Supplementary Information

First Example of a Di-Cadmium Tris-Phthalocyanine Triple-Decker Sandwich Complex

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Experimental Procedure

All solvents were SLR or analytical grade and were used as supplied. Commercially available materials were used without further purification. Infrared spectra were recorded as powders on a Perkin Elmer Spectrum BX equipped with a DuraSamplIR II ATR attachment. NMR spectra were recorded at 400 MHz for ^{1}H and 75.4 MHz for ^{13}C on a Varian Unity plus spectrometer. The residual solvent peak was used as reference (7.15 ppm for benzene-d$_6$ and 7.23 ppm for chloroform-d$_3$). UV-vis spectra were recorded on a Hitachi U-3000 spectrophotometer in the solvent stated. Melting points and phase transition temperatures of **2** (crystal, K; discotic mesophase, D; isotropic liquid, I) were recorded using an Olympus BH-2 polarising microscope fitted with a Linkham THM 600 hotstage. DSC (Differential Scanning Calorimetry) was performed using a TA-910 thermal analysis instrument. Microanalysis data were obtained using a Carlo Erda 1106 Elemental Analyzer and are quoted to the nearest 0.01%. Maldi-TOF mass spectra were recorded using an Applied Biosystems Voyager-DE-STR at the EPSRC National Mass Spectrometry Service Centre at the University of Wales in Swansea, U.K., using DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile) as matrix. EPR measurements were carried out at 295 K on a Bruker E500 continuous wave X-band EPR spectrometer fitted with a Bruker ER4123D dielectric room temperature resonator. MTSL, [1-oxyl-2,2,5,5-tetramethyl-d-pyrroline-3-methyl] methanethiosulfonate, was used as standard. X-ray crystallography was performed using a Rigaku R-Axis IIc image plate diffractometer equipped with a rotating anode X-ray source (Mo-Kα radiation) and graphite monochromator.

Electrochemical experiments were controlled with a BAS 100 potentiostat using anhydrous dichloromethane as solvent and $[NBu_4][B\{C_6H_3(CH_3)_2\}_4]$ as supporting electrolyte. A three electrode cell utilising a glassy carbon working electrode, a silver/silver chloride reference electrode and a platinum wire auxiliary electrode were used. Data, uncorrected for junction potentials, were collected with BAS software and exported to a Microsoft Excel spreadsheet for manipulation.

2: 1,4,8,11,15,18,22,25-Octakis(hexyl)phthalocyanine (500 mg, 0.42 mmol) in pentan-1-ol (20ml) was brought to reflux. Cadmium acetate hydrate (99.99+%) (2 eq., excess) was added and reflux continued for 45 minutes. The hot mixture was added to excess cold MeOH (150 ml) and the flask left in the fridge overnight. The green solid was filtered and washed with MeOH. The green solid was redissolved in THF and the solution filtered to remove the insoluble cadmium salt residue. The solvent was then removed under reduced pressure and the solid reprecipitated from excess MeOH to yield a green powder (350 mg, 64%). [MALDI-MS: isotopic cluster at 1298 [M, 100%]. λ_{max} (*n*-hexane): 709, 643 nm. Found: C, 74.15; H, 8.72; N, 8.47%. $C_{80}H_{112}N_8Cd$ requires: C, 74.01; H, 8.69; N, 8.63%. δ_H (400 MHz, C_6D_6 containing pyridine-d$_5$) 7.75 (s, 8H), 4.63 (t, 16H), 2.2 (m, 16H), 1.6 (m, 16H), 1.1-1.3 (m, 32H), 0.75 (t, 24H) ppm. δ_C (75.4 MHz, C_6D_6 containing pyridine-d$_5$) 155.38, 138.55, 136.68, 130.21, 33.02, 32.43, 31.3, 29.34, 22.85, 14.05 ppm. M.p. (DSC transition energies) K-D 131.1 ºC (0.75 J/g) D-D 166 ºC (1.34 J/g) D-D 192.8 ºC (undetected) D-I 244.4 ºC (0.19 J/g). ν_{max} (neat, ATR) 2952.61, 2920.92, 2851.56, 1313.26, 1151.81, 1084.52, 883.15 cm^{-1}]

3: 1,4,8,11,15,18,22,25-Octakis(hexyl)phthalocyaninato cadmium (350 mg, 0.27 mmol) was recrystallised thrice from THF-MeOH to afford a dark blue crystalline material (150 mg, 44%). [MALDI-MS: isotopic clusters at 2598.7 [M-Pc, 10%], 2484.8 [M-CdPc, 55%], 1299.1 [M-CdPc$_2$, 100%], 1187.1 [M-Cd$_2$Pc$_2$, 55%]. λ_{max} (*n*-hexane): 718 (ε= 1.3x10^5), 599 (ε = 0.6x10^5), 550, 484 nm. Found: C, 76.06; H, 8.95; N, 8.79%. $C_{240}H_{336}N_{24}Cd_2$ requires: C, 76.17; H, 8.95; N, 8.88%. M.p. 220 ºC (dec.). ν_{max} (neat, ATR) 2950.75, 2918.0, 2849.64, 1604.2, 1365.16, 1287.22, 1266.26, 1189.81, 1093.03 cm^{-1}]

Crystal structure

The central ligand, Figure 1, is approximately planar; the two independent rings are tilted 3.76(11)° and 1.90(10)° from the central N4 plane and opposite rings are, by symmetry, parallel. The outer rings, Figure 2, have an ‘inverted umbrella’ conformation; the four benzenoid rings tilt away from the N4 mean plane by angles of 12.57(12)°, 8.72(12 °, 13.17(12)° and 8.65(12)°. Within the triclinic cell, Figure 3, all the molecules of **3** lie parallel. There is stacking along the α axis, with substantial overlap of the cores of the outer ligands with their symmetrically related neighbours.

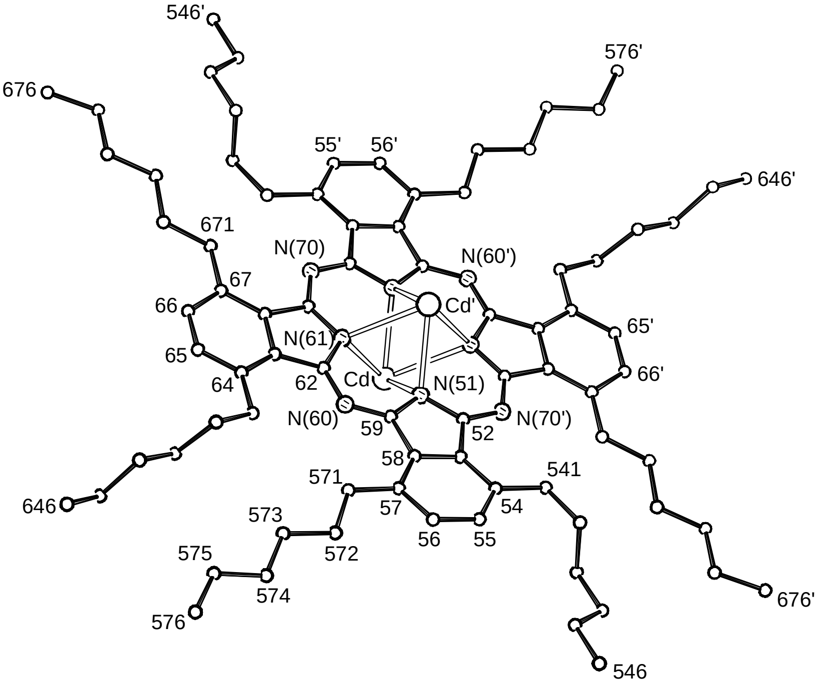

Figure 1. Central ligand

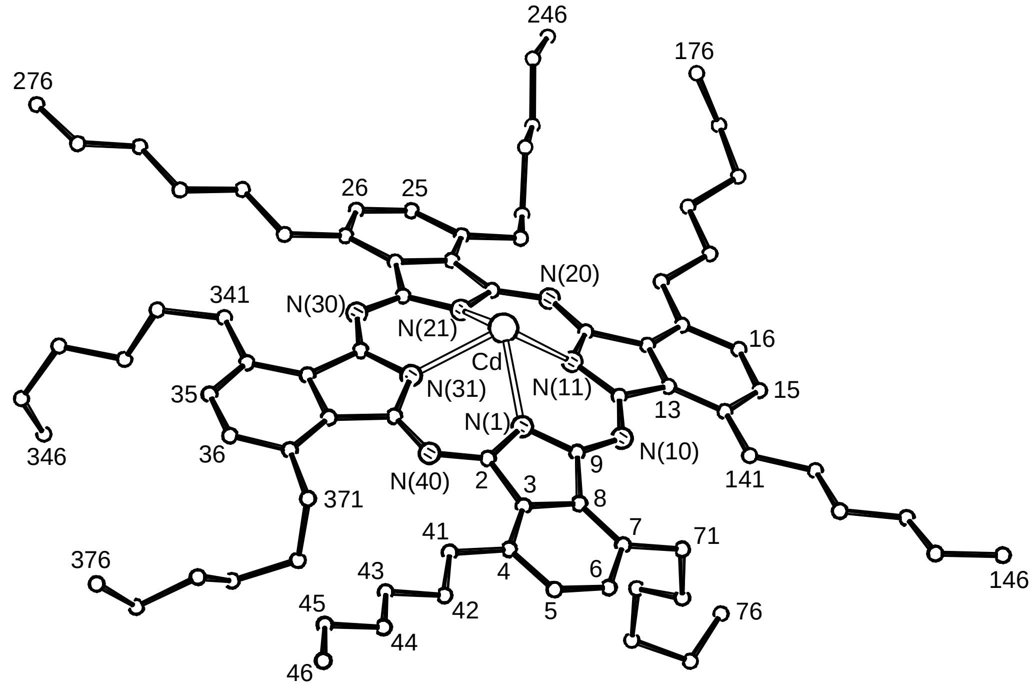

Figure 2: Outer ligand

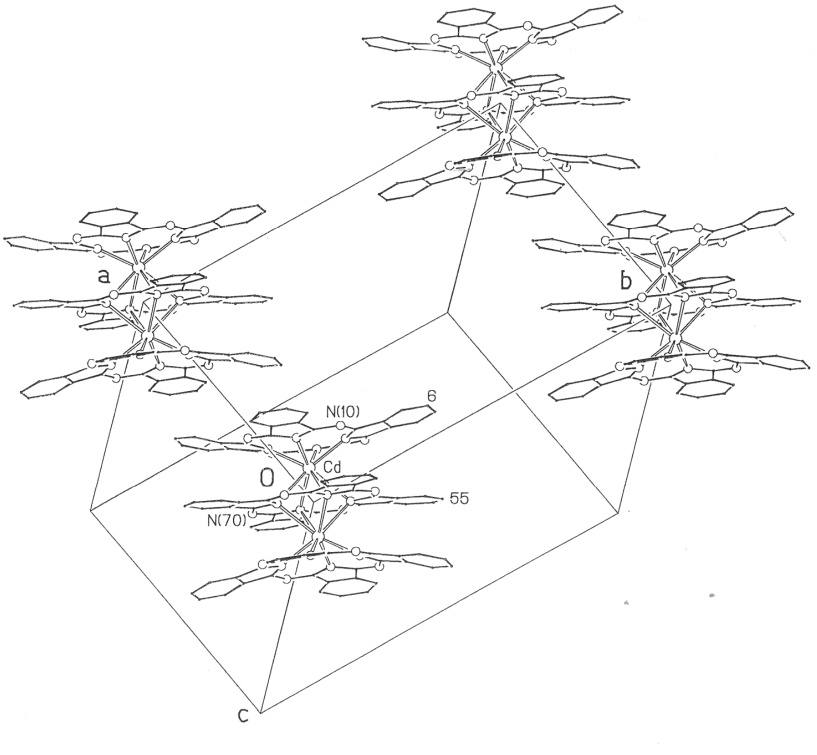

Figure 3. Crystal packing