Supplementary Information

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

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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.

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-Kα radiation (γ = 0.7107) or mirror monochromatic CuKα radiation (γ = 1.5418). The standard data collection temperature was 120 K, maintained using an open flow N2 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 and developed using conventional alternating cycles of least-squares refinement with SHELXL-97 and difference Fourier synthesis with the aid of the graphical interface program X-Seed. 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. The inclusion of the more rigid CS2 and I2 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.

N,N’-(1,2-phenylene)diisonicotinamide, Ligand 1.

This ligand has been synthesised previously for coordination studies, 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$_4$O$_2$) Calc. (%): C 67.92, H 4.44, N 17.60; Found (%): C 67.70, H 4.46, N 17.24.

$^1$H NMR (d$_6$-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$_6$-DMSO, 400 MHz), $\delta$(ppm): 164.1, 150.4, 141.6, 131.2, 126.3, 126.0, 121.6.

IR $\nu$ / cm$^{-1}$: 3280 (s), 3050 (m), 1670 (s), 1600 (s), 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].
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 \([\text{Hg}_2\text{Cl}_4\text{I}_2]\); TGA (EtOH solvate): 40 – 220 °C, -5.8 % wet mass, 1.5 mol EtOH per mol \([\text{Hg}_2\text{Cl}_4\text{I}_2]\); SQUEEZE (EtOH solvate): 68 electrons per cell, 1.2 mol EtOH per mol \([\text{Hg}_2\text{Cl}_4\text{I}_2]\), void volume 331.0 Å³ per cell.

IR ν / cm⁻¹ (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): C₄₀H₄₀Cl₄Hg₂N₈O₆, M = 1258.64, colourless needle, 0.23 x 0.16 x 0.15 mm³, monoclinic, space group P2₁/n (No. 14), a = 7.5177(2), b = 11.6687(3), c = 24.2254(7) Å, β = 95.782(2)°, V = 2114.28(10) Å³, Z = 2, Dc = 1.853 g/cm³, F₀₀₀ = 1199, Xcalibur, Eos, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120.1K, 2θmax = 50.0°, 10725 reflections collected, 3703 unique (R(int) = 0.0389). Final Goof = 1.019, R₁ = 0.0254, wR2 = 0.0586, R indices based on 3254 reflections with I >2σ(I) (refinement...
on $F^2$), 236 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 7.552$ mm$^{-1}$.

$[\text{Hg}_2\text{Cl}_4\text{I}_2] \cdot n(\text{I}_2)$ (A.I$_2$) and $[\text{Hg}_2\text{Cl}_4\text{I}_2] \cdot n(\text{CS}_2)$ (A.CS$_2$)

Macrocycle $[\text{Hg}_2\text{Cl}_4\text{I}_2]$ was desolvated by vacuum/N$_2$ 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$_2$ adducts were obtained by placing the desolvated crystals in a sealed vial with iodine or CS$_2$ pellets for 3 days.

$[\text{Hg}_2\text{Cl}_4\text{I}_2] \cdot n(\text{I}_2)$. SQUEEZE: 112 electrons per cell, 0.53 moles I$_2$ per mole [Hg$_2$Cl$_4$I$_2$]. Refinement of occupancy of I$_2$ gave 0.59 moles. Elemental Analysis (Hg$_2$Cl$_4$C$_{36}$H$_{28}$N$_8$O$_4$. nI$_2$) Found (%): C 32.45, H 2.45, N 8.21; Calc. (%) for $n = 0.64$: C 32.21, H 2.10, N 8.34.

$[\text{Hg}_2\text{Cl}_4\text{I}_2] \cdot n(\text{CS}_2)$. TGA (Figure S?) analysis indicated 0.61 moles CS$_2$ per moles of [Hg$_2$Cl$_4$I$_2$], which matches well with the crystallographic determination of the mole ratio (0.6 moles).

Crystal data for A.I$_2$ (851194): C$_{36}$H$_{28}$Cl$_4$Hg$_2$I$_{1.18}$N$_8$O$_4$, $M = 1328.88$, colourless needle, 0.5205 × 0.1823 × 0.1106 mm$^3$, monoclinic, space group $P2_1/n$ (No. 14), $a = 7.4703(2)$, $b = 11.6228(3)$, $c = 24.2709(6)$ Å, $\beta = 96.023(3)$°, $V = 2095.71(9)$ Å$^3$, $Z = 2$, $D_c = 2.096$ g/cm$^3$, $F_{000} = 1247.2$, Xcalibur, Eos, Gemini ultra, Mo K$\alpha$ radiation, $\lambda = 0.7107$ Å, $T = 120(2)$K, $2\theta_{\text{max}} = 50.0$°, 12682 reflections collected, 3676 unique ($R_{\text{int}} = 0.0404$). Final $GooF = 2.443$, $R_1 = 0.0893$, $wR2 = 0.1619$, $R$ indices based on 3498 reflections with $I > 2\sigma(I)$ (refinement on $F^2$), 253 parameters, 1 restraint. Lp and absorption corrections applied, $\mu = 8.448$ mm$^{-1}$.

Crystal data for A.CS$_2$ (851193): C$_{36.60}$H$_{28}$Cl$_4$Hg$_2$N$_8$O$_4$S$_{1.20}$, $M = 1225.33$, colourless needle, 0.26 × 0.18 × 0.15 mm$^3$, monoclinic, space group $P2_1/n$ (No. 14), $a = 7.4559(2)$, $b = 11.6141(2)$, $c = 24.2824(5)$ Å, $\beta = 96.263(2)$°, $V = 2090.15(8)$ Å$^3$, $Z = 2$, $D_c = 1.947$ g/cm$^3$, $F_{000} = 1165.6$, Xcalibur, Eos, Gemini ultra, MoK$\alpha$ radiation, $\lambda = 0.7107$ Å, $T = 120(2)$K, $2\theta_{\text{max}} = 50.0$°, 16684 reflections collected, 3654 unique ($R_{\text{int}} = 0.0404$). Final $GooF = 1.194$, $R_1 = 0.0362$, $wR2 = 0.1078$, $R$ indices based on 3457 reflections with $I > 2\sigma(I)$ (refinement on $F^2$), 250 parameters, 1 restraint. Lp and absorption corrections applied, $\mu = 7.700$ mm$^{-1}$. 
**Figure S3.** Typical colourless crystal of $[\text{Hg}_2\text{Cl}_4\text{I}_2] \cdot \text{MeOH}$ (Material A).

**Figure S4.** Typical crystal of $[\text{Hg}_2\text{Cl}_4\text{I}_2] \cdot \text{I}_2$ (A.I$_2$).

**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$_2$ (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$_2$ and A-I$_2$. Note that the I$_2$ is disordered over two positions. A-CS$_2$ and A-I$_2$ were synthesised by desolvation of A and exposure to vapours of CS$_2$ and I$_2$ via a single-crystal-to-single-crystal transformation.
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): C₁₈H₁₄Cl₂HgN₄O₂, M = 589.82, colourless block, 0.35 × 0.28 × 0.21 mm³, monoclinic, space group P2₁/c (No. 14), a = 10.3530(10), b = 11.0411(8), c = 16.2530(12) Å, β = 93.079(7)°, V = 1855.2(3) Å³, Z = 4, Dc = 2.112 g/cm³, F₀₀₀ = 1120, Xcalibur, Eos, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 173(2)K, 2θmax = 52.0°, 8150 reflections collected, 3629 unique (Rint = 0.0956). Final GooF = 0.944, RI = 0.0604, wR2 = 0.1025, R indices based on 2309 reflections with I >2σ(I) (refinement on F²), 244 parameters, 54 restraints. Lp and absorption corrections applied, μ = 8.606 mm⁻¹.
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.
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): C73H60Br8Hg4N16O9, $M = 2747.01$, colourless block, $0.24 \times 0.21 \times 0.19 \text{ mm}^3$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.2403(3)$, $b = 11.5470(3)$, $c = 17.2774(4) \text{ Å}$, $\alpha = 98.323(2)$, $\beta = 95.234(2)$, $\gamma = 95.764(2)^\circ$, $V = 1999.58(9) \text{ Å}^3$, $Z = 1$, $D_c = 2.281 \text{ g/cm}^3$, $F_{000} = 1282$, Xcalibur, Eos, Gemini ultra, Mo Kα radiation, $\lambda = 0.7107 \text{ Å}$, $T = 120.0K$, $2\theta_{\text{max}} = 50.0^\circ$, 24197 reflections collected, 7033 unique (Rint = 0.0342). Final $GooF = 1.027$, $RI = 0.0245$, $wR2 = 0.0499$, $R$ 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 x 4 metallocycle formed by ligand 1 and HgBr₂ in material C. Atoms of the asymmetric unit are labelled. Atoms are shown as ellipsoids at 50% probability.
Ligand $\text{I}$ (22 mg, 69 $\mu$mol) 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 $\mu$mol) 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 $\mu$mol, 48%), m.p. 318 - 322 °C (from DSC).

TGA: 30 – 70 °C, -4.8 % wet mass, 0.98 mol EtOH per mol $[\text{Co}_2\text{Cl}_4\text{I}_2]$; SQUEEZE: 68 electrons per cell, 1.3 mol EtOH per mol $[\text{Co}_2\text{Cl}_4\text{I}_2]$, void volume 298.3 Å$^3$ per cell.

IR: ν / cm$^{-1}$: 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 $\text{D}$ (851197): $\text{C}_{36}\text{H}_{28}\text{Cl}_4\text{Co}_2\text{N}_8\text{O}_4$, $M = 896.32$, blue flat needles, 0.31 × 0.18 × 0.11 mm$^3$, monoclinic, space group $P2_1/n$ (No. 14), $a = 7.3899(5)$, $b = 11.5287(10)$, $c = 23.764(2)$ Å, $\beta = 94.810(6)$°, $V = 2017.5(3)$ Å$^3$, $Z = 2$, $D_c = 1.475$ g/cm$^3$, $F_{000} = 908$, Xcalibur, Eos, Gemini ultra, Cu Kα radiation, $\lambda = 1.5418$ Å, $T = 120.1$K, $2\theta_{\text{max}} = 141.1$°, 6884 reflections collected, 3725 unique ($R_{\text{int}} = 0.0489$). Final $\text{GooF}^2 = 1.009$, $R1 = 0.0482$, $wR2 = 0.1154$, $R$ 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$^{-1}$.

$[\text{Co}_2\text{Cl}_4\text{I}_2] \cdot \text{I}_2$

Macrocycle $[\text{Co}_2\text{Cl}_4\text{I}_2] \cdot \text{EtOH}$ was desolvated by vacuum/N$_2$ 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$_2$ per mol $[\text{Co}_2\text{Cl}_4\text{I}_2]$. Elemental Analysis ($\text{Co}_2\text{Cl}_4\text{C}_{36}\text{H}_{28}\text{N}_8\text{O}_4 \cdot n\text{I}_2$) Found (%): C 39.61, H 2.86, N 10.10; Calc. (%) for $n = 0.78$: C39.61, 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.I₂ (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.
Zn₂Cl₂I₄ · 5MeOH (Material E)

Ligand 1 (6.0 mg, 19 µmol) 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 µmol) in ethanol (4 ml). The product formed over 3 days as colourless or pale yellow needle-like crystals (3.5 mg, 3.8 µmol, 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 Å³ per cell. ν / cm⁻¹ (EtOH solvate): 3240 (br), 3050 (br), 1650 (m), 1600 (m), 1520 (s), 1450
Crystal data for E (857511): C₃₆H₂₈Cl₄N₈O₄Zn₂, M = 909.20, colourless needle, 0.5505 × 0.1604 × 0.0505 mm³, monoclinic, space group P2₁/n (No. 14), a = 7.3482(5), b = 11.3708(6), c = 23.8973(16) Å, β = 94.865(6)°, V = 1989.5(2) Å³, Z = 2, Dc = 1.514 g/cm³, F₀₀₀ = 920, Xcalibur, Eos, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120.0K, 2θmax = 50.0°, 6435 reflections collected, 3487 unique (Rint = 0.0526). Final GooF = 1.140, R₁ = 0.0947, wR2 = 0.2363, R indices based on 2573 reflections with I >2sigma(I) (refinement on F²), 244 parameters, 0 restraints. Lp and absorption corrections applied, μ = 1.523 mm⁻¹.

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. CS₂ bubbling from A at 153°C. I₂ bubbling from A at 160°C. I₂ bubbling from A at 160°C after the end tips of the crystals have stopped bubbling.

References

5 POV-Ray The Persistence of Vision RayTracer – 2010