

## Supplementary Information

# Supramolecular Isomerism of a Metallocyclic Dipyridyldiamide Ligand Metal Halide System generating Isostructural (Hg, Co and Zn) Porous Materials.

Christopher Jones, Jin Chong Tan and Gareth O. Lloyd\*

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, United Kingdom, CB2 1EW. Fax: +44 1223 336362; Tel: + 44 1223 763989; E-mail: [gol20@cam.ac.uk](mailto:gol20@cam.ac.uk)

CCDC 851192 – 851197, 857511 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Suitable single crystals were mounted using perflouropolyether on a thin glass fibre. Crystallographic measurements were carried out using an Agilent Gemini Diffractometer. The instruments were equipped with a graphite monochromatic Mo-K $\alpha$  radiation ( $\gamma = 0.7107$ ) or mirror monochromatic CuK $\alpha$  radiation ( $\gamma = 1.5418$ ). The standard data collection temperature was 120 K, maintained using an open flow N<sub>2</sub> Oxford Cryostream device. Integration was carried out using CrysAlisPro software. Data sets were corrected for Lorentz and polarization effects and for the effects of absorption using SCALE3 ABSPACK. Structures were solved using direct methods in SHELXS-97<sup>1</sup> and developed using conventional alternating cycles of least-squares refinement with SHELXL-97<sup>1</sup> and difference Fourier synthesis with the aid of the graphical interface program X-Seed.<sup>2,3</sup> All non-hydrogen atoms were treated as anisotropic. In all cases hydrogen atoms were fixed in idealised positions and allowed to ride on the parent atom to which they were attached. Hydrogen atom thermal parameters were tied to those of the parent atom. Crystals of **A**, **D** and **E** had the Squeeze routine within Platon performed on the structure to take into account the highly disordered solvent guests after attempts to model the guests were unsuccessful.<sup>4</sup> The inclusion of the more rigid CS<sub>2</sub> and I<sub>2</sub> allowed for the modelling, however, soft restraints were necessary to keep the bond distances within reasonable values. Molecular graphics were produced using the program POV-Ray.<sup>5</sup>

### N,N'-(1,2-phenylene)diisonicotinamide, Ligand **1**.

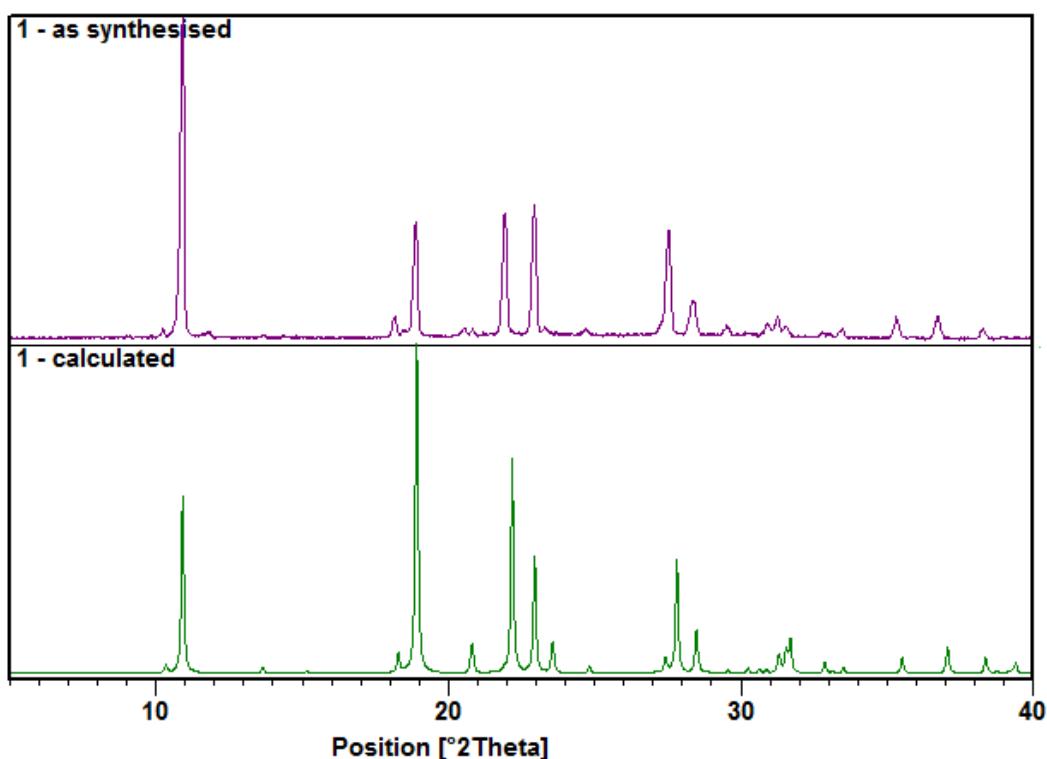
This ligand has been synthesised previously for coordination studies,<sup>6</sup> but a novel, relatively simple synthetic procedure was devised for this study. Isonicotinyl chloride hydrochloride (1.70 g, 9.6 mmol) was added to a stirred solution of o-phenylenediamine (0.52 g, 4.8 mmol) and triethylamine (3 g, 29.6 mmol) in THF (50 ml) at 0 °C. The suspension was heated under nitrogen at 80 °C for 48 h. The resulting off-white precipitate was stirred in ice-water (300 ml) then washed with ice-cold acetone (10 ml). The product was obtained as a white to pale yellow solid (0.538 g, 35 %), m.p. 288 - 290 °C (from DSC). If necessary, recrystallisation from MeOH gave pure materials.

Elemental Analysis ( $C_{18}H_{14}N_4O_2$ ) Calc. (%): C 67.92, H 4.44, N 17.60; Found (%): C 67.70, H 4.46, N 17.24.

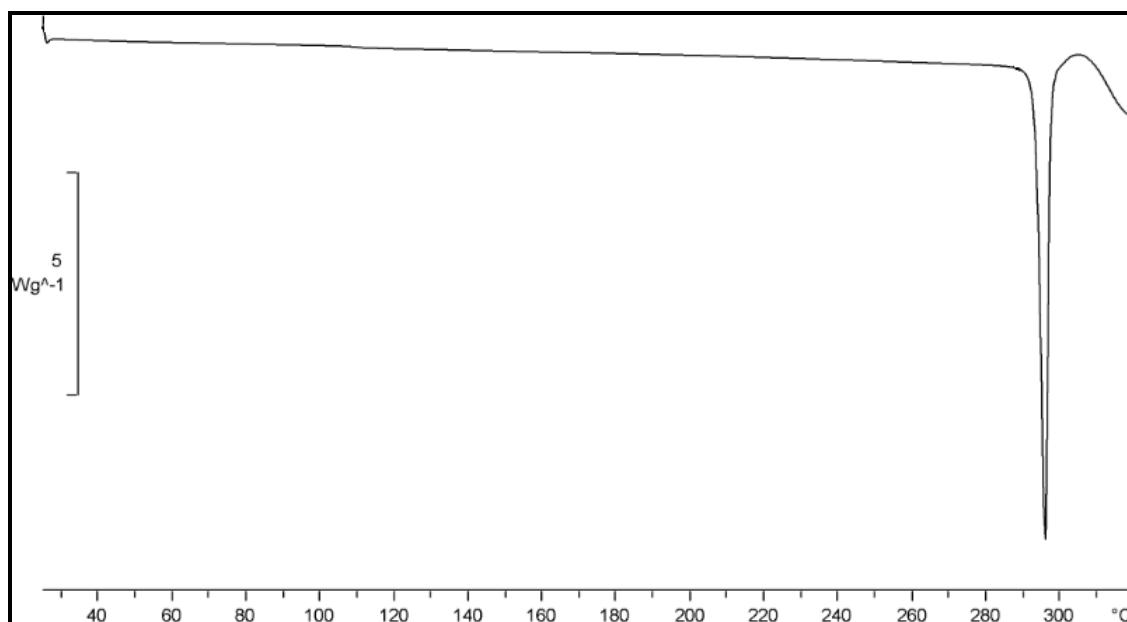
$^1H$  NMR (d<sub>6</sub>-DMSO, 400 MHz),  $\delta$ (ppm): 8.74 (dd, 4H, J 4.4 and 1.6 Hz), 8.71 (dd, 4H, J 4.4 and 1.6 Hz), 7.64 (dd, 2H, J 6.0 and 3.6 Hz), 7.30 (dd, 2H, J 6.0 and 3.6 Hz).

$^{13}C$  NMR (d<sub>6</sub>-DMSO, 400 MHz),  $\delta$ (ppm): 164.1, 150.4, 141.6, 131.2, 126.3, 126.0, 121.6.

IR  $\nu$  / cm<sup>-1</sup>: 3280 (s), 3050 (m), 1670 (s), 1600 (m), 1530 (s), 1490 (s), 1440 (m), 1410 (s), 1310 (s), 1280 (s), 1230 (m), 1110 (m), 1060 (m), 993 (m), 914 (s), 874 (w), 839 (m), 756 (s).



**Figure S1.** PXRD pattern of **1** compared with the pattern modelled from single-crystal data [CCDC ref. code BAXNIY].



**Figure S2.** DSC thermogram of **1** (3.36 mg) recorded with a linear temperature increase of 5 °C/min.

[Hg<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>] · MeOH or EtOH (Material A)

Ligand **1** (22 mg, 69 µmol) was dissolved in boiling methanol (10 ml) and the hot solution added through a filter to a solution of mercury (II) chloride (18 mg, 66 µmol) in methanol (7 ml). Crystallisation began almost immediately and continued over 3 days to yield the product as colourless needle-like crystals (23 mg, 19 µmol, 28 %) up to 1 cm in length, with m.p. 260 - 262 °C (from DSC). Alternative solvates were prepared in similar yields from ethanol (20 ml) and a 3:1 methanol : dichloromethane mixture (17 ml total). TGA (MeOH solvate): 40 – 170 °C, -5.2 % wet mass, 1.9 mol MeOH per mol [Hg<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>]; TGA (EtOH solvate): 40 – 220 °C, -5.8 % wet mass, 1.5 mol EtOH per mol [Hg<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>]; SQUEEZE (EtOH solvate): 68 electrons per cell, 1.2 mol EtOH per mol [Hg<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>], void volume 331.0 Å<sup>3</sup> per cell.

IR  $\nu$  / cm<sup>-1</sup> (EtOH solvate): 3250 (br), 1660 (s), 1600 (m), 1540 (m), 1520 (s), 1470 (m), 1420 (s), 1310 (s), 1270 (m), 1210 (w), 1060 (m), 1010 (w), 901 (w), 837 (m), 754 (s), 685 (m), 669 (m).

Crystal data for **A** (851192): C<sub>40</sub>H<sub>40</sub>Cl<sub>4</sub>Hg<sub>2</sub>N<sub>8</sub>O<sub>6</sub>,  $M = 1258.64$ , colourless needle, 0.23 × 0.16 × 0.15 mm<sup>3</sup>, monoclinic, space group  $P2_1/n$  (No. 14),  $a = 7.5177(2)$ ,  $b = 11.6687(3)$ ,  $c = 24.2254(7)$  Å,  $\beta = 95.782(2)$ °,  $V = 2114.28(10)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.853$  g/cm<sup>3</sup>,  $F_{000} = 1199$ , Xcalibur, Eos, Gemini ultra, Mo K $\alpha$  radiation,  $\lambda = 0.7107$  Å,  $T = 120.1$ K,  $2\theta_{\max} = 50.0$ °, 10725 reflections collected, 3703 unique ( $R_{\text{int}} = 0.0389$ ). Final  $GooF = 1.019$ ,  $RI = 0.0254$ ,  $wR2 = 0.0586$ ,  $R$  indices based on 3254 reflections with  $I > 2\sigma(I)$  (refinement

on  $F^2$ ), 236 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 7.552 \text{ mm}^{-1}$ .

[Hg<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>] . n(I<sub>2</sub>) (**A.I<sub>2</sub>**) and [Hg<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>] . n(CS<sub>2</sub>) (**A.CS<sub>2</sub>**)

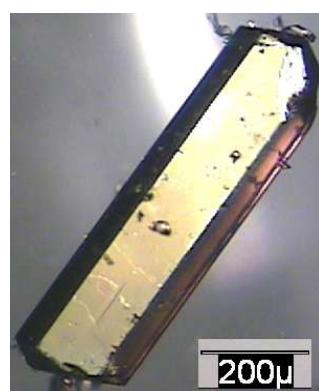
Macrocycle [Hg<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>] was desolvated by vacuum/N<sub>2</sub> cycling and heating to 80 °C over 6 hours. The PXRD after this procedure was identical to the pattern of the solvated structure, indicating that no decomposition or phase change occurred. The iodine and CS<sub>2</sub> adducts were obtained by placing the desolvated crystals in a sealed vial with iodine or CS<sub>2</sub> pellets for 3 days.

[Hg<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>] . n(I<sub>2</sub>). SQUEEZE: 112 electrons per cell, 0.53 moles I<sub>2</sub> per mole [Hg<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>]. Refinement of occupancy of I<sub>2</sub> gave 0.59 moles. Elemental Analysis (Hg<sub>2</sub>Cl<sub>4</sub>C<sub>36</sub>H<sub>28</sub>N<sub>8</sub>O<sub>4</sub> . nI<sub>2</sub>) Found (%): C 32.45, H 2.45, N 8.21; Calc. (%) for n = 0.64: C 32.21, H 2.10, N 8.34.

[Hg<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>] . n(CS<sub>2</sub>). TGA (Figure S?) analysis indicated 0.61 moles CS<sub>2</sub> per moles of [Hg<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>], which matches well with the crystallographic determination of the mole ratio (0.6 moles).

Crystal data for **A.I<sub>2</sub>** (851194): C<sub>36</sub>H<sub>28</sub>Cl<sub>4</sub>Hg<sub>2</sub>I<sub>1.18</sub>N<sub>8</sub>O<sub>4</sub>,  $M = 1328.88$ , colourless needle,  $0.5205 \times 0.1823 \times 0.1106 \text{ mm}^3$ , monoclinic, space group  $P2_1/n$  (No. 14),  $a = 7.4703(2)$ ,  $b = 11.6228(3)$ ,  $c = 24.2709(6) \text{ \AA}$ ,  $\beta = 96.023(3)^\circ$ ,  $V = 2095.71(9) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 2.096 \text{ g/cm}^3$ ,  $F_{000} = 1247.2$ , Xcalibur, Eos, Gemini ultra, Mo K $\alpha$  radiation,  $\lambda = 0.7107 \text{ \AA}$ ,  $T = 120(2)\text{K}$ ,  $2\theta_{\max} = 50.0^\circ$ , 12682 reflections collected, 3676 unique ( $R_{\text{int}} = 0.0404$ ). Final  $GooF = 2.443$ ,  $R1 = 0.0893$ ,  $wR2 = 0.1619$ ,  $R$  indices based on 3498 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ), 253 parameters, 1 restraint. Lp and absorption corrections applied,  $\mu = 8.448 \text{ mm}^{-1}$ .

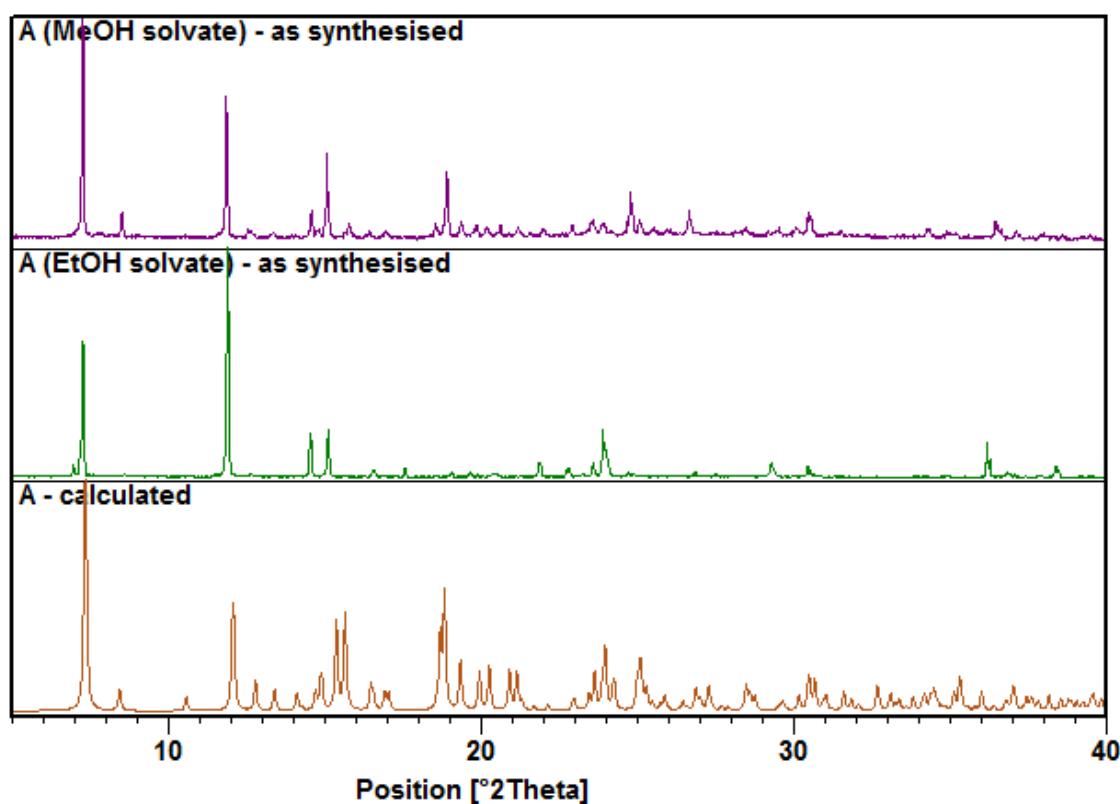
Crystal data for **A.CS<sub>2</sub>** (851193): C<sub>36.60</sub>H<sub>28</sub>Cl<sub>4</sub>Hg<sub>2</sub>N<sub>8</sub>O<sub>4</sub>S<sub>1.20</sub>,  $M = 1225.33$ , colourless needle,  $0.26 \times 0.18 \times 0.15 \text{ mm}^3$ , monoclinic, space group  $P2_1/n$  (No. 14),  $a = 7.4559(2)$ ,  $b = 11.6141(2)$ ,  $c = 24.2824(5) \text{ \AA}$ ,  $\beta = 96.263(2)^\circ$ ,  $V = 2090.15(8) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.947 \text{ g/cm}^3$ ,  $F_{000} = 1165.6$ , Xcalibur, Eos, Gemini ultra, MoK $\alpha$  radiation,  $\lambda = 0.7107 \text{ \AA}$ ,  $T = 120(2)\text{K}$ ,  $2\theta_{\max} = 50.0^\circ$ , 16684 reflections collected, 3654 unique ( $R_{\text{int}} = 0.0375$ ). Final  $GooF = 1.194$ ,  $R1 = 0.0362$ ,  $wR2 = 0.1078$ ,  $R$  indices based on 3457 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ), 250 parameters, 1 restraint. Lp and absorption corrections applied,  $\mu = 7.700 \text{ mm}^{-1}$ .



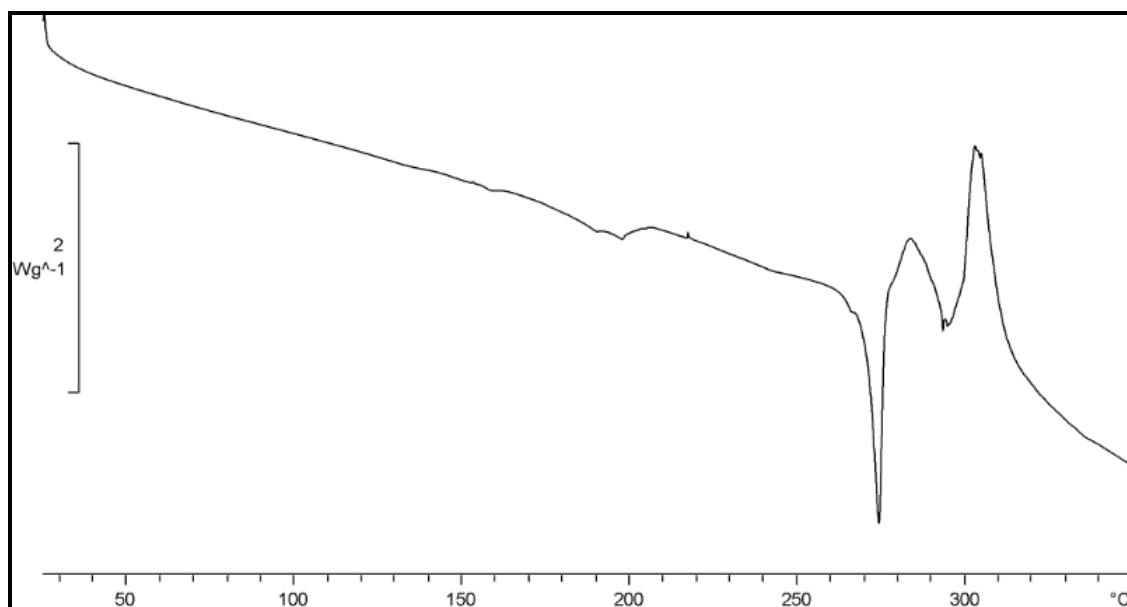
**Figure S3.** Typical colourless crystal of  $[\text{Hg}_2\text{Cl}_4\mathbf{1}_2] \cdot \text{MeOH}$  (Material A)



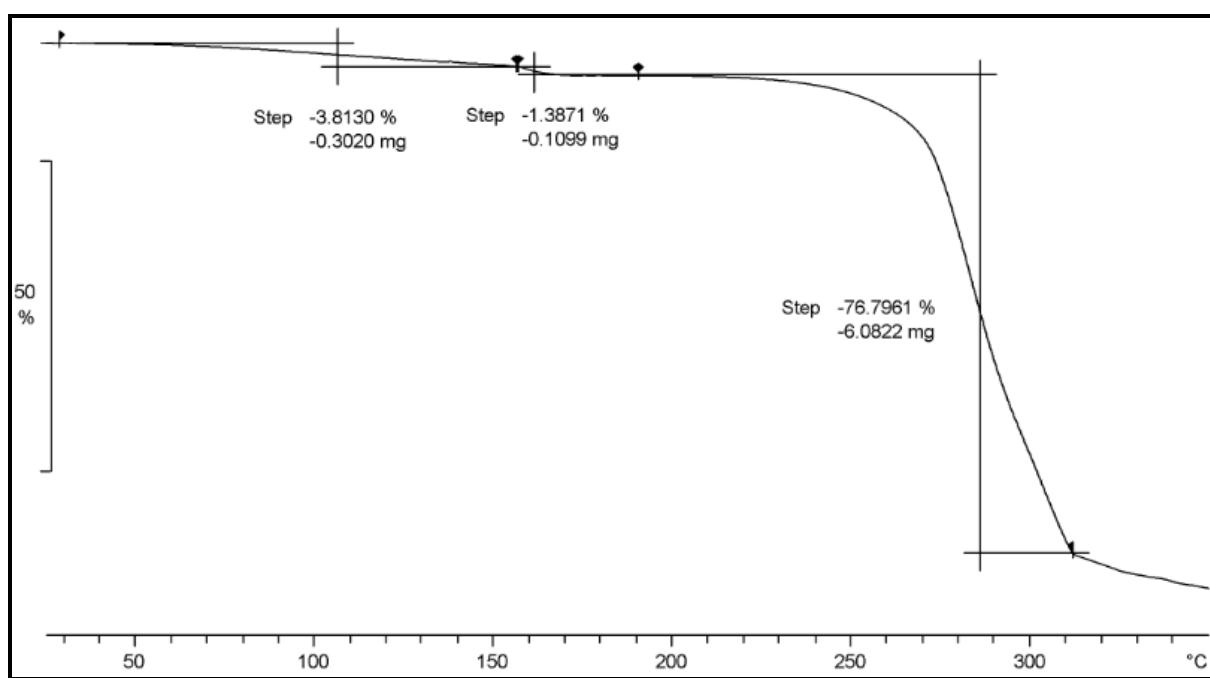
**Figure S4.** Typical crystal of  $[\text{Hg}_2\text{Cl}_4\mathbf{1}_2] \cdot \text{I}_2$  (A.I<sub>2</sub>).



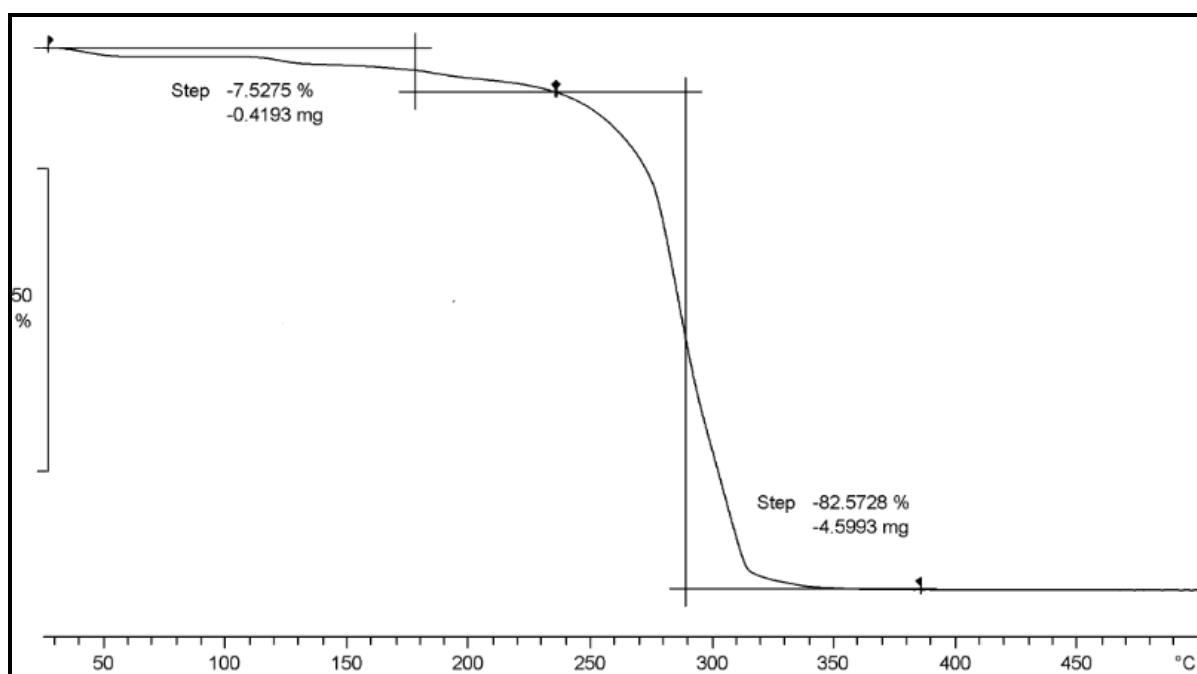
**Figure S5.** PXRD pattern of solvates of A compared with the modelled pattern. Real samples showed preferred orientation [010].



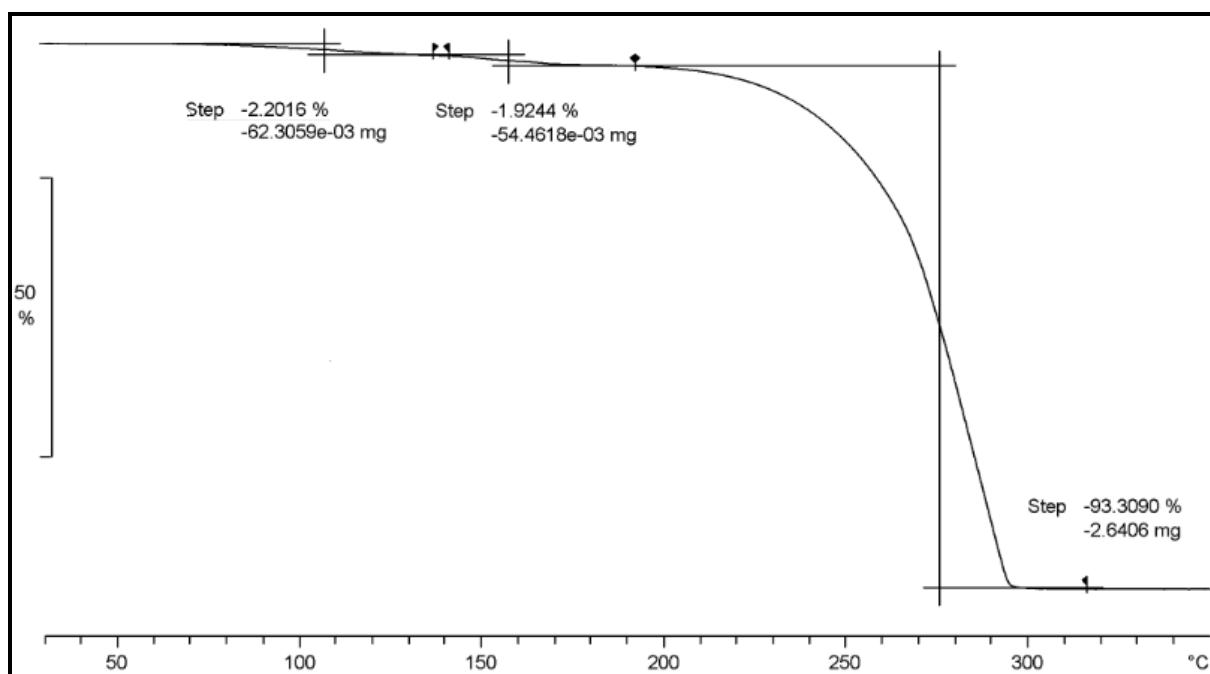
**Figure S6.** DSC thermogram of **A** methanol solvate (3.85 mg) recorded with a linear temperature increase of 5 °C/min.



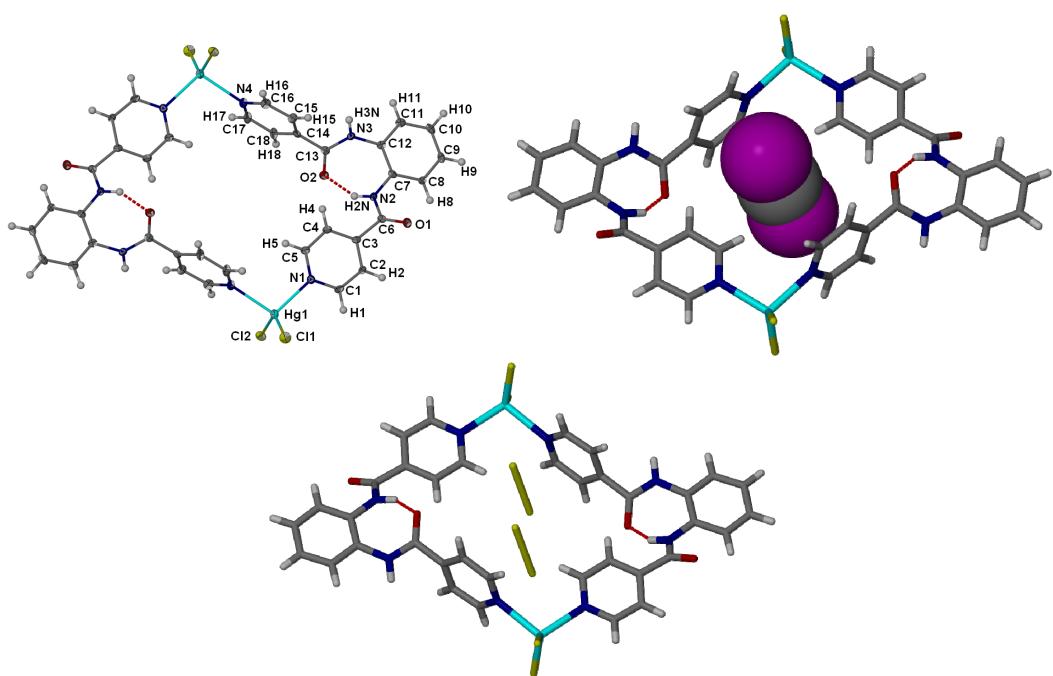
**Figure S7.** TGA trace of **A** (MeOH solvate, 7.92 mg) recorded with a linear temperature increase of 10 °C/min.



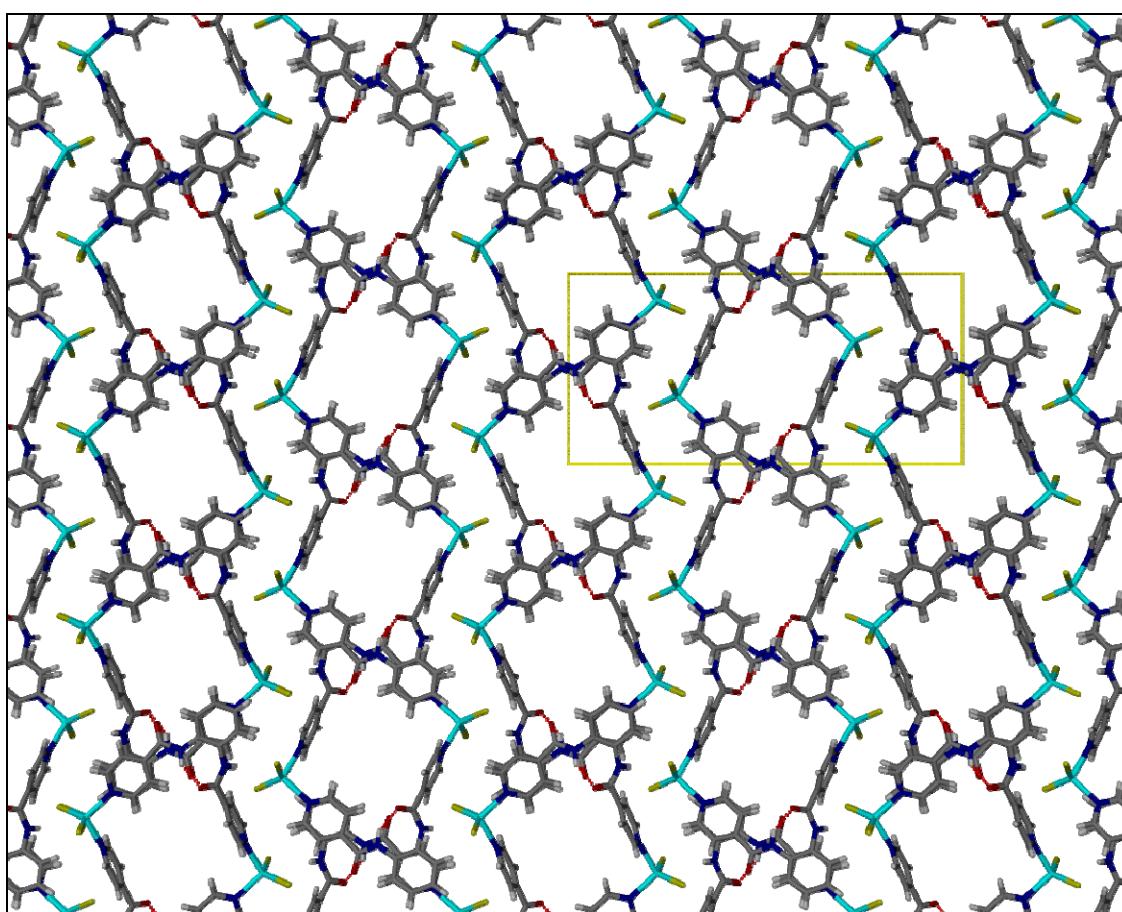
**Figure S8.** TGA trace of **A** (EtOH solvate, 5.57 mg) recorded with a linear temperature increase of 10 °C/min.



**Figure S9.** TGA trace of **A.CS<sub>2</sub>** (2.83 mg) recorded with a linear temperature increase of 10 °C/min.



**Figure S10.** Metallocycles of material **A**. The asymmetric unit is labelled. Atoms are shown as ellipsoids at 50% probability in as-synthesised **A**, and closed-stick representation in the structures of **A-CS<sub>2</sub>** and **A-I<sub>2</sub>**. Note that the I<sub>2</sub> is disordered over two positions. **A-CS<sub>2</sub>** and **A-I<sub>2</sub>** were synthesised by desolvation of **A** and exposure to vapours of CS<sub>2</sub> and I<sub>2</sub> via a single-crystal-to-single-crystal transformation.

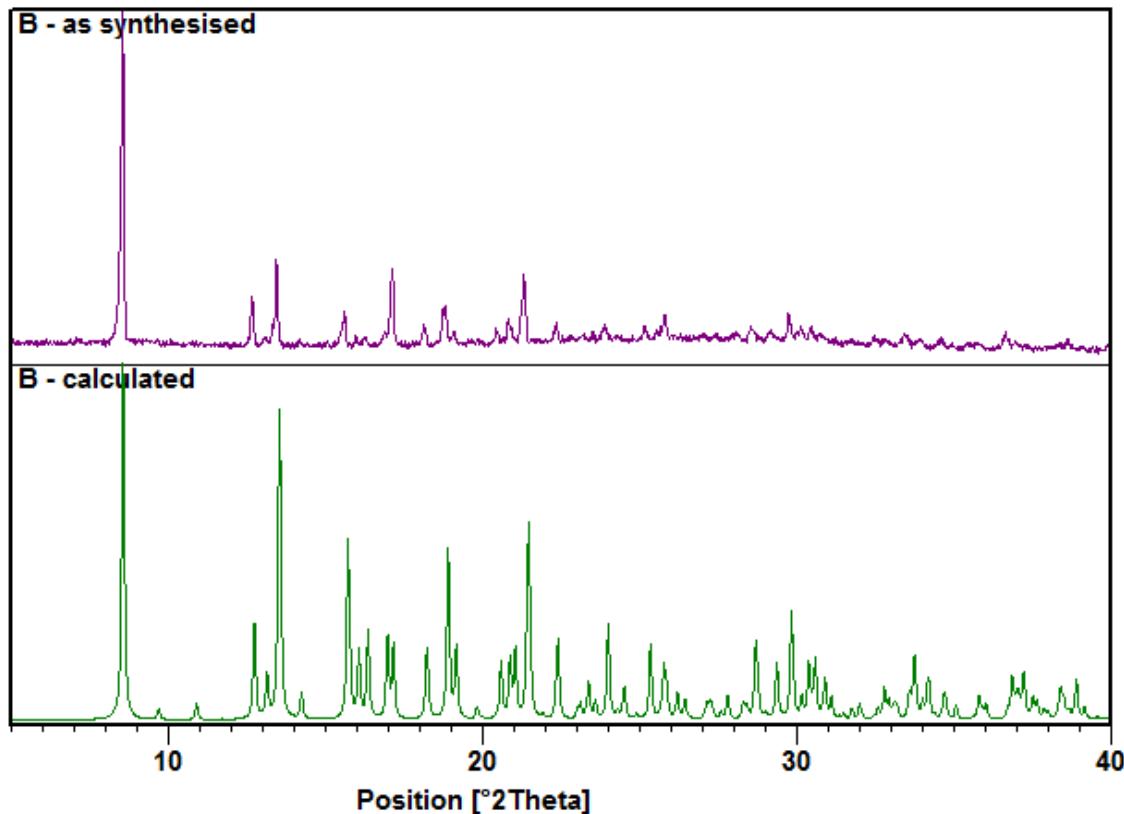


**Figure S11.** Packed out structure of **A** showing the channels. Yellow lines show unit cell. Structure viewed down [100]. Atoms shown in capped stick representation.

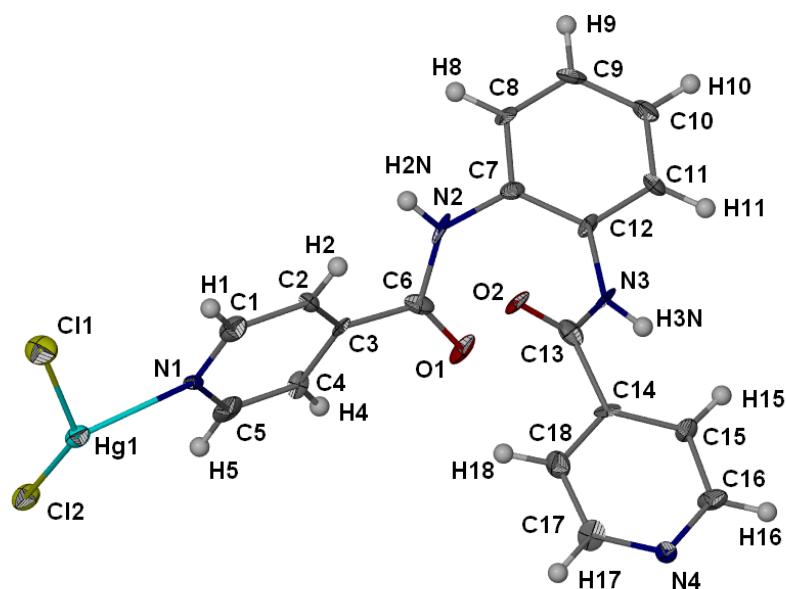
#### [HgCl<sub>2</sub>1]<sub>n</sub> (Material **B**)

Ligand **1** (2.8 mg, 8.8 µmol) was dissolved in boiling methanol (0.5 ml). The hot solution was added immediately to a suspension of mercury chloride (2.4 mg, 8.8 µmol) in dichloromethane (1.5 ml), and the hot mixture shaken to dissolve. The white product precipitated over 2 hours as a microcrystalline powder and small block-like crystals.

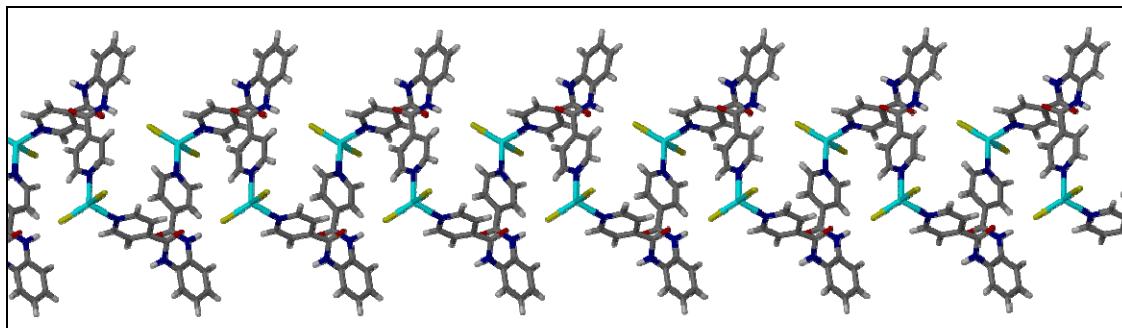
Crystal data for **B** (851195): C<sub>18</sub>H<sub>14</sub>Cl<sub>2</sub>HgN<sub>4</sub>O<sub>2</sub>,  $M = 589.82$ , colourless block, 0.35 × 0.28 × 0.21 mm<sup>3</sup>, monoclinic, space group  $P2_1/c$  (No. 14),  $a = 10.3530(10)$ ,  $b = 11.0411(8)$ ,  $c = 16.2530(12)$  Å,  $\beta = 93.079(7)^\circ$ ,  $V = 1855.2(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.112$  g/cm<sup>3</sup>,  $F_{000} = 1120$ , Xcalibur, Eos, Gemini ultra, Mo K $\alpha$  radiation,  $\lambda = 0.7107$  Å,  $T = 173(2)$ K,  $2\theta_{\max} = 52.0^\circ$ , 8150 reflections collected, 3629 unique ( $R_{\text{int}} = 0.0956$ ). Final  $GooF = 0.944$ ,  $R1 = 0.0604$ ,  $wR2 = 0.1025$ ,  $R$  indices based on 2309 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ), 244 parameters, 54 restraints. Lp and absorption corrections applied,  $\mu = 8.606$  mm<sup>-1</sup>.



**Figure S12.** PXRD pattern of **B** compared with the pattern modelled from single-crystal data.



**Figure S13.** Asymmetric unit of the material **B**. Atoms are shown as ellipsoids at 50% probability.

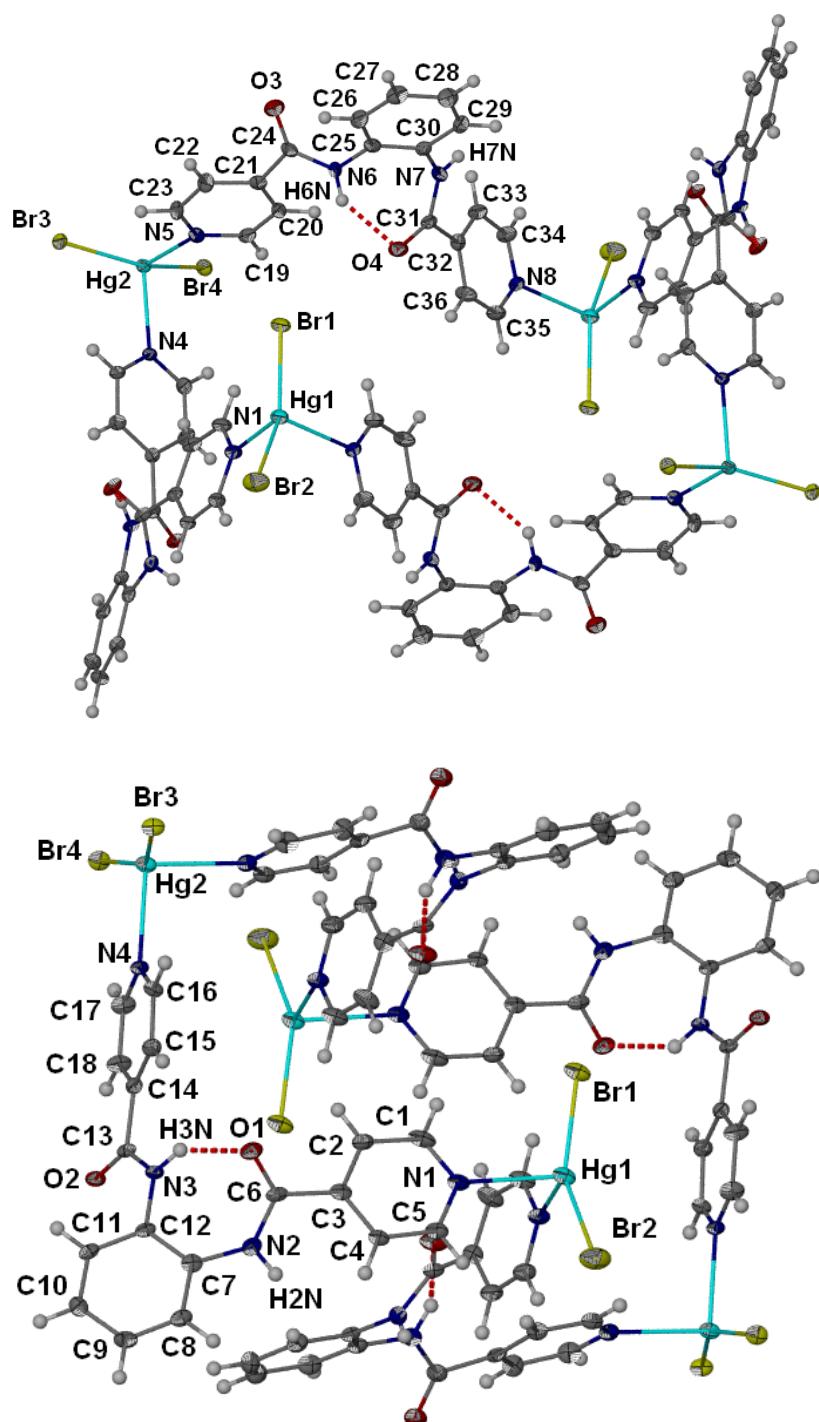


**Figure S14.** One-dimensional chain of **B**. Atoms are shown in capped-stick representation.

[Hg<sub>4</sub>Br<sub>8</sub>**1**<sub>4</sub>] . MeOH (Material C)

Ligand **1** (37 mg, 0.12 mmol) and mercury (II) bromide (43 mg, 0.12 mmol) were stirred in a 5:1 methanol : dichloromethane mixture (30 ml total) at 80°C for 30 minutes. The solution was separated into vials and left to stand for 7 days, to yield the product as colourless block-like crystals.

Crystal data for **C** (851196): C<sub>73</sub>H<sub>60</sub>Br<sub>8</sub>Hg<sub>4</sub>N<sub>16</sub>O<sub>9</sub>,  $M = 2747.01$ , colourless block,  $0.24 \times 0.21 \times 0.19 \text{ mm}^3$ , triclinic, space group P-1 (No. 2),  $a = 10.2403(3)$ ,  $b = 11.5470(3)$ ,  $c = 17.2774(4) \text{ \AA}$ ,  $\alpha = 98.323(2)$ ,  $\beta = 95.234(2)$ ,  $\gamma = 95.764(2)^\circ$ ,  $V = 1999.58(9) \text{ \AA}^3$ ,  $Z = 1$ ,  $D_c = 2.281 \text{ g/cm}^3$ ,  $F_{000} = 1282$ , Xcalibur, Eos, Gemini ultra, Mo K $\alpha$  radiation,  $\lambda = 0.7107 \text{ \AA}$ ,  $T = 120.0 \text{ K}$ ,  $2\theta_{\max} = 50.0^\circ$ , 24197 reflections collected, 7033 unique ( $R_{\text{int}} = 0.0342$ ). Final  $GooF = 1.027$ ,  $R1 = 0.0245$ ,  $wR2 = 0.0499$ ,  $R$  indices based on 5996 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ), 508 parameters, 2 restraints. Lp and absorption corrections applied,  $\mu = 11.717 \text{ mm}^{-1}$ .



**Figure S15.** Two different views of the  $4 \times 4$  metallocycle formed by ligand **1** and  $\text{HgBr}_2$  in material **C**. Atoms of the asymmetric unit are labelled. Atoms are shown as ellipsoids at 50% probability.

### [Co<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>] . EtOH (Material **D**)

Ligand **1** (22 mg, 69 µmol) was dissolved in boiling ethanol (10 ml) and the hot solution added through a filter to a solution of cobalt chloride hexahydrate (16 mg, 67 µmol) in ethanol (7 ml). The solution formed a gel on cooling, which returned to a solution after 1 day. The product formed over 3 days as blue needle-like crystals (29 mg, 32 µmol, 48 %), m.p. 318 - 322 °C (from DSC).

TGA: 30 – 70 °C, -4.8 % wet mass, 0.98 mol EtOH per mol [Co<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>]; SQUEEZE: 68 electrons per cell, 1.3 mol EtOH per mol [Co<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>], void volume 298.3 Å<sup>3</sup> per cell.

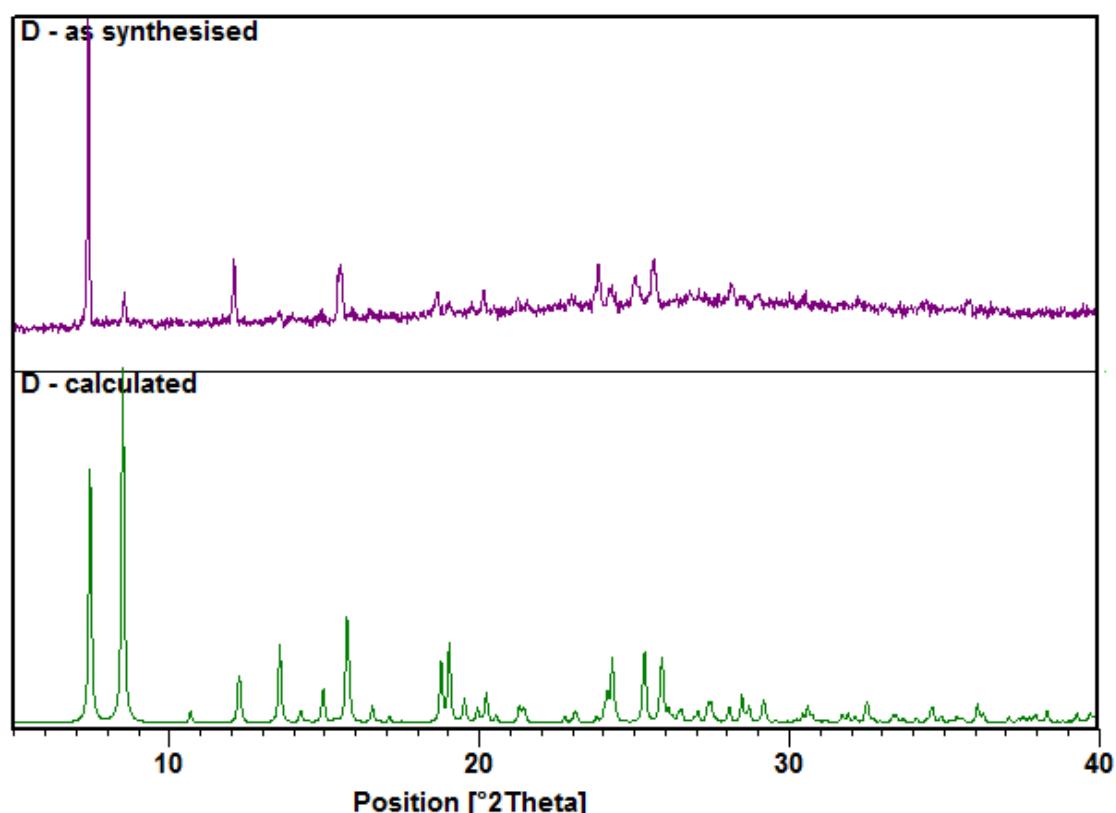
IR:  $\nu$  / cm<sup>-1</sup>: 3220 (br), 3040 (m), 1650 (s), 1600 (m), 1520 (s), 1480 (m), 1430 (m), 1420 (s), 1310 (s), 1270 (w), 1210 (w), 1060 (s), 1030 (w), 899 (w), 843 (m), 768 (s), 688 (m), 677 (s).

Crystal data for **D** (851197): C<sub>36</sub>H<sub>28</sub>Cl<sub>4</sub>Co<sub>2</sub>N<sub>8</sub>O<sub>4</sub>,  $M = 896.32$ , blue flat needles, 0.31 × 0.18 × 0.11 mm<sup>3</sup>, monoclinic, space group  $P2_1/n$  (No. 14),  $a = 7.3899(5)$ ,  $b = 11.5287(10)$ ,  $c = 23.764(2)$  Å,  $\beta = 94.810(6)^\circ$ ,  $V = 2017.5(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.475$  g/cm<sup>3</sup>,  $F_{000} = 908$ , Xcalibur, Eos, Gemini ultra, Cu K $\alpha$  radiation,  $\lambda = 1.5418$  Å,  $T = 120.1$ K,  $2\theta_{\max} = 141.1^\circ$ , 6884 reflections collected, 3725 unique ( $R_{\text{int}} = 0.0489$ ). Final  $GooF = 1.009$ ,  $R1 = 0.0482$ ,  $wR2 = 0.1154$ ,  $R$  indices based on 2957 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ), 244 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 9.280$  mm<sup>-1</sup>.

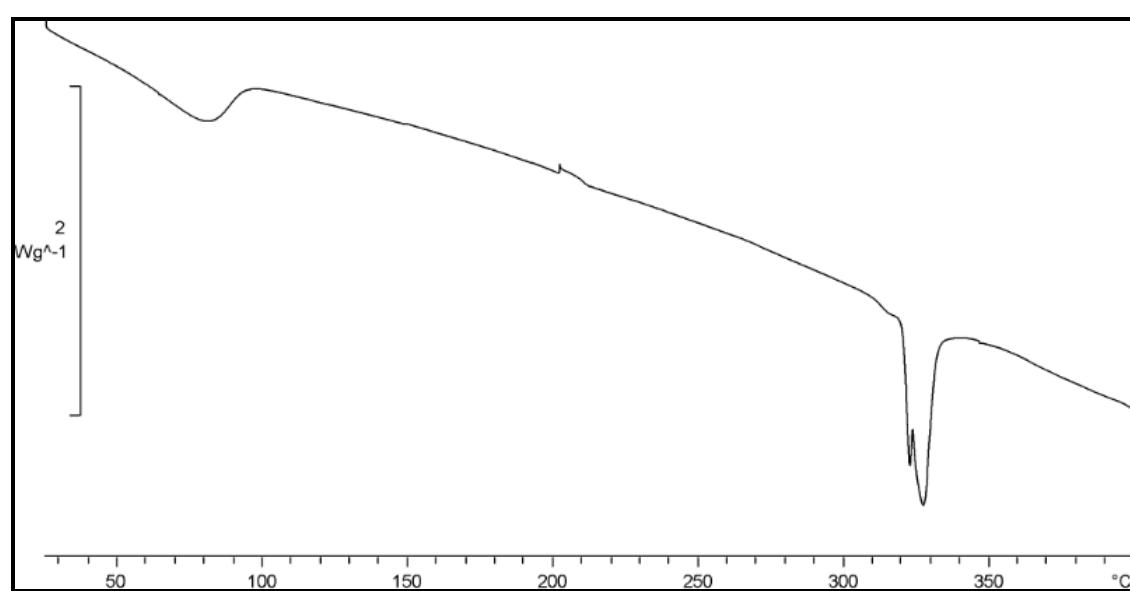
### [Co<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>] . I<sub>2</sub>

Macrocycle [Co<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>] . EtOH was desolvated by vacuum/N<sub>2</sub> cycling and heating to 80 °C. The PXRD pattern after this procedure was the same as that of the pattern of the solvated structure, indicating that no decomposition or phase change occurred. The iodine adduct was obtained by placing the desolvated crystals in a sealed vial with iodine pellets for 3 days.

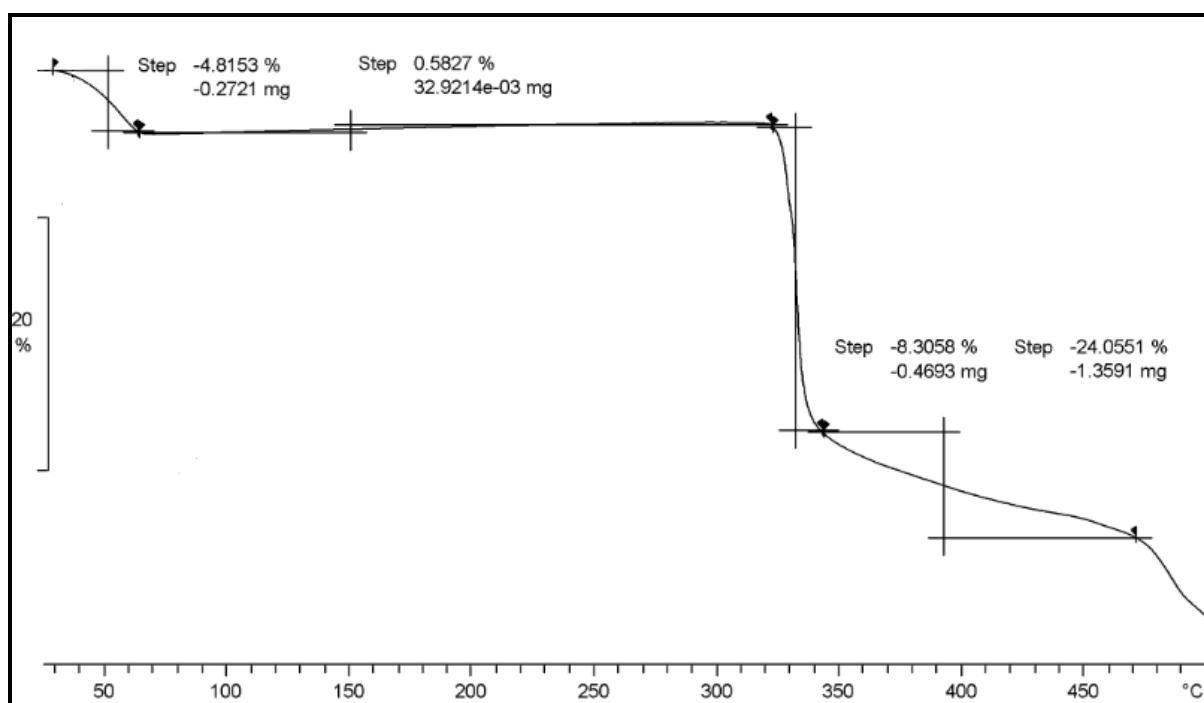
TGA: 40 – 290 °C, -9.4 % initial mass, 0.37 mol I<sub>2</sub> per mol [Co<sub>2</sub>Cl<sub>4</sub>**1**<sub>2</sub>]. Elemental Analysis (Co<sub>2</sub>Cl<sub>4</sub>C<sub>36</sub>H<sub>28</sub>N<sub>8</sub>O<sub>4</sub> . nI<sub>2</sub>) Found (%): C 39.61, H 2.86, N 10.10; Calc. (%) for  $n = 0.78$ : C 39.61, H 2.86, N 10.1.



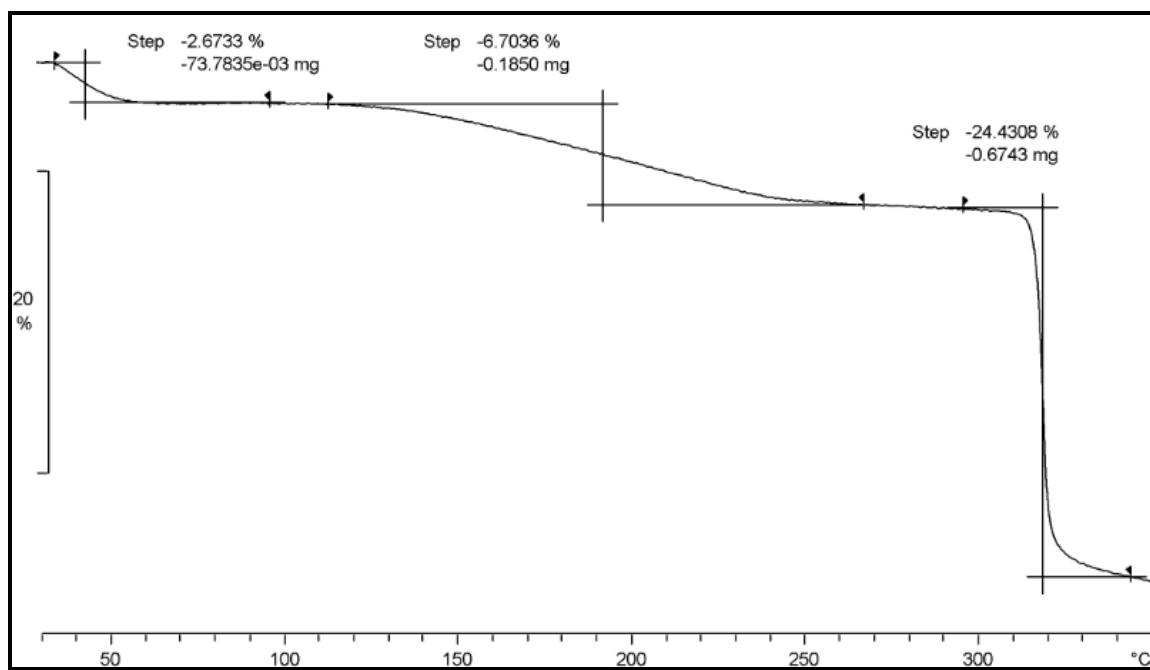
**Figure S16.** PXRD pattern of **D** compared with the pattern modelled from single-crystal data.



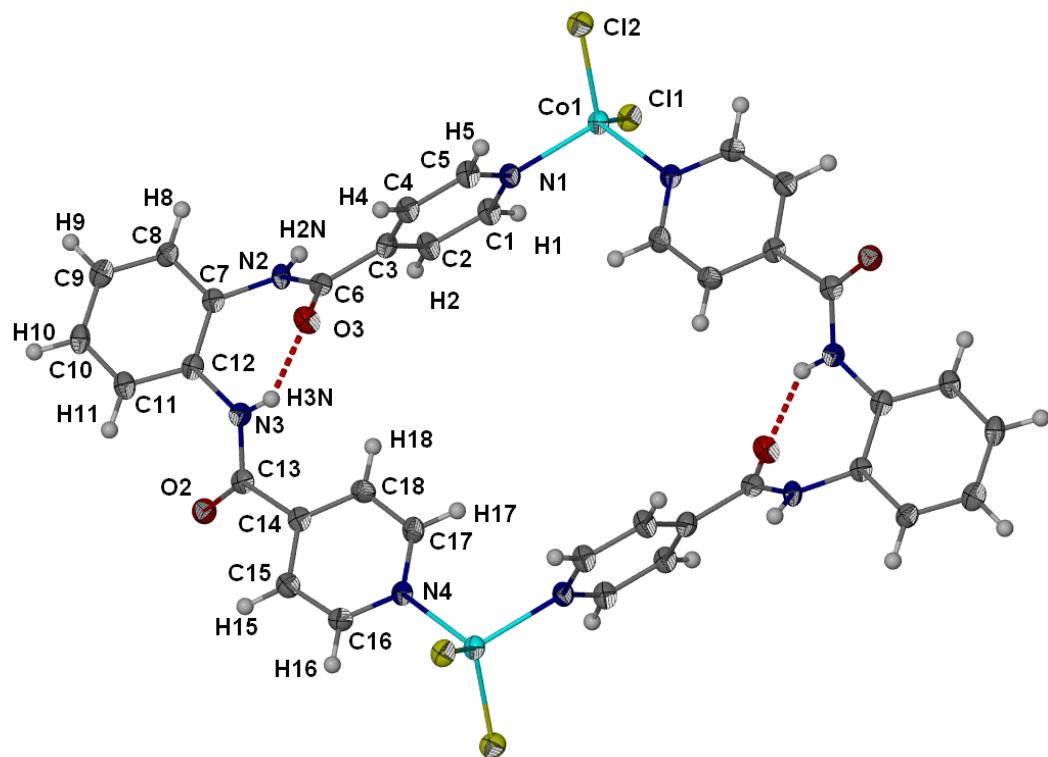
**Figure S17.** DSC thermogram of **D** (3.76 mg) recorded with a linear temperature increase of 5 °C/min.



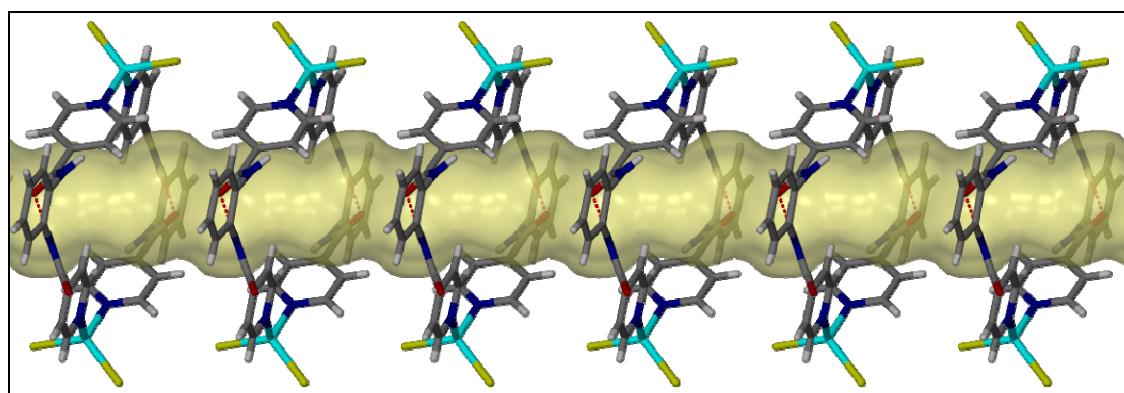
**Figure S18.** TGA trace of D (5.65 mg) recorded with a linear temperature increase of 10 °C/min.



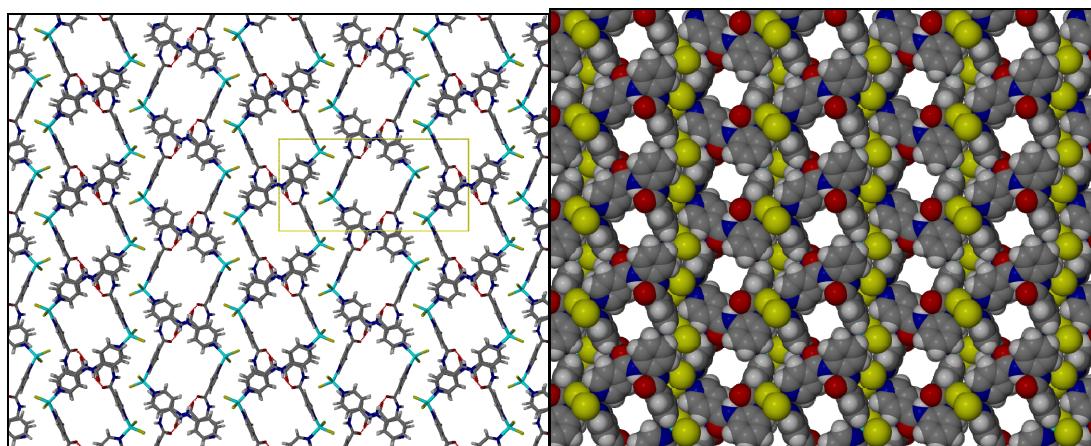
**Figure S19.** TGA trace of D.I<sub>2</sub> (2.76 mg) recorded with a linear temperature increase of 10 °C/min.



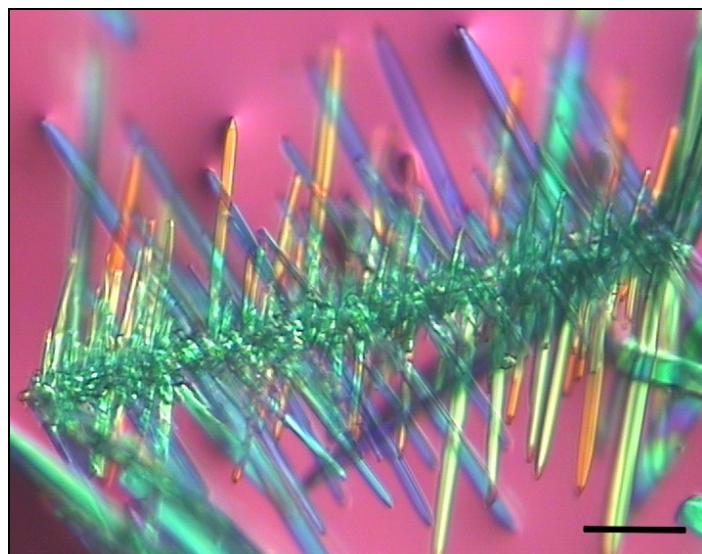
**Figure S20.** Metallocycle of material **D**. The asymmetric unit is labelled. Atoms are shown as ellipsoids at 50% probability.



**Figure S21.** The packing of the metallocycles in **D** results in a one-dimensional column which is represented in this figure by the yellow surface.



**Figure S22.** Packing of the metallocycles in **D** results in one-dimensional columns running along [100]. Molecules shown in capped stick representation on the left and spheres of van der Waal's radii on the right.



**Figure S23.** Optical micrograph showing the branching morphology of crystalline **D**. Scale bar represents 30  $\mu\text{M}$ .

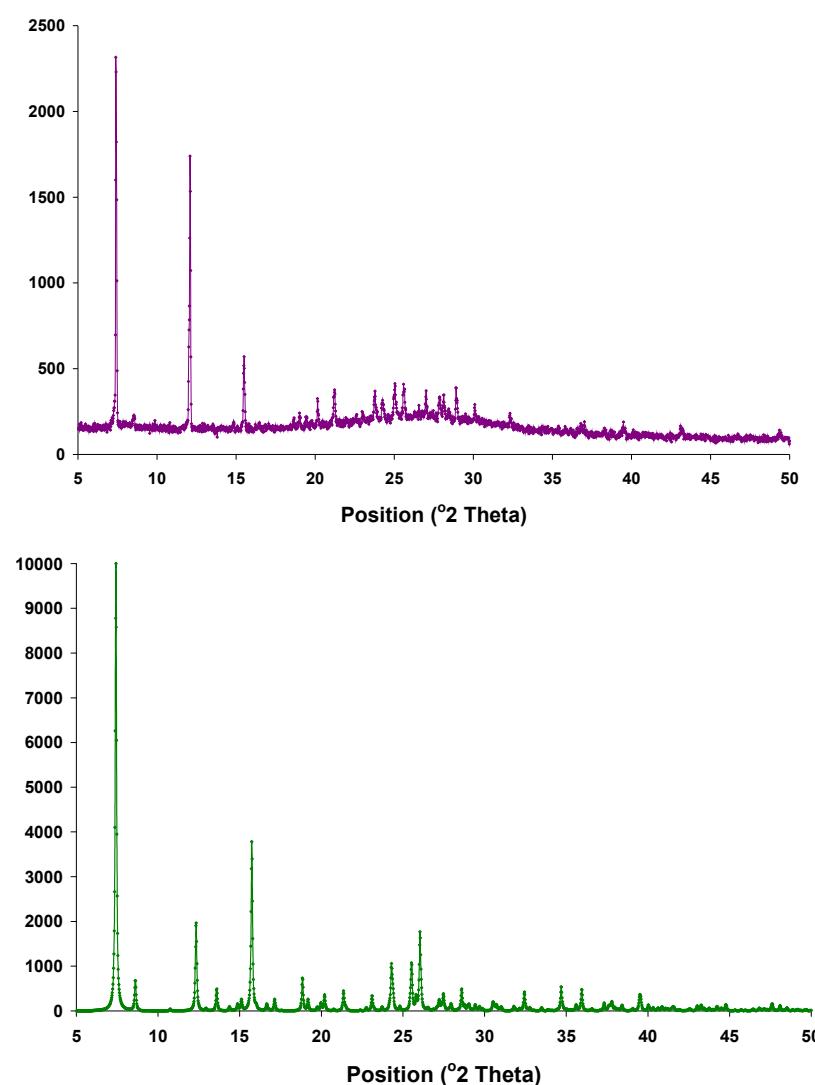
#### $\text{Zn}_2\text{Cl}_2\mathbf{1}_4 \cdot 5\text{MeOH}$ (Material **E**)

Ligand **1** (6.0 mg, 19  $\mu\text{mol}$ ) was dissolved in boiling ethanol (4 ml) and the hot solution added through a filter to a solution of zinc chloride (3.0 mg, 22  $\mu\text{mol}$ ) in ethanol (4 ml). The product formed over 3 days as colourless or pale yellow needle-like crystals (3.5 mg, 3.8  $\mu\text{mol}$ , 20 %), m.p. 316 – 319 °C (from DSC).

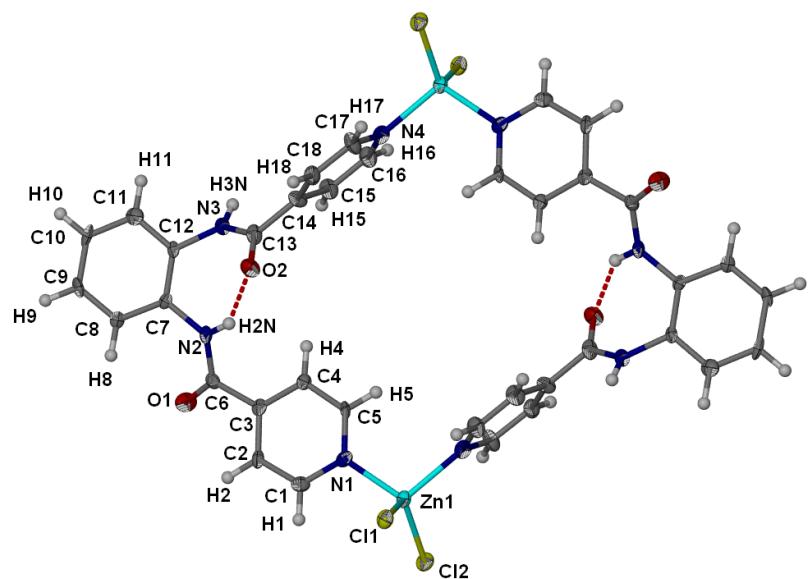
TGA (EtOH solvate): 30 – 140°C, -6.5 % wet mass, 1.4 mol EtOH per mol **8**; SQUEEZE (EtOH solvate): 58 electrons per cell, 1.1 mol EtOH per mol **8**, void volume 290.2 Å<sup>3</sup> per cell.  $\nu$  / cm<sup>-1</sup> (EtOH solvate): 3240 (br), 3050 (br), 1650 (m), 1600 (m), 1520 (s), 1450

(m), 1420 (s), 1310 (s), 1270 (m), 1210 (w), 1070 (s), 1030 (s), 901 (m), 849 (s), 769 (s), 690 (s).

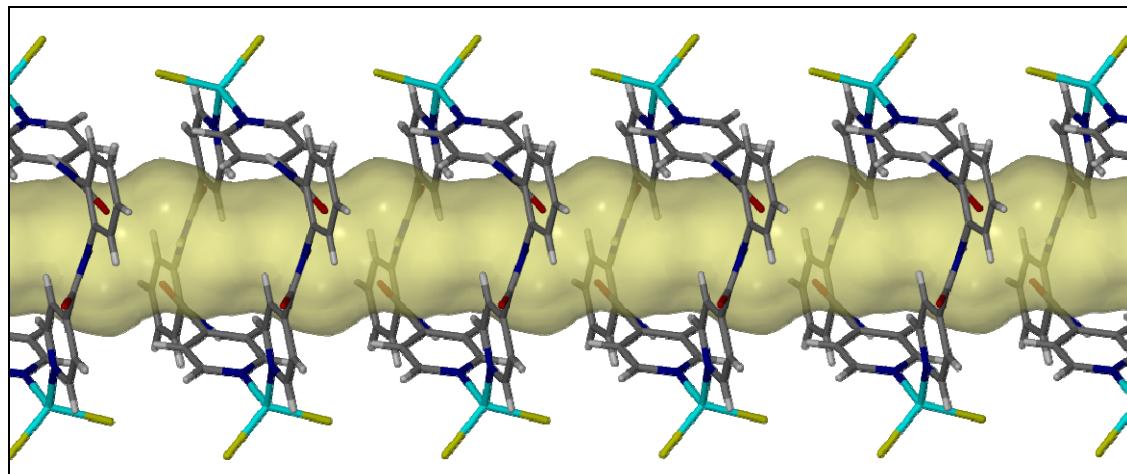
Crystal data for **E** (857511):  $C_{36}H_{28}Cl_4N_8O_4Zn_2$ ,  $M = 909.20$ , colourless needle,  $0.5505 \times 0.1604 \times 0.0505$  mm<sup>3</sup>, monoclinic, space group  $P2_1/n$  (No. 14),  $a = 7.3482(5)$ ,  $b = 11.3708(6)$ ,  $c = 23.8973(16)$  Å,  $\beta = 94.865(6)^\circ$ ,  $V = 1989.5(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.514$  g/cm<sup>3</sup>,  $F_{000} = 920$ , Xcalibur, Eos, Gemini ultra, Mo K $\alpha$  radiation,  $\lambda = 0.7107$  Å,  $T = 120.0$  K,  $2\theta_{\max} = 50.0^\circ$ , 6435 reflections collected, 3487 unique ( $R_{\text{int}} = 0.0526$ ). Final  $GooF = 1.140$ ,  $RI = 0.0947$ ,  $wR2 = 0.2363$ ,  $R$  indices based on 2573 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ), 244 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 1.523$  mm<sup>-1</sup>.



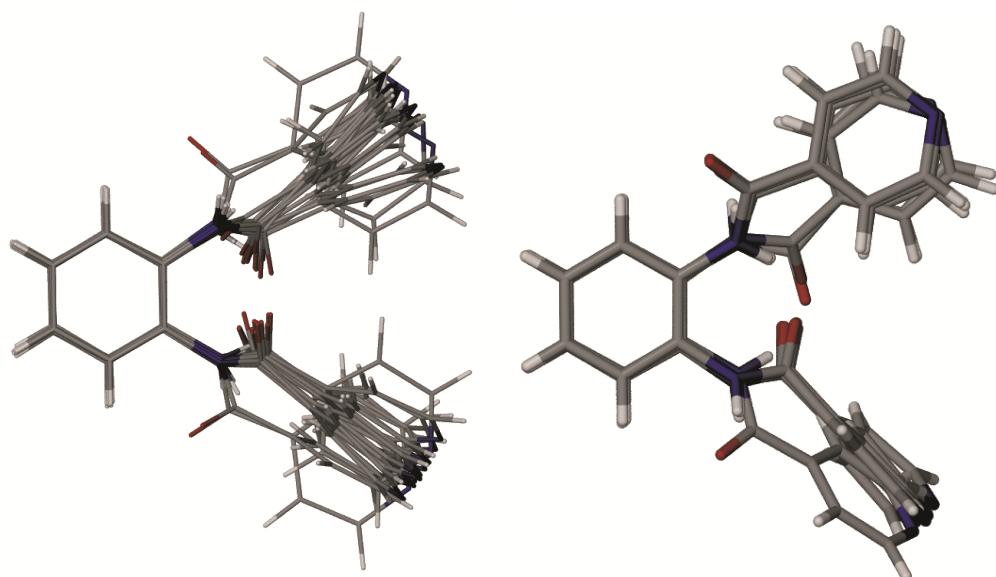
**Figure S24.** PXRD patterns of **E**. Experimental pattern top and simulated pattern from single crystal data with a preferred orientation of [010] bottom.



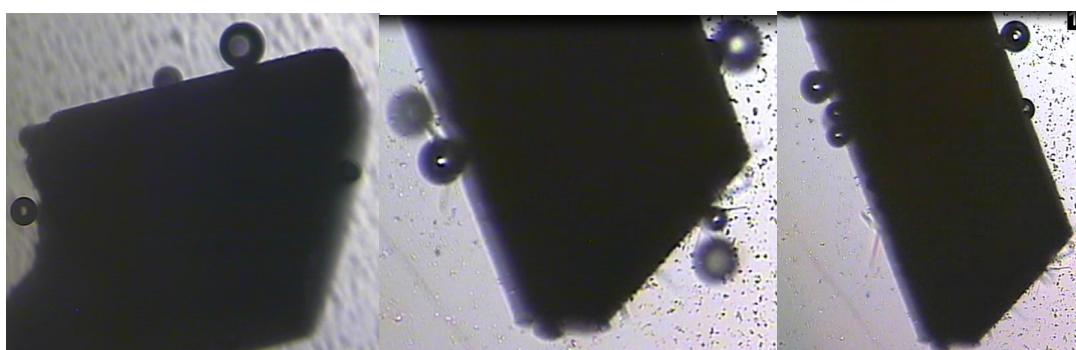
**Figure S25.** Metallocycle of material **E**. The asymmetric unit is labelled. Atoms are shown as ellipsoids at 50% probability.



**Figure S26.** The packing of the metallocycles in **E** results in a one-dimensional column which is represented in this figure by the yellow surface.



**Figure S27.** Overlays of the structures of ligand 1. Left, published structures. The majority show anti-parallel hydrogen bonding and parallel pyridyl rings. The two significantly different examples show hydrogen bonding to trifluoroacetate anion (CCDC ref. code BAXNOE) and show a parallel hydrogen bonding tape with intramolecular NH O and intermolecular CH O hydrogen bonding (CCDC ref. code XAHRUU). Right, structures from this publication. The intramolecular hydrogen bonding and the orthogonal pyridyl rings can be easily noted and their structural difference to the “normal” anti-parallel hydrogen bonding and parallel pyridyl rings.



**Figure S28.** From left to right.  $\text{CS}_2$  bubbling from **A** at  $153^\circ\text{C}$ .  $\text{I}_2$  bubbling from **A** at  $160^\circ\text{C}$ .  $\text{I}_2$  bubbling from **A** at  $160^\circ\text{C}$  after the end tips of the crystals have stopped bubbling.

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