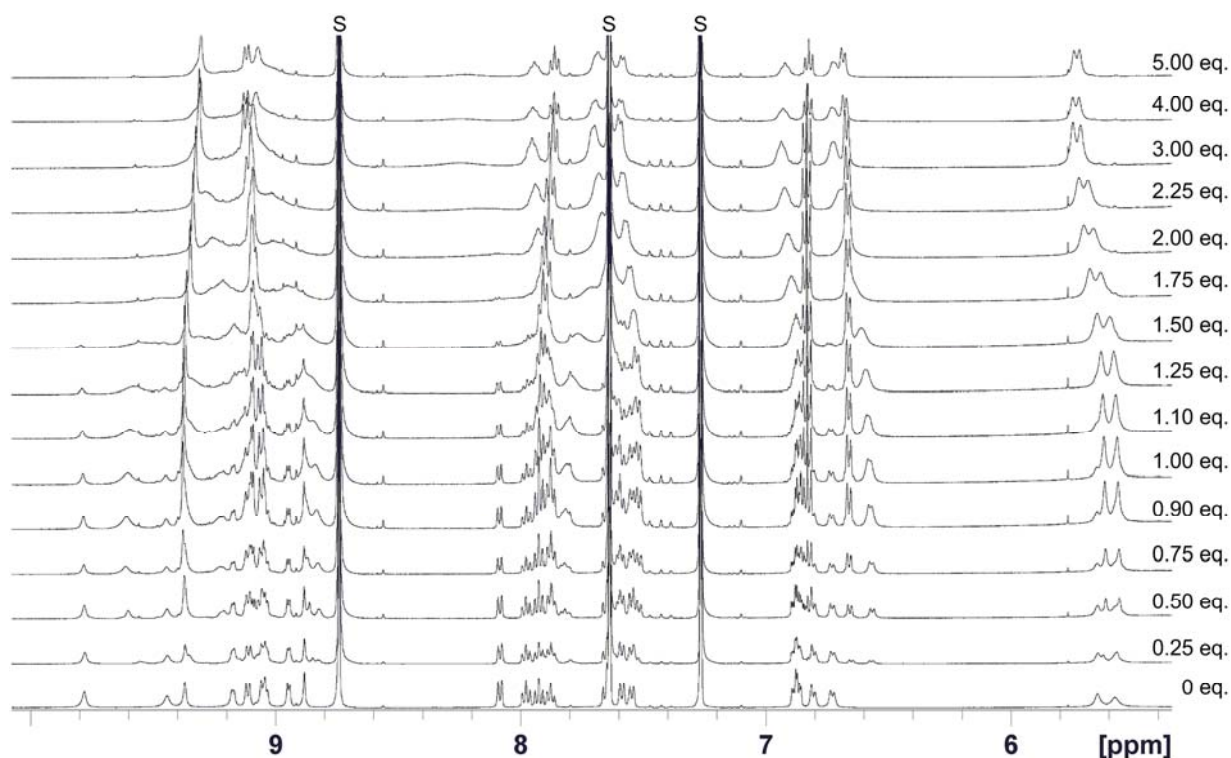
Figure S20. ^{1}H NMR spectra (500 MHz, 298 K) for the titration of **1** with Hg(OAc)$_2$ in pyridine-d_5/DMSO-d_6 (9:1), selected area. S = solvent.

Additional comment: it is noteworthy that the average NMR spectrum of **1Hg** and **1Hg$_2$** displays a selective broadening of one of the two sets of signals of a strap (*i.e.*, protons labeled "a" *vs* "b" in Scheme 1 in the text). This uncommon, selective broadening of the ligand NMR signals should correlate with a constrained conformation of one half of a strap (a well resolved NMR spectrum was obtained at 333 K).
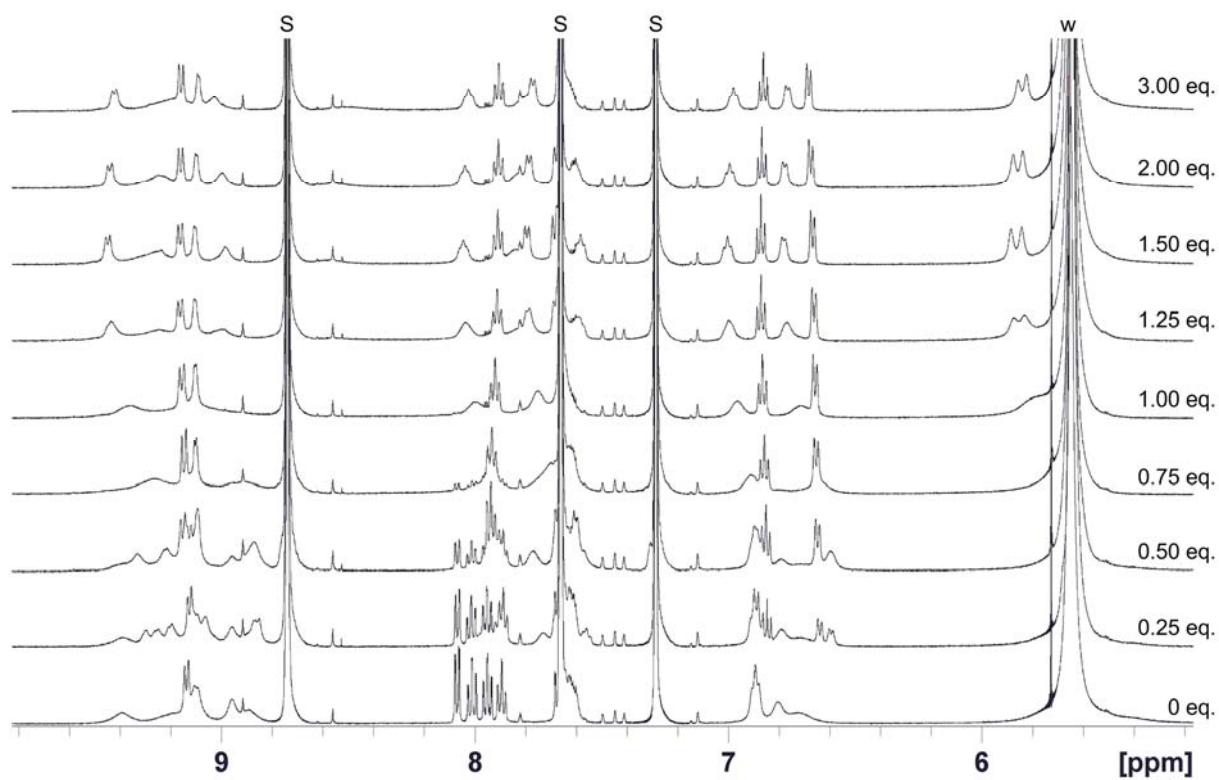
Figure S21. ^{1}H NMR spectra (500 MHz, 298 K) for the titration of **1** with Hg(OAc)$_2$ in pyridine-d_5/CD$_3$OD (9:1), selected area. S = solvent, w = water.

Total energy and cartesian coordinates of the complexes optimized at the B88P86/SDD level of theory.

- **1Hg₂(DMSO)₃**

Energy : -6087.288710 a.u.

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C   -5.287744    2.545914    3.056125
C   -6.642247    2.898661    2.814408
C   -7.546266    1.932071    2.322201
C   -7.110781    0.607001    2.082583
C   -5.763477    0.228819    2.332432
C   -4.391897    3.618516    3.631530
O   -4.880810    4.643042    4.209645
C   -5.296134   -1.203975    2.107586
C   -5.218263   -1.624714    0.605548
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C   -4.760546   -3.702920   -0.896229
C   -5.991936   -4.138040   -1.455793
C   -6.033626   -4.749149   -2.731516
C   -4.841891   -4.938063   -3.464662
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C   -3.572916   -3.873034   -1.653036
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C    2.390967   -3.302036   -3.905363
C    2.764970   -4.295262   -4.838529
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C    0.448607   -2.577220   -1.107019
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- **1Hg$_2$(DMSO)$_2$**

Energy : -5534.124276 a.u.

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C	0.674964	2.375058	-3.591886
C	0.726683	3.459441	-2.721640
Hg	-1.476341	0.636348	-0.358460
N	0.097941	1.876934	1.468255
C	0.014813	1.842096	2.874549
C	0.120539	3.201486	3.415969
C	0.258402	4.059585	2.339731
C	0.247072	3.236021	1.125490
C	-0.171766	0.674681	3.670586
C	-0.191593	0.866751	5.171347
C	1.037885	0.935280	5.871886
C	1.080934	1.145504	7.269562
C	-0.132822	1.299051	7.980962
C	-1.374097	1.247196	7.310803
C	-1.412719	1.025500	5.904144
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N	2.923118	5.142225	-0.489436
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