In-situ coordination chemistry within cobalt-containing phthalocyanine nanoporous crystals.

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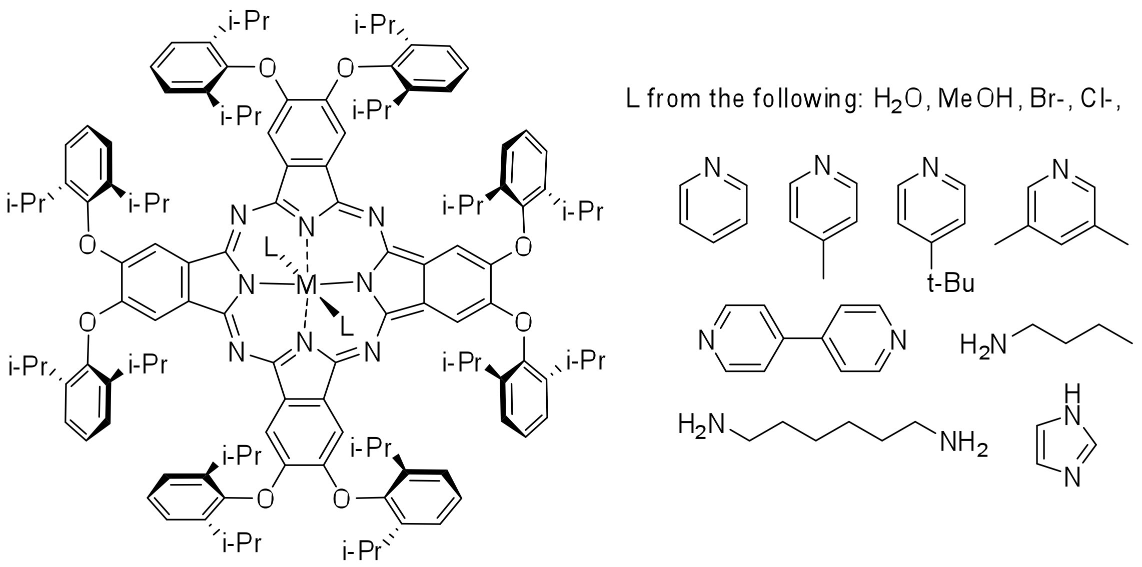
Supplemental Information

1. Experimental procedures.

1.1. General methods.

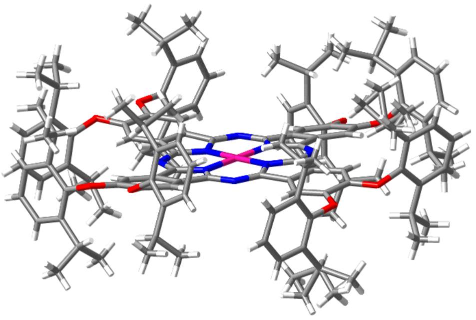
Infra-red spectra were recorded in the range 4000-600 cm^{-1} using a Perkin-Elmer 1600 series FTIR instrument. All absorption bands are quoted in cm^{-1}. Elemental analysis was carried out with a Carlo Erba EA1101 elemental analyser. UV/vis absorption spectra were recorded in the range 200-800 nm using a Jasco V-570 UV/vis/NIR spectrophotometer. Volumetric N_2 sorption studies were undertaken at 77 K using a Beckman Coulter 3100 Surface Area Analyzer (Fullerton, California, USA) and performed on samples that had been previously placed under vacuum (10-6 bar) at 25 °C for 8 hours to remove residual solvent and other adsorbates. The TGA was performed using the device Thermal Analysis SDT Q600. MALDI-TOF mass spectroscopic analyses were performed with a Waters MALDI Micro MX spectrometer.

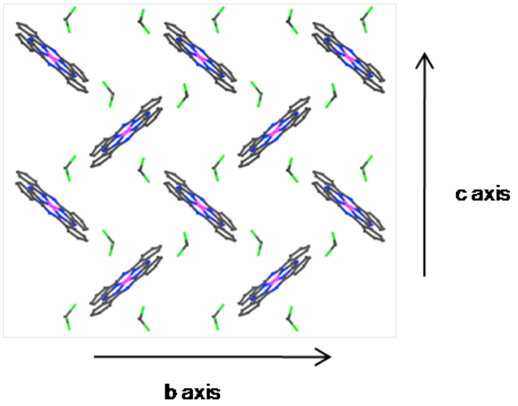


Synthesis of 2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato cobalt (PcCo). PcCo was prepared by using a slightly modified procedure compared to the one previously reported.[25] A stirred solution of 4,5-bis(2,6-di-*iso*-propylphenoxy)-phthalonitrile (1.00 g, 2.08 mmol) and cobalt(II)acetate (0.18 g, 1.04 mmol) in anhydrous NMP (2 ml) was heated at 180 °C for 3 h under nitrogen. The reaction mixture was cooled to room temperature and poured into water (15 ml). The crude product was collected by filtration then solubilised in the minimum amount of DCM and reprecipitated with MeOH. A second reprecipitation from DCM solution with MeOH gave the title compound as a green solid (0.62 g, 60%). M.p. >300 °C; IR (film)/cm^{-1} 2961, 1612, 1456, 1462, 1413, 1353, 1269, 1186, 1095, 1050, 904, 864, 799, 777, 755, 729; ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.6 (br s, 8H, Ar*H*), 7.30 (br s, 8 H, Ar*H*), 5.4 (br s, 16 H, Ar*H*), 1.0-2.5 (br m, 112H, CH_3CHCH_3), paramagnetic (Fig. S2a); UV/vis (DCM): λ_{max} 673, 608, 404, 331, 302, 229 nm (Fig. S1a); MS (MALDI-TOF): cluster centred at m/z 1982.055 (MH^+); elemental analysis calc (%) for $C_{128}H_{144}N_8O_8Co$: C 77.59, H 7.32, N 5.66 found C 77.68, H 7.52, N 5.52.

Single crystal XRD analysis

Data were collected at 100 K (nitrogen cryogen), unless otherwise stated, using synchrotron radiation at either the CCLRC Daresbury Laboratory ('Daresbury') or the Diamond Light Source ('Diamond') or at Manchester University X-Ray Crystallography Facility. A Bruker APEX CCD diffractometer (graphite monochromated MoKα radiation) was used at Daresbury and Manchester, whereas at Diamond (Station I19) a Rigaku Saturn 724 CCD diffractometer (graphite monochromated radiation) was used. The structures were solved by direct methods. All calculations were carried out by using the SHELX-97 package. Non-H atoms were refined anisotropically, except some of the disordered atoms. H atoms were included in calculated positions, except those bonded to the solvent molecules. For some of PNCs and PUNCs, a number of the C atoms of the phenoxy substituents were disordered over 2 sites, whose occupancies were constrained to sum to unity. The phenyl component of the disordered phenoxyl groups was constrained to be a regular hexagon. The electron count due to disorder solvent or adsorbed molecules in the void space of the crystals was calculated using the SQUEEZE software package. A common feature in all the structures is the weakness of data at high diffraction angles, ascribed to the disorder in the ligands and solvent molecules, often leading to higher than usual R-factors and goodness of fit values.



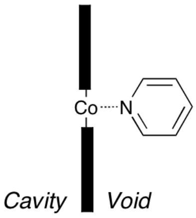


2,3,9,10,16,17,23,24-octa(2’,6’-di-*iso*-propylphenoxy)phthalocyaninato cobalt.2($CHCl_3$) (PcCo).

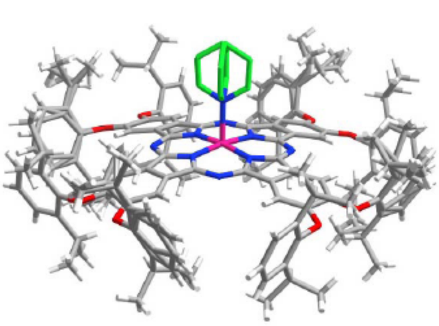
The crystals were obtained by simple crystallisation of PcCo by the slow diffusion of acetone into a solution of chloroform. Data were collected at 150 K at Diamond (λ = 0.6889 Å). Crystal size 0.15 x 0.15 x 0.05 mm, $C_{128}H_{144}CoN_8O_8.2(CHCl_3)$, M = 2220.18 monoclinic, space group $P2_1/c$, a = 21.336(8) Å, b = 16.819(6) Å, c = 18.474(7) Å, β = 114.455(5) , V = 6035(4) Å^3, Z = 2, μ(0.6889) = 0.334 µm^{-1}, 27489 reflections measured, 8610 unique reflections (R_{int} = 0.1014), 7766 reflections with $I > 2\sigma(I)$, R = 0.0684 and $\omega R2$ = 0.1882 (observed data), R = 0.0732 and $\omega R2$ = 0.1949 (all data). The asymmetric unit contains 0.5 molecules of **PcCo** with 1 chloroform solvent molecule; the entire PcCo molecule is generated by inversion. The data were cut at 0.9 Å resolution because the crystal diffracted poorly beyond this point. CCDC deposition number 900380.

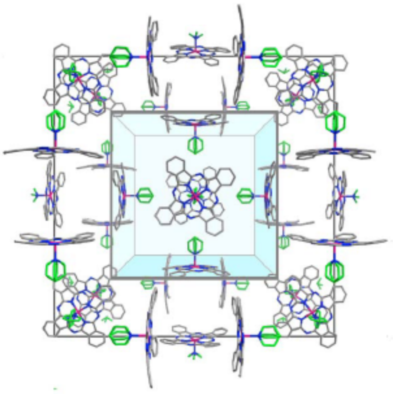
Structures for Figure 2

The following cubic **PcCo** crystals with different axial ligands were obtained for slow diffusion of a non solvent (methanol or acetone) in a solution of **PcCo (**about 0.01 g, 0.005 mmol) in chloroform (0.5 ml), to which an excess of the appropriate ligand had been added.

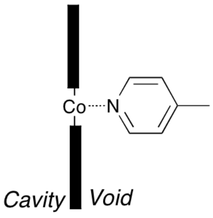


PNC[Co-*v*Py]

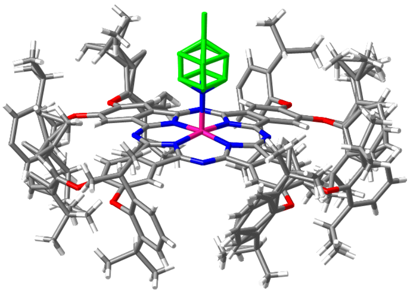


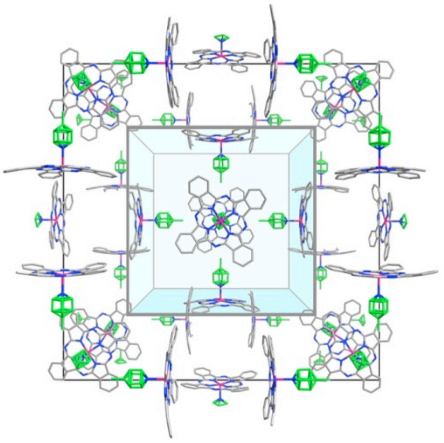


2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato pyridyl cobalt (PNC[Co-*v*Py]).[1] Data were collected at 100 K at Daresbury ($\lambda = 0.69050$Å). Crystal size 0.70 x 0.60 x 0.50 mm, $C_{173.50}H_{225}CoN_9O_{21.50}$, M = 2839.55, cubic, $Pn\bar{3}n$, $a = 37.5596(4)$ Å, $V = 52986.2(10)$ Å^3, $Z = 12$, $\mu(0.69050) = 0.159$ µm^{-1}, 192955 reflections measured, 7836 unique reflections ($R_{int} = 0.1292$), 6213 reflections with $I > 2\sigma(I)$, $R = 0.0625$ and $\omega R2 = 0.1819$ (observed data), $R = 0.0746$ and $\omega R2 = 0.1913$ (all data). The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. The disordered solvent was modelled with SQUEEZE which found 5166 electrons equivalent to 162 acetone molecules to be included in the solvent accessible voids of 20906 Å^3. The presence of disorder solvent (acetone/$CHCl_3$) in the voids was indicated by TGA analysis (nitrogen): 25.8% loss of weight occurs below 50 °C. A pyridine molecule is coordinated to Co in the apical site. CCDC deposition number 761407.



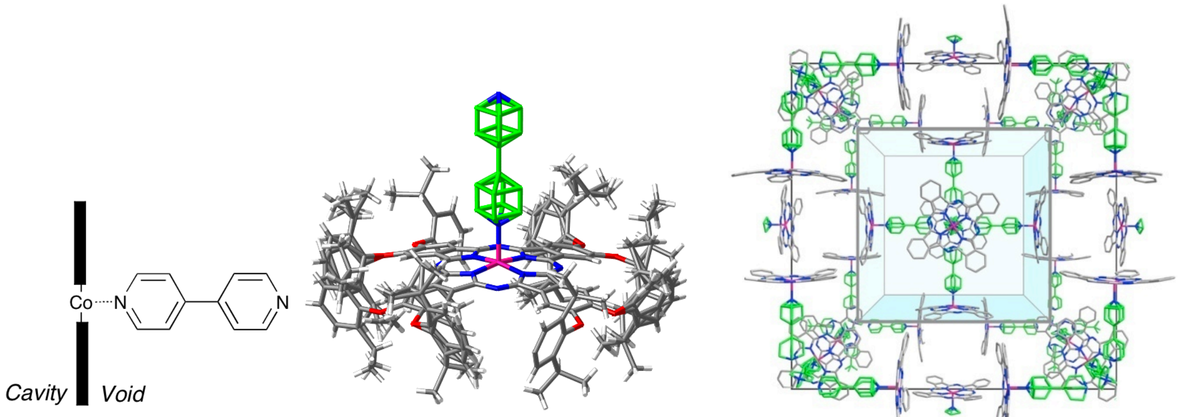
PNC[Co-*v*Pic]





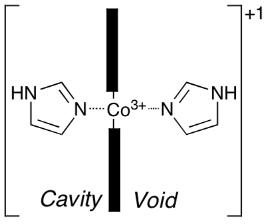
2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato picolyl cobalt (PNC[Co-*v*Pic)]). Data were collected at 150 K at Daresbury($\lambda = 0.69050$Å). Crystal size 0.90 x 0.60 x 0.60 mm, $C_{147.33}H_{174.33}Cl_{10.08}CoN_9O_{11.33}$, M = 2669.01, cubic, $Pn\bar{3}n$, $a =$

37.5208(2) Å, V = 52822.2(5) Å^3, Z = 12, μ(0.69050) = 0.300 µm^{-1}, 191856 reflections measured, 7810 unique reflections (R_{int} = 0.1041), 6722 reflections with $I > 2\sigma(I)$, R = 0.0611 and $\omega R2$ = 0.1842 (observed data), R = 0.0676 and $\omega R2$ = 0.1901 (all data). The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules; there was also a large peak in the voids assumed to be a Cl atom from the solvent. In the axial site there is a picoline molecule disordered about a 4-fold axis through the axial atoms N1S, C3S and C4S. Modelling the disordered solvent with SQUEEZE found 3636 electrons equivalent to 40 (acetone + $CHCl_3$) molecules to be included in the solvent accessible voids of 20412 Å^3. CCDC deposition number 900366.

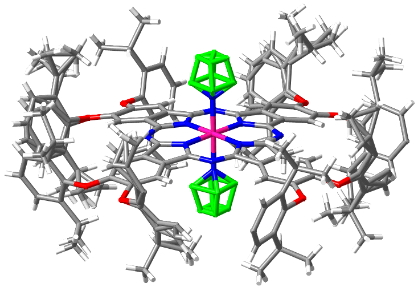


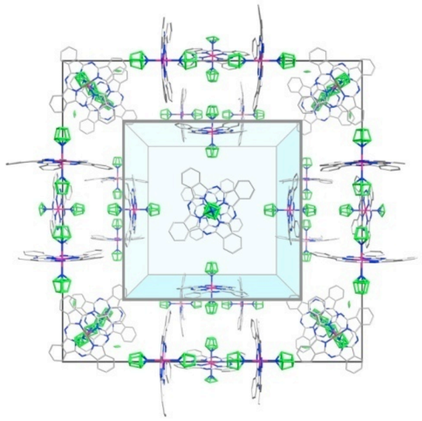
PNC[Co-*v*BiPy]

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(4,4'-bipyridyl) cobalt (PNC[Co-*v*Bipy]). Data were collected at 120 K using synchrotron radiation at Daresbury (λ = 0.68840 Å). Crystal size 0.80 x 0.60 x 0.60 mm, $C_{141.17}H1_{56.92}Cl_{7.75}CoN_{10}O_{8.58}$, M = 2464.68, cubic, $Pn\bar{3}n$, a = 37.4921(9) Å, V = 52701(2) Å^3, Z = 12, μ(0.68840) = 0.256 µm^{-1}, 130816 reflections measured, 7777 unique reflections (R_{int} = 0.12), 4688 reflections with $I > 2\sigma(I)$, R = 0.1455 and $\omega R2$ = 0.4179 (observed data), R = 0.1797 and $\omega R2$ = 0.4358 (all data). The asymmetric unit contains ¼ of the molecule together with a chloroform molecule at 0.5 occupancy. A 4,4-bipyridyl molecule is axially coordinated to the metal in the apical position and is disordered about a 4-fold through the axial atoms N1S and N2S. Modelling the disordered solvent with SQUEEZE found 541 electrons equivalent to 7($CHCl_3$ + MeOH) molecules to be included in the solvent accessible voids of 13159 Å^3. CCDC deposition number 900365.

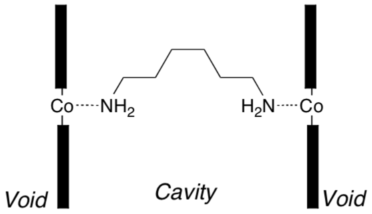


PNC[*c*Im-Co-*v*Im]

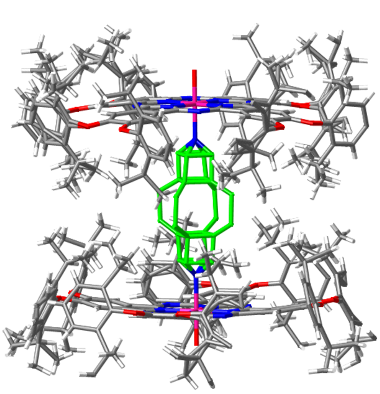


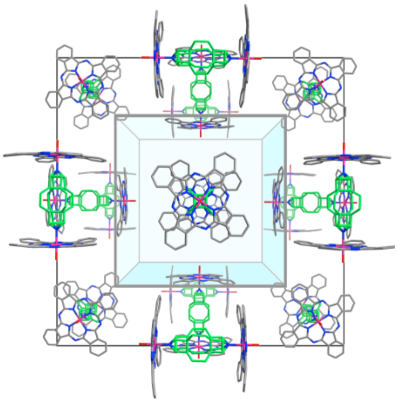


2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(imidazole)$_2$ cobalt (PNC[*c*Im-Co-*v*Im]) ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.04 (s, 8H, Ar*H*), 7.49 (t, 8 H, *J* = 7.8 Hz, Ar*H*), 7.39 (d, 16 H, *J* = 7.8 Hz, Ar*H*), 4.39 (s, 2H, Ar*H*), 3.46 (s, 36H, MeOH), 3.33 (m, 16 H, $CH_3C\mathit{H}CH_3$), 1.61 (br s, 40 H, H_2O), 1.20 (br m, 98 H, $C\mathit{H}_3CHC\mathit{H}_3$) (Fig. S2); UV/vis (DCM): λ_{max} 678, 609, 422, 367, 299, 232 nm (Fig. S1b) Data were collected at 150 K at Daresbury (λ = 0.69390 Å). Crystal size 0.25 x 0.20 x 0.15 mm, $C_{135.50}H_{157.17}CoN_{12}O_{8.75}$, M = 2152.83, cubic, $Pn\bar{3}n$, a = 37.5719(16) Å, V = 53038(4) Å^3, Z = 12, μ(0.69390) = 0.140 μm^{-1}, 130673 reflections measured, 7811 unique reflections (R_{int} = 0.075), 5594 reflections with $I > 2\sigma(I)$, R = 0.0835 and $\omega R2$ = 0.2717 (observed data), R = 0.1037 and $\omega R2$ = 0.2950 (all data). The asymmetric unit contains ¼ of the molecule together with a solvent atom, assumed to be water at 0.5 occupancy. Imidazole is axially coordinated in both sides of the metal and both are disordered about a 4-fold through the axial atoms N2S and N3S. Modelling the disordered solvent with SQUEEZE found 670 electrons equivalent to 9($CHCl_3$ + MeOH) molecules to be included in the solvent accessible voids of 17786 Å^3. The counteranion is likely to be deprotonated imidazole. CCDC deposition number 900376.

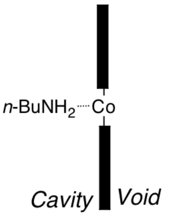


PNC[Co-*c*DAH-Co]

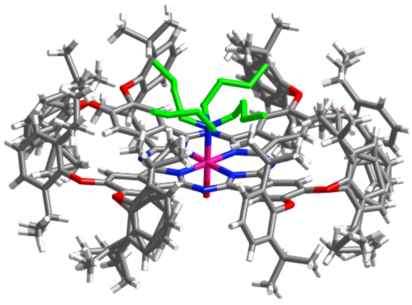


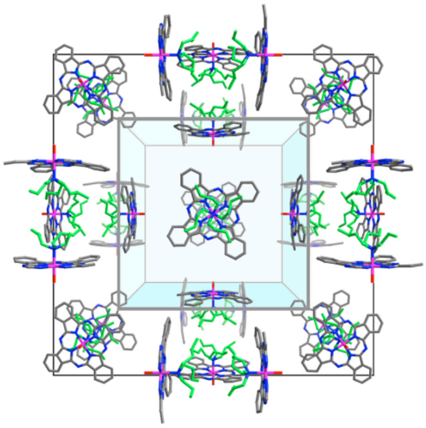


2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(1,6-diamino-hexane) cobalt (PNC[*v*H_2O-Co-*c*DAH-Co-*v*H_2O]) Data were collected at 100 K at Daresbury (λ = 0.67100 Å). Crystal size 0.35 x 0.28 x 0.1 mm, $C_{132}H_{155}Cl_3CoN_9O_9$, M = 2176.93, cubic, $Pn\bar{3}n$, a = 37.4908(2) Å, V = 52695.6(5) Å^3, Z = 12, μ(0.67100) = 0.185 μm^{-1}, 226206 reflections measured, 7453 unique reflections (R_{int} = 0.0968), 5513 reflections with $I > 2\sigma(I)$, R = 0.1458 and $\omega R2$ = 0.4153 (observed data), R = 0.1843 and $\omega R2$ = 0.4590 (all data). The asymmetric unit contains ¼ of the molecule together with a $CHCl_3$ solvent molecule at 0.25 occupancy. A 1,6-diaminohexane molecule which links together two **PcCo** is in the non-apical axial site of the metal and a water molecule is in the apical axial site, and is disordered about a 4-fold through the wall-tied Co atoms. CCDC deposition number 900379.



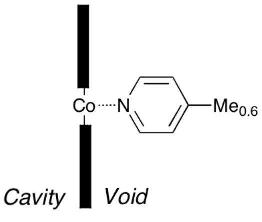
PNC[*c*BuNH$_2$-Co]



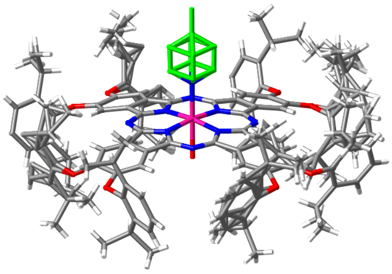


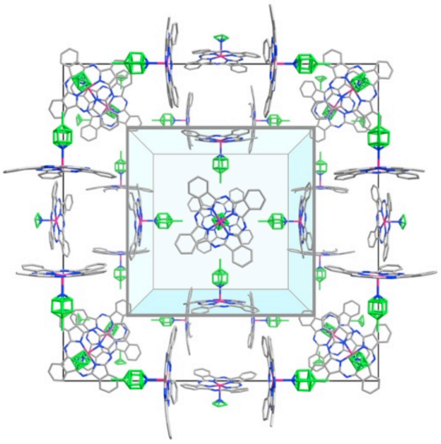
2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(1-butylamine) cobalt (PNC[cBuNH_2-Co-vH_2O]) Data were collected at 100 K at Diamond (λ = 0.6889 0 Å). Crystal size 0.11 x 0.11 x 0.10 mm, $C_{132}H_{157}CoN_9O_8$, M = 2056.60, cubic, $Pn\bar{3}n$, a = 37.458(5) Å, V = 52556(12) Å^3, Z = 12, μ(0.68890) = 0.138μm^{-1}, 212805 reflections measured, 8973 unique reflections (R_{int} = 0.0885), 7516 reflections with $I > 2\sigma(I)$, R = 0.1354 and $\omega R2$ = 0.3890 (observed data), R = 0.1497 and $\omega R2$ = 0.3993 (all data). The asymmetric unit contains ¼ of **PcCo** molecule together with a solvent atom, assumed to be water at 0.25 occupancy. A 1-butylamine molecule disordered over 4 positions and a water molecule are coordinated in the cavity axial site and in the void axial site of the metal, respectively. CCDC deposition number 900372.

Structures for Scheme 1

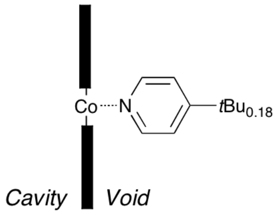


PNC[Co-*v*-Pic$_{0.6}$Py$_{0.4}$]

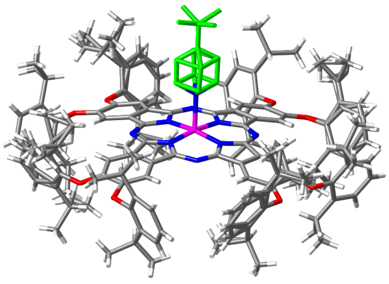


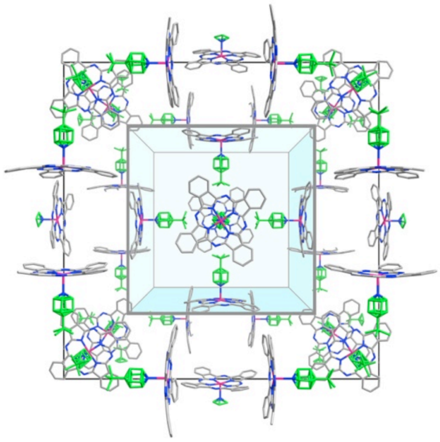


2,3,9,10,16,17,23,24-octa(2’,6’-di-*iso*-propylphenoxy)phthalocyaninato picolyl cobalt (PNC[Co-*v*Pic$_{0.60}$Py$_{0.40}$]). An excess of 4-picoline was added to some **Pc1Co(Py)** in contact with the crystallization solvent. Approx. 60% exchange of pyridine by 4-picoline. Data were collected at 100 K at Daresbury (λ = 0.67090Å). Crystal size 0.25 x 0.25 x 0.20 mm, $C_{136.33}H_{155.33}Cl_{0.17}CoN_9O_{13.33}$, M = 2198.20, cubic, $Pn\bar{3}n$, a = 37.1172(4) Å, V = 51135.8(10) Å^3, Z = 12, μ(0.67090) = 0.150 μm^{-1}, 269869 reflections measured, 7520 unique reflections (R_{int} = 0.0843), 5226 reflections with $I > 2\sigma(I)$, R = 0.1444 and $\omega R2$ = 0.4132 (observed data), R = 0.1838 and $\omega R2$ = 0.4396 (all data). The asymmetric unit contains ¼ of the molecule together with a solvent atom, assumed to be water at an occupancy of 0.5 and a heavier atom assumed to be Cl, on a -3 special position.. 4-Picoline and pyridine 60:40 ratio, are axially bonded to Co in the apical position and are disordered about a 4-fold axis through the axial atoms N1S, C3S. A water molecule is axially bonded in the other side of the metal at 0.5 occupancy. Modelling the disordered solvent with SQUEEZE found 617 electrons equivalent to 34 MeOH molecules to be included in the solvent accessible voids of 16288 Å^3. CCDC deposition number 900367.

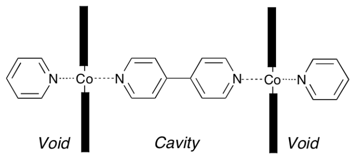


PNC[Co-*v*-*t*$Bu_{0.18}Py_{0.82}$]

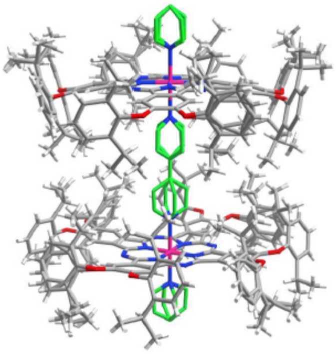


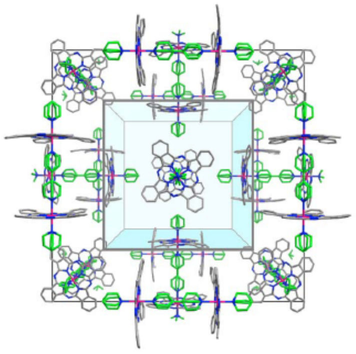


2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato t-butylpyridyl cobalt (PNC[Co-*v*$Py_{0.82}Bupy_{0.18}$]). An excess of 4-*t*-butylpyridine was added to some **Pc1Co(Py)** in contact with the crystallization solvent. 18% exchange of pyridine by 4-*t*-butylpyridine. Data were collected at 100 K at Daresbury (λ = 0.69050Å). Crystal size 0.60 x 0.60 x 0.50 mm, $C_{169.08}H_{215.58}CoN_9O_{20.75}$, M = 2765.02, cubic, $Pn\bar{3}n$, a = 37.5512(3) Å, V = 52950.7(7) Å^3, Z = 12, μ(0.69050) = 0.157 µm^{-1}, 187976 reflections measured, 7836 unique reflections (R_{int} = 0.1323), 6662 reflections with $I > 2\sigma(I)$, R = 0.0876 and $\omega R2$ = 0.2881 (observed data), R = 0.0944 and $\omega R2$ = 0.3008 (all data). The asymmetric unit contains ¼ of the molecule together with some disordered solvent molecules. The solvent in the voids was modelled with SQUEEZE that found 4520 electrons equivalent to 141 acetone molecules to be included in the solvent accessible voids of 17423 Å^3. *t*-Butylpyridine and pyridine in 18:82 ratio, are axially bonded to Co in the apical position and are disordered about a 4-fold axis through the axial atoms N1S, C3S. CCDC deposition number 900368.

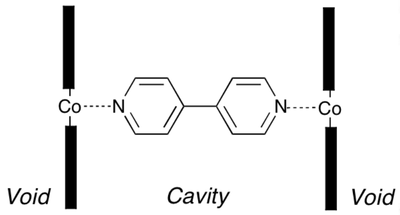


PNC[*v*$Py_{0.6}H_2O_{0.4}$-Co-*c*BiPy-Co-*v*$Py_{0.6}H_2O_{0.4}$]

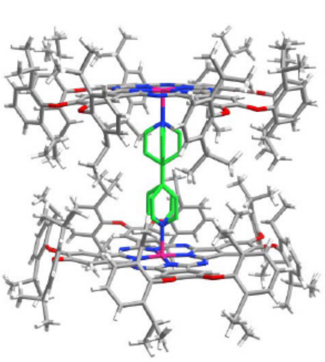


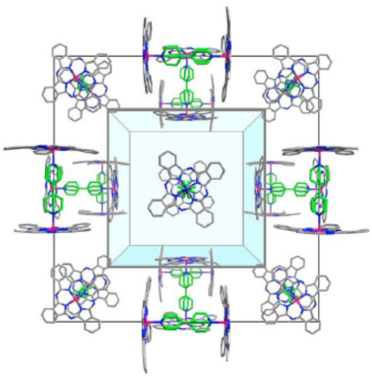


2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(pyridine)(4,4'-bipyridyl)cobalt (PNC[*v*$Py_{0.6}H_2O_{0.4}$-Co-*c*Bipy-Co-*v*$Py_{0.6}H_2O_{0.4}$]).[1] An excess of 4,4-bipyridyl was added to some **Pc1Co(Py)** in contact with the crystallization solvent. Data were collected at 150 K at Daresbury (λ = 0.69450 Å). Crystal size 0.22 x 0.22 x 0.22 mm, cubic, $C_{137.50}H_{157.58}Cl_{2.25}CoN_{9.60}O_{10.15}$, M = 2245.81, $Pn\bar{3}n$, a = 37.647(3) Å, V = 53.359(7) Å^3, Z = 12, μ(0.69450) = 0.174 µm^{-1}, 130465 reflections measured, 7862 unique reflections (R_{int} = 0.0874), 4878 reflections with $I > 2\sigma(I)$, R = 0.1051 and $\omega R2$ = 0.3332 (observed data), R = 0.1404 and $\omega R2$ = 0.3642 (all data). A 4,4-bipyridyl molecule which links together two **PcCo** is in the non-apical axial site of the metal and pyridine/water in 60/40 ratio are in the apical axial site. The axial ligands display symmetry induced four-fold disorder. Modelling the disordered solvent with SQUEEZE found 690 electrons equivalent to 9($CHCl_3$ + MeOH) molecules to be included in the solvent accessible voids of 17539 Å^3. TGA analysis (nitrogen): 22.5% loss of weight occurred at ~ 27 °C, 6.2% loss of weight occurred at ~ 193 °C. Initial weight loss due to thermal degradation commences at ~ 450 °C. CCDC deposition number 761419.



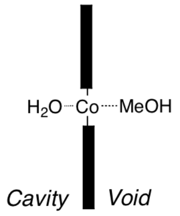
PUNC[Co-*c*BiPy-Co]



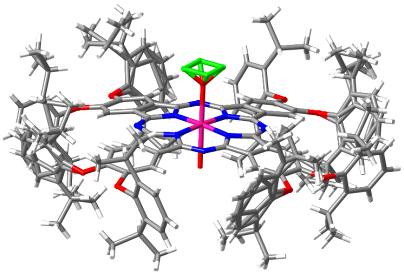


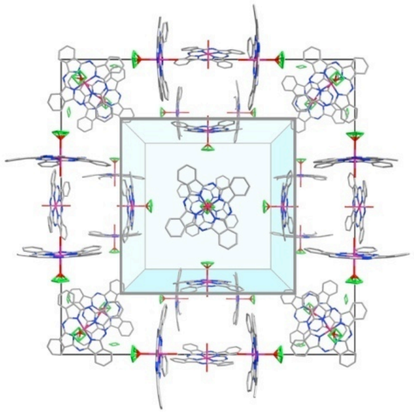
2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(4,4'-bipyridyl) cobalt (PUNC[Co-*c*BiPy-Co]).[1] The crystals were prepared by exposing crystals of **PNC[*v*(py)$_{0.6}$(H$_2$O)$_{0.4}$-Co-*c*bipy-Co-*v*(py)$_{0.6}$(H$_2$O)$_{0.4}$]** to a stream of dry nitrogen at 20 °C. Data were collected at 100 K at Diamond (λ = 0.68890 Å). Crystal size 0.70 x 0.45 x 0.40 mm, $C_{134.08}H_{154.8}Cl_{1.50}CoN_9O_{10.58}$, M = 2173.94, cubic, $Pn\bar{3}n$, a = 37.698(14) Å, V = 53574(34) Å^3, Z = 12, μ(0.68890) = 0.161 µm^{-1}, 216513 reflections measured, 7808 unique reflections (R_{int} = 0,0336), 6921 reflections with $I > 2\sigma(I)$, R = 0.1243 and $\omega R2$ = 0.3720 (observed data), R = 0.1320 and $\omega R2$ = 0.3825 (all data). A disordered over 2 positions 4,4-bipyridyl molecule which links together two **PcCo** is in the non-apical axial site of the metal. CCDC deposition number 761420. BET surface area = 845 m^2/g; total pore volume = 0.44 cm^3/g at (P/P_0) 0.98, adsorption. TGA analysis (nitrogen): 8% loss of weight occurred at ~ 230 °C. Initial weight loss due to thermal degradation commences at ~ 437 °C.

Structures for Scheme 2

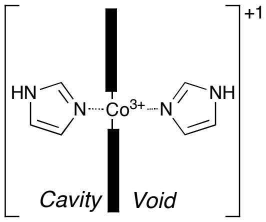


PNC[cH$_2$O-Co-vMeOH]

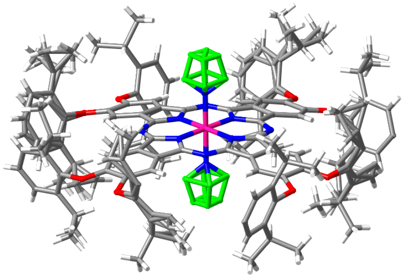


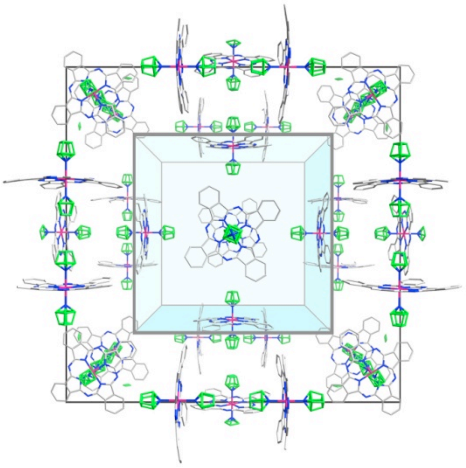


2,3,9,10,16,17,23,24-octa(2’,6’-di-*iso*-propylphenoxy)phthalocyaninato(H_2O)(MeOH) cobalt (**PNC[*c*H_2O-Co-*v*MeOH]).** The crystals were obtained by repeated washing with methanol (5 x 2 ml) of some **(PNC[Co-*v*Py])**. The crystals were kept in contact with methanol until XRD analysis. Data were collected at 100 K at DIAMOND (λ = 0.6889 Å). Crystal size 0.25 x 0.25 x 0.2 mm, $C_{130}H_{157.17}Cl_{1.50}CoN_8O_{12.67}$, M = 2146.58, cubic, space group $Pn\bar{3}n$, a = 37.6395(3) Å, V = 53325.1(7) Å, Z = 12, μ(0.6889) = 0.162 μm^{-1}, 134288 reflections measured, 7866 unique reflections (R_{int} = 0.047), 7012 reflections with $I > 2\sigma(I)$, R = 0.1043 and $\omega R2$ = 0.3445 (observed data), R = 0.1101 and $\omega R2$ = 0.3528 (all data). The asymmetric unit contains ¼ of **PcCo** molecule together with a solvent atom, assumed to be water at an occupancy of 0.5. In the axial sites there is a water molecule at one site and a disordered over 4 positions MeOH at the other site. Modelling the disordered solvent with SQUEEZE found 501 electrons equivalent to about 8MeOH + 6 $CHCl_3$ molecules to be included in the solvent accessible voids of 18734.2 Å^3. CCDC deposition number 900375.

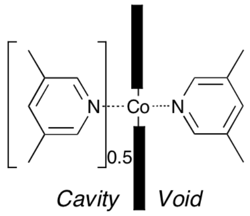


PNC[*c*Im-Co-*v*Im]

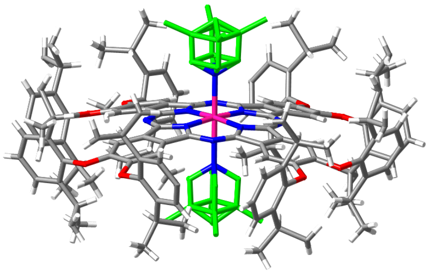


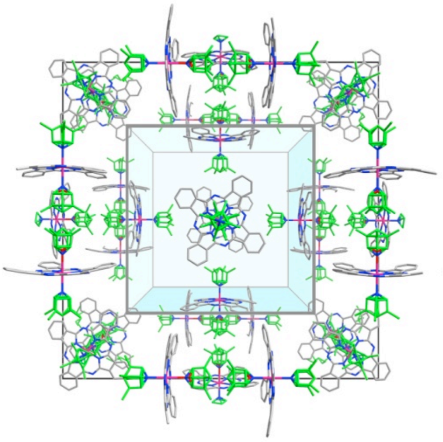


2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(imidazole)$_2$ cobalt (PNC[*c*Im-Co-*v*Im]$_2$). An excess of imidazole was added to the MeOH in contact with **PNC[*c*H$_2$O-Co-*v*MeOH]** crystals. ^{1}H NMR (400 MHz; CDCl$_3$) δ 8.04 (s, 8H, Ar*H*), 7.49 (t, 8 H, *J* = 7.8 Hz, Ar*H*), 7.39 (d, 16 H, *J* = 7.8 Hz, Ar*H*), 4.39 (s, 2H, Ar*H*), 3.46 (s, 36H, MeOH), 3.33 (m, 16 H, CH$_3$C*H*CH$_3$), 1.61 (br s, 40 H, H$_2$O), 1.20 (br m, 98 H, C*H*$_3$CHC*H*$_3$) (Fig. S3); UV/vis (DCM): λ_{max} 678, 609, 422, 367, 299, 232 nm (Fig. S2); Data were collected at 100 K at Diamond (λ = 0.68890 Å) Crystal size 0.07 x 0.07 x 0.07 mm, $C_{144.50}H_{184.25}Cl_{9.75}CoN_{12}O_{15.25}$, M = 2737.86, cubic, $Pn\bar{3}n$, *a* = 37.603(3) Å, *V* = 53170(8) Å^3, *Z* = 12, μ(0.68890) = 0.296 μm^{-1}, 181954 reflections measured, 7645 unique reflections (R_{int} = 0.096), 6962 reflections with $I > 2\sigma(I)$, *R* = 0.1171 and $\omega R2$ = 0.3932 (observed data), *R* = 0.1223 and $\omega R2$ = 0.4004 (all data). The asymmetric unit contains ¼ of the molecule and two methanol molecules at 0.5 occupancy each. Imidazole is axially bonded to both sides of the metal and both are disordered about a 4-fold through the axial atoms N1S and N3S. Modelling the disordered solvent with SQUEEZE found 2964 electrons equivalent to 39 (CHCl$_3$ + MeOH) molecules to be included in the solvent accessible voids of 13766.1Å^3. The counteranion is likely to be deprotonated imidazole. CCDC deposition number 900377.

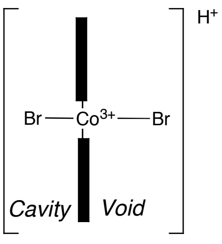


PNC[*c*Lu$_{0.5}$-Co-*v*Lu]

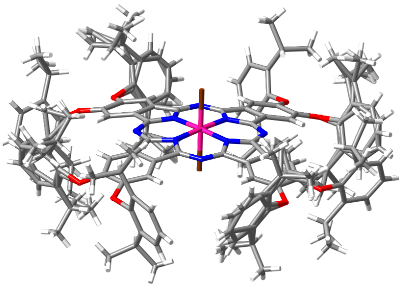


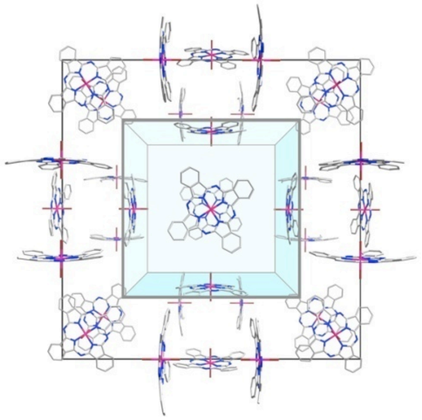


2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(3,5-lutidine)$_2$ cobalt (PNC[*c*Lu$_{0.5}$-Co-*v*Lu]). An excess of 3,5-lutidine was added to some **PNC[*c*H$_2$O-Co-*v*MeOH]** crystals in MeOH. Data were collected at 100 K at Diamond (λ = 0.68890 Å) Crystal size 0.09 x 0.09 x 0.09 mm, $C_{152.50}H_{176.50}CoN_{11.50}O_{8.50}$, M = 2365.48, cubic, $Pn\bar{3}n$, a = 37.3922(2) Å, V = 52280.9(5) Å^3, Z = 12, μ(0.68890) = 0.146 μm^{-1}, 204441 reflections measured, 8991 unique reflections (R_{int} = 0.1189), 8109 reflections with $I > 2\sigma(I)$, R = 0.1508 and $\omega R2$ = 0.4504 (observed data), R = 0.1611 and $\omega R2$ = 0.4565 (all data). The asymmetric unit contains ¼ of the molecule and a 3,5-lutedine molecule at 0.5 occupancy. The 3,5-lutidine is axially coordinated at both sides of the metal, but at 0.5 partial occupancy in the cavity side. Both lutidine ligands are disordered in two perpendicular orientations dictated by symmetry. Both diisopropylphenoxy groups are disordered with two components of occupancies 73/27% and 59/41%. CCDC deposition number 900378.



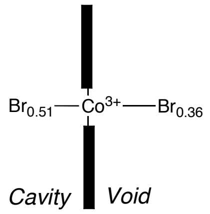
PNC[*c*Br-Co^{3+}-*v*Br]



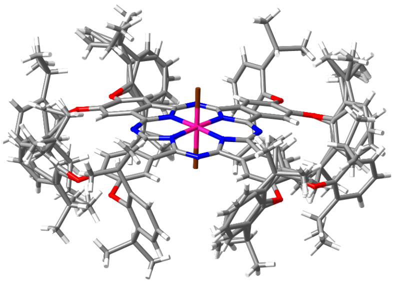


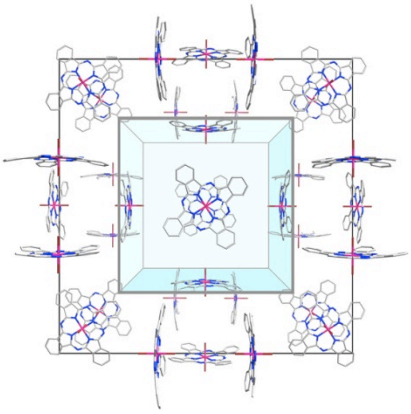
2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(Br)$_2$cobalt (PNC[*c*Br-Co^{3+}-*v*Br]). An excess of HBr (48% w/w aqueous solution) was added to some **PNC[*c*H$_2$O-Co-*v*MeOH]** crystals in MeOH. Data were collected at 150 K at Diamond (λ = 0.68890 Å). Crystal size 0.15 x 0.15 x 0.12 mm, $C_{130.83}H_{150.25}Br_2Cl_{4.25}CoN_8O_{9.42}$, M =

2354.92, cubic, $Pn\bar{3}n$, a = 37.627(4) Å, V = 53272(10) Å^3, Z = 12, μ(0.68890) = 0.652 µm^{-1}, 105222 reflections measured, 7813 unique reflections (R_{int} = 0.082), 6049 reflections with I $>2\sigma(I)$, R = 0.1172 and $\omega R2$ = 0.3544 (observed data), R = 0.1351 and $\omega R2$ = 0.3724 (all data). The asymmetric unit contains ¼ of the molecule. Br$^-$ is axially bonded in both sides of the metal. Modelling the disordered solvent with SQUEEZE found 1299 electrons equivalent to 17($CHCl_3$ + MeOH) molecules to be included in the solvent accessible voids of 16985 Å^3. CCDC deposition number 900369.

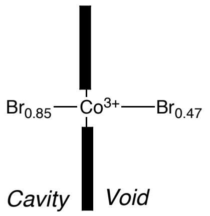


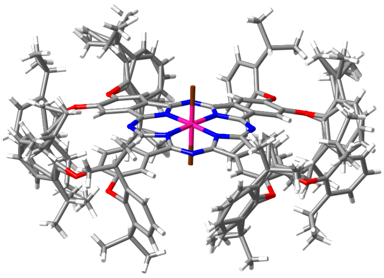
PNC[cBr$_{0.51}$-Co^{3+}-vBr$_{0.36}$]

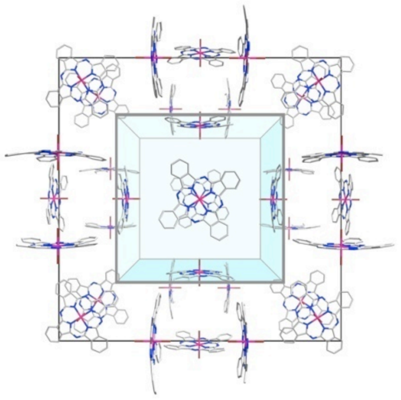




2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(Br)$_2$cobalt (PNC[*c*Br$_{0.51}$-Co^{3+}-*v*Br$_{0.36}$]). These crystals were obtained by washing **(PNC[*c*Br-Co^{3+}-*v*Br])** with MeOH (3 x 2 ml) 24h after the addition of HBr. The crystals were then kept in MeOH until XRD analysis was performed. Data were collected at 100 K at Diamond (λ = 0.68890 Å). Crystal size 0.05 x 0.05 x 0.05 mm, $C_{130.83}H_{155.08}Br_{0.88}Cl_{4.25}CoN_8O_{11.42}$, M = 2302.16, cubic, $Pn\bar{3}n$, a = 37.2791(3) Å, V = 51807.9(7) Å^3, Z = 12, μ(0.68890) = 0.412 µm^{-1}, 223415 reflections measured, 7625 unique reflections (R_{int} = 0.110), 5329 reflections with I $>2\sigma(I)$, R = 0.1025 and $\omega R2$ = 0.3268 (observed data), R = 0.1228 and $\omega R2$ = 0.3473 (all data). The asymmetric unit contains ¼ of the molecule and 2 solvent atoms assumed to be water at 0.25 and 0.5 occupancy. Br$^-$ is coordinated to the metal in both axial positions at occupancies of 51% in the cavity and 37% in the void sites, respectively. We assume charge balance is maintained by some residual unoxidised Co^{2+}. Modelling the disordered solvent with SQUEEZE found 1326 electrons equivalent to 17($CHCl_3$ + MeOH) molecules to be included in the solvent accessible voids of 17073.7Å^3. CCDC deposition number 900370.

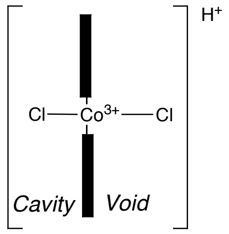


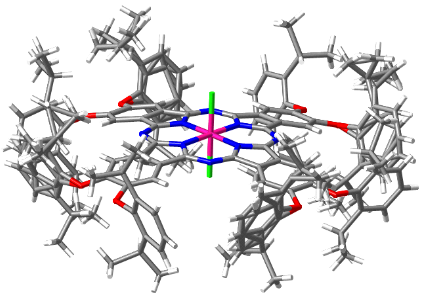


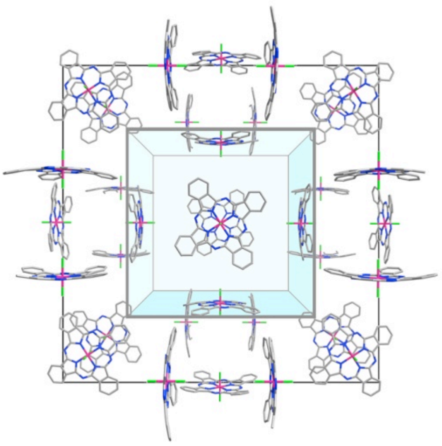


PNC[cBr$_{0.85}$-Co^{3+}-vBr$_{0.47}$]

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(Br)$_2$cobalt (PNC[cBr$_{0.85}$-Co^{3+}-vBr$_{0.47}$]). An excess of Br$_2$ was added to some **PNC[cH$_2$O-Co-vMeOH]** crystals in MeOH. 24h after the addition of Br$_2$ the crystals were washed with MeOH (3x2ml) and kept in MeOH until XRD analysis was performed. Data were collected at 100 K at Diamond (λ = 0.68890 Å). Crystal size 0.05 x 0.05 x 0.05 mm, $C_{130.17}H_{153.42}Br_{1.32}Cl_{3.25}CoN_8O_{11.08}$, M = 2286.65, cubic, $Pn\bar{3}n$, a = 37.017(4) Å, V = 50723(9) Å^3, Z = 12, μ(0.68890) = 0.508 μm^{-1}, 141321 measured reflections, 5287 unique reflections (R_{int} = 0.118), 3715 reflections with $I > 2\sigma(I)$, R = 0.1359 and $\omega R2$ = 0.3776 (observed data), R = 0.1580 and $\omega R2$ = 0.4015 (all data). The asymmetric unit contains ¼ of the molecule and 2 solvent atoms assumed to be water at 0.25 occupancy each. Br$^-$ is present in both axial positions at occupancies of 85% in the cavity and 47% in the void sites, respectively. We assume charge balance is maintained by some residual protonation of the phthalocyanine. Modelling the disordered solvent with SQUEEZE found 977 electrons equivalent to 13(CHCl$_3$ + MeOH) molecules to be included in the solvent accessible voids of 14797.9 Å^3. CCDC deposition number 900371.

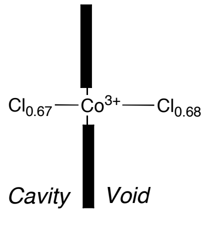




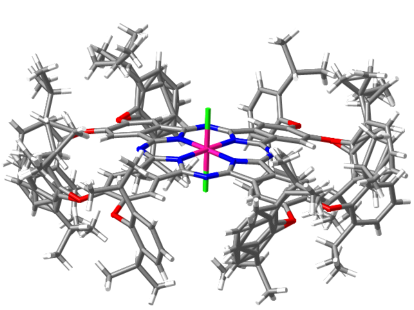


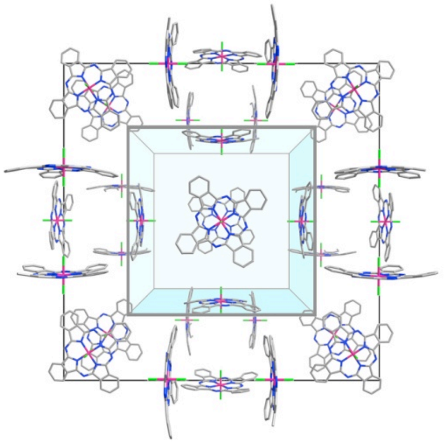
PNC[cCl-Co^{3+}-vCl]

2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(Cl)$_2$cobalt (PNC[*c*Cl-Co^{3+}-*v*Cl]). An excess of HCl (37% w/w) was added to some **PNC[*c*H$_2$O-Co-*v*MeOH]** crystals in MeOH. Data were collected at 100 K at Diamond (λ = 0.68890 Å). Crystal size 0.25 x 0.15 x 0.10 mm, $C_{128}H_{146}Cl_2CoN_8O_{10}$, M = 2086.36, cubic, $Pn\bar{3}n$, a = 37.230(4) Å, V = 51605(10) Å^3, Z = 12, μ(0.68890) = 0.172 µm^{-1}, 106091 reflections measured, 7600 unique reflections (R_{int} = 0.0667), 6274 reflections with I $>2\sigma(I)$, R = 0.1749 and $\omega R2$ = 0.4650 (observed data), R = 0.1885 and $\omega R2$ = 0.4650 (all data). The asymmetric unit contains ¼ of the molecule a solvent atom, assumed to be water at an occupancy of 0.5. A chloride is axially bonded to both sides of the metal. CCDC deposition number 900373.



PNC[cCl$_{0.67}$-Co^{3+}-vCl$_{0.68}$]





2,3,9,10,16,17,23,24-octa(2',6'-di-*iso*-propylphenoxy)phthalocyaninato(Cl)$_2$cobalt (PNC[*c*Cl$_{0.67}$-Co^{3+}-*v*Cl$_{0.68}$]). These crystals were obtained by washing some **PNC[*c*Cl-Co^{3+}-*v*Cl]** with MeOH (3 x 2 ml) after 24 h from the addition of HCl. The crystals were then kept in MeOH until XRD analysis was performed. Data were collected at 100 K at Diamond (λ = 0.68890 Å). Crystal size 0.05 x 0.05 x 0.05 mm, $C_{130.50}H_{154.25}Cl_{3.75}Cl_{1.27}CoN_8O_{11.25}$, M = 2251.88, cubic, $Pn\bar{3}n$, a = 37.365(4) Å, V = 52166(10) Å^3, Z = 12, μ(0.68890) = 0.219 µm^{-1}, 141171 measured reflections, 5324 unique reflections (R_{int} = 0.095), 4044 reflections with I $>2\sigma(I)$, R = 0.1318 and $\omega R2$ = 0.3742 (observed data), R = 0.1491 and $\omega R2$ = 0.3949 (all data). The asymmetric unit contains ¼ of the molecule and 2 solvent atoms assumed to be water at 0.25 occupancy each. In both axial positions Cl$^-$ is present at occupancies of 67% in the cavity and 68% in the void sites, respectively. We assume charge balance is maintained by some residual protonation of the phthalocyanine. Modelling the disordered solvent with SQUEEZE found 1147 electrons equivalent to 15(CHCl$_3$ + MeOH) molecules to be included in the solvent accessible voids of 15616.1 Å^3. CCDC deposition number 900374.

References.

1. C. G. Bezzu, J. E. Warren, M. Helliwell, D. R. Allan and N. B. McKeown, *Science*, 2010, **327**, 1627-1630.

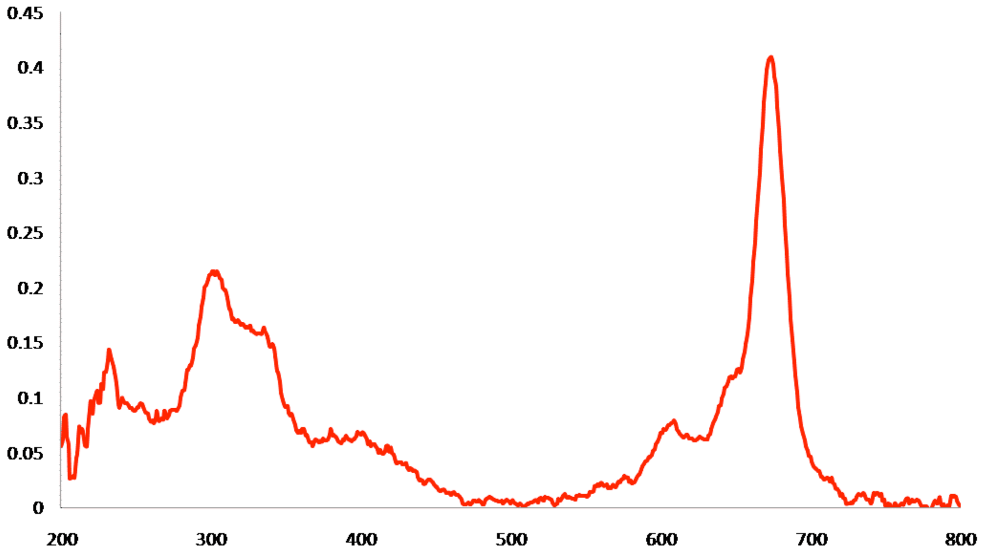


Fig. S1. **a)** UV-vis spectrum of PcCo in DCM solution with λ_{max} = 673 nm

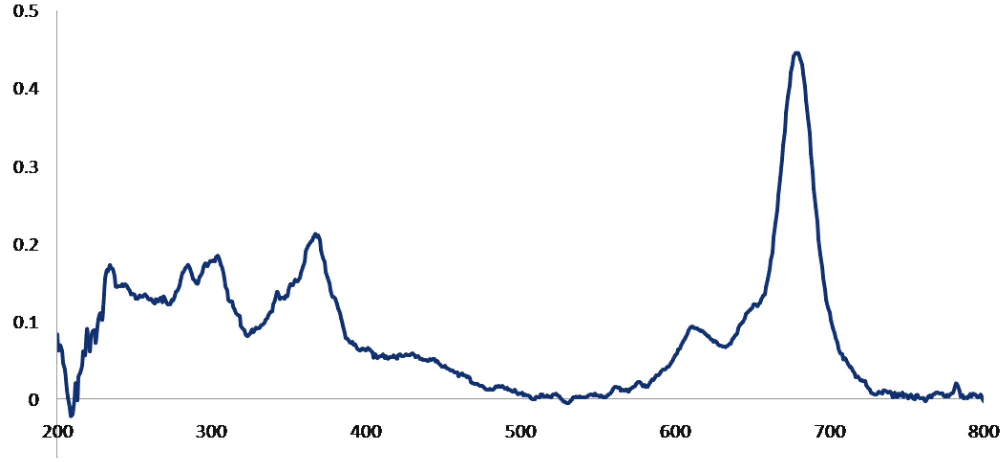


Fig. S1. **b)** UV-vis spectrum of a dissolved sample of **PNC[*c*Im-Co-*v*Im]$_2$** in DCM solution with λ_{max} = 678 nm

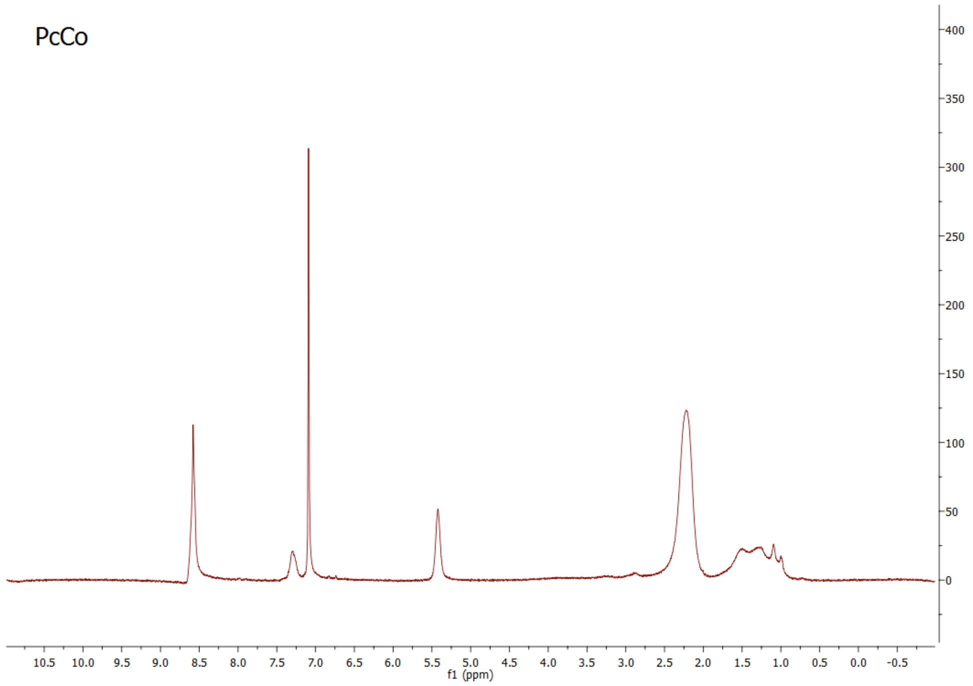


Fig. S2 a) ^{1}H NMR spectrum of PcCo showing broad peaks due to the paramagnetic nature of the Co^{2+} cation.

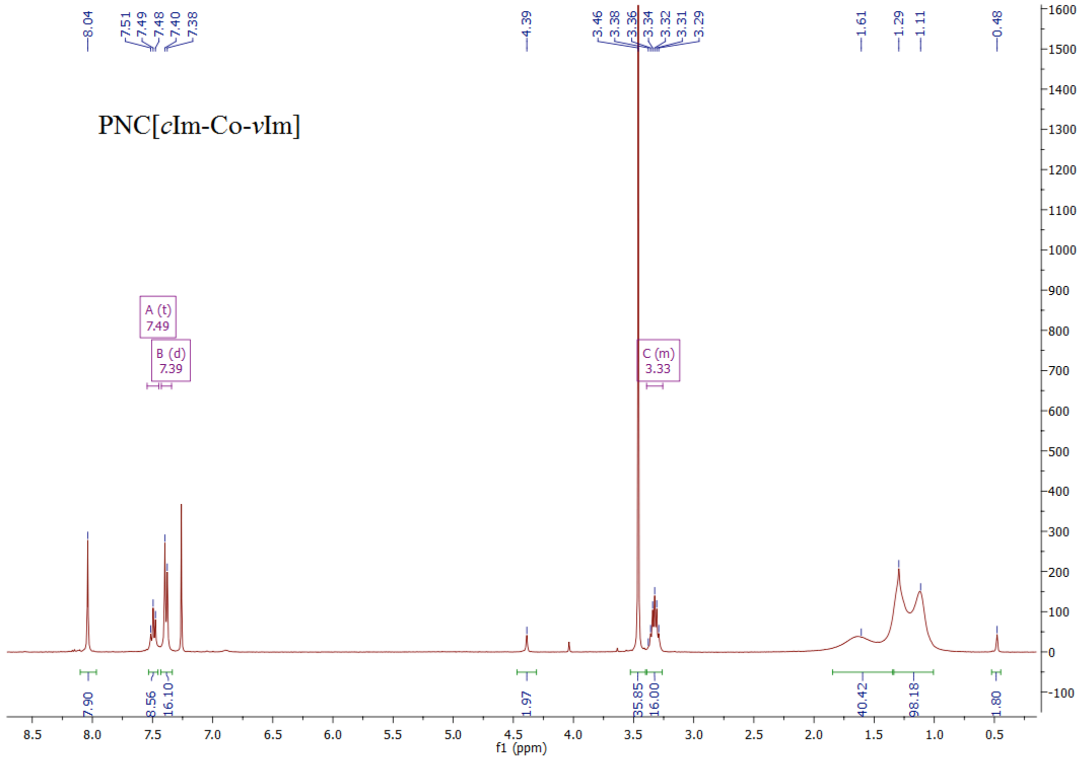


Fig. S2 b) ^{1}H NMR spectrum of a dissolved sample of **PNC[*c*Im-Co-*v*Im]$_2$** showing sharp peaks due to the diamagnetic nature of the Co^{3+} cation. The large peak at 3.5 ppm is due to the included methanol.