

Supporting Information File

**Encapsulation of transition metal atoms into carbon nanotubes:
a supramolecular approach**

**Jian Fan, Thomas W. Chamberlain, Yu Wang, Sihai Yang, Alexander J. Blake, Martin Schröder
and Andrei N. Khlobystov**

Synthesis of Bis(2,2'-bipyridin-5-ylmethyl)malonate:

A solution of malonyl dichloride (1.1 g, 7.8 mmol) in dichloromethane (50 mL) was added dropwise to a solution of 5-hydroxymethyl-2,2'-bipyridine (3.0 g, 16.1 mmol) and triethylamine (5 mL) in dichloromethane (100 mL) at room temperature. The mixture was stirred overnight, and then washed with water (3×50 mL). The organic phase was dried over anhydrous Na_2SO_4 , filtered and evaporated to dryness. The residue was purified by column chromatography (SiO_2 ; acetone) to afford the product as pale yellow crystals (1.1 g, 33 %).

^1H NMR (270 MHz, CDCl_3): δ (ppm) = 8.68 (m, 4H), 8.42 (m, 4H), 7.81 (m, 4H), 7.33 (ddd, $J = 7.6$ Hz, $J = 4.8$ Hz, $J = 1.1$ Hz, 2H), 5.27 (s, 4H), 3.54 (s, 2H). ^{13}C NMR (68 MHz, CDCl_3): δ (ppm) = 166.02, 156.46, 155.69, 149.29, 149.19, 137.11, 137.00, 130.79, 123.97, 121.30, 120.94, 64.76, 41.44. ESI-MS: m/z 441 [$\text{M}+\text{H}]^+$. Elemental analysis (%) calcd for this product: C 68.18, H 4.55, N 12.73; found: C 67.87, H 4.65, N 12.75. IR (CHCl_3): ν (cm^{-1}) 2980m, 2929m, 2855m, 1737s, 1602s, 1591m, 1463s, 1330m, 1257m, 1093m, 929m.

Bis(2,2'-bipyridin-5-ylmethyl)-3'H-cyclopropano[1,9]($\text{C}_{60}\text{-I}_h$)[5,6]fullerene-3',3'-dicarboxylate (1):
A solution of C_{60} (100 mg, 0.138 mmol), bis(2,2'-bipyridin-5-ylmethyl)malonate (60.7 mg, 0.138 mmol) and iodine (35.3 mg, 0.138 mmol) in toluene (200 mL) was stirred at room temperature for 30 minutes. 1,8-Diazabicycloundec-7-ene (21.1 mg, 0.138 mmol) was then added and the mixture stirred for a further 2 days. The solvent was removed under reduced pressure at room temperature and the product was then isolated by column chromatography (SiO_2 ; toluene, then chloroform/acetone 7:3) as a dark brown powder (39.9 mg, 25 %).

^1H NMR (270 MHz, CDCl_3): δ (ppm) = 8.78 (d, $J = 2.2$ Hz, 2H), 8.67 (ddd, $J = 4.8$ Hz, $J = 1.6$ Hz, $J = 0.8$ Hz, 2H), 8.41 (d, $J = 8.1$ Hz, 2H), 8.38 (d, $J = 7.6$ Hz, 2H), 7.90 (dd, $J = 8.1$ Hz, $J = 2.2$ Hz, 2H), 7.80 (td, $J = 7.6$ Hz, $J = 1.6$ Hz, 2H), 7.32 (ddd, $J = 7.6$ Hz, $J = 4.8$ Hz, $J = 1.1$ Hz, 2H), 5.56 (s, 4H). ^{13}C NMR (68 MHz, CDCl_3): δ (ppm) = 163.29, 156.85, 155.54, 149.71, 149.30, 145.33, 145.26, 145.08, 144.99, 144.75, 144.72, 144.58, 143.91, 143.07, 142.26, 141.86, 141.06, 139.10, 137.67, 137.00, 130.17, 124.05, 121.39, 121.03, 77.28, 71.26, 66.37. MALDI-MS: m/z 1158 [$\text{M}]^+$. Elemental analysis (%) calcd for this product: C 88.08, H 1.55, N 4.84; found: C 88.13, H 1.51, N 4.84. IR (KBr disc): ν (cm^{-1}) 2959m, 2924m, 2853m, 1745s, 1636m, 1460s, 1384m, 1230m, 793w, 673w, 507m.

Complex formation and crystal growth (2):

A solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (3 mg, 0.01 mmol) in MeOH (8.0 mL) was added to **1** (12 mg, 0.01 mmol) in CH_2Cl_2 (10 mL). The resulting red solution was stirred at room temperature for 1 hour, filtered and then left undisturbed in the dark. Red platy single crystals (5 mg, 35%) suitable for X-ray crystallographic study were isolated by filtration after several days. Elemental analysis (%) calcd for this product: C 69.96, H 1.09, N 5.69; found: C 70.35, H 1.35, N 5.35. IR (KBr disc): ν (cm^{-1}) 2961m, 2923m, 2852m, 1744s, 1627s, 1435s, 1265w, 1173w, 1096w, 839w, 581w, 526m.

X-ray crystal crystallography.

X-ray diffraction data for a single crystal of **2** were collected at 120(2) K on Station 9.8 of the Synchrotron Radiation Source at STFC Daresbury Laboratory. The structure was solved by direct methods and developed by difference Fourier techniques using the SHELXTL software package.^[1] The hydrogen atoms on the ligands were placed geometrically and refined using a riding model. Geometric restraints were applied to the phenyl ring and the carboxylate group of the organic ligand.

The unit cell volume includes a large region of disordered solvents which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE^[2] to calculate the contribution to the diffraction from the solvent region (18% voids) and thereby produced a set of solvent-free diffraction intensities. SQUEEZE estimated a total count of 310 electrons per unit cell, which were assigned to be 1.0 DCM molecule per cadmium. The final formula was calculated from the SQUEEZE^[2] results combined with elemental analysis and TGA data: the contents of the solvent/cation region are therefore represented in the unit cell contents but were not included in the refinement model.

Crystal structure of Cd(II) complex 2:

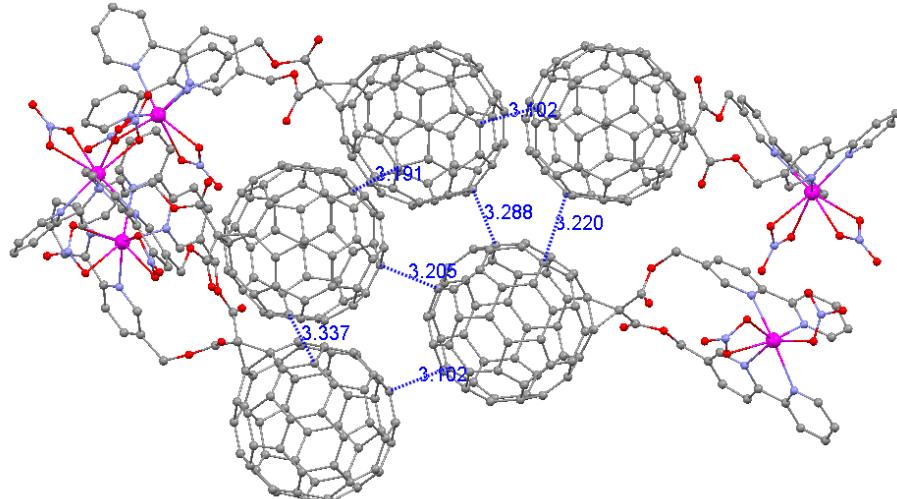


Figure S1: (top) Single-crystal XRD structure of Cd(II) complex **2** showing the packing of the fullerene molecules in the 3D lattice. The distances indicated in blue (Å) show the closest fullerene to fullerene contacts in the structure.

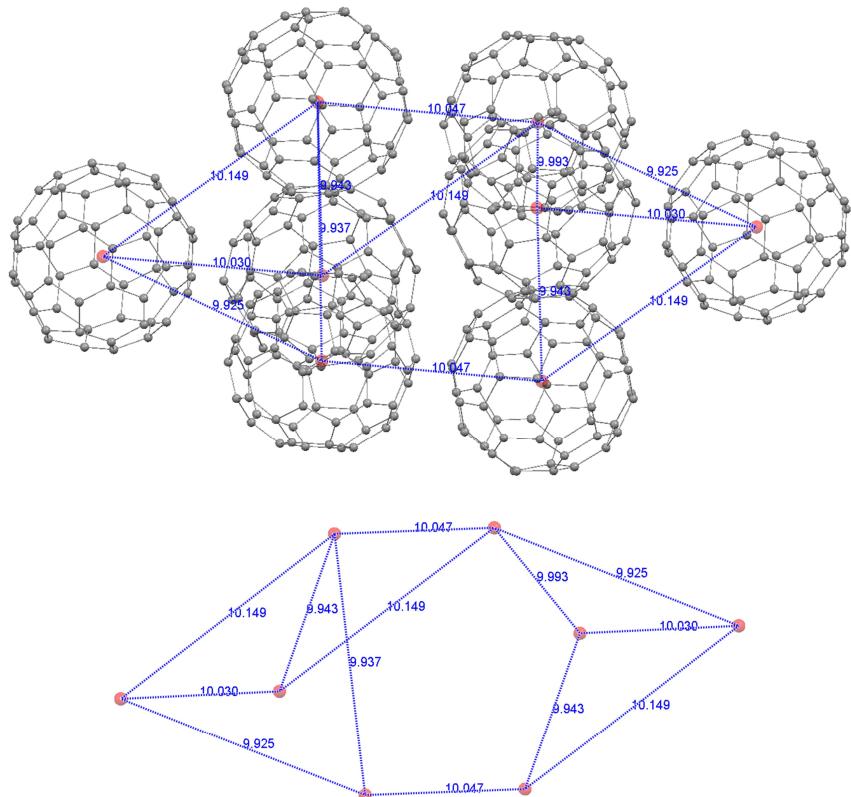


Figure S2: (top) Single-crystal XRD structure of Cd(II) complex **2** showing the packing of the fullerene cages (the functional groups have been removed for clarity). (bottom) Centroid to centroid distances (\AA) between neighbouring fullerene molecules in the crystal lattice.

Crystal data for 2:

[Cd(C₈₅H₁₈N₄O₄)(NO₃)₂]·CH₂Cl₂: Red plate (0.08 x 0.05 x 0.003 mm). $P2_1/c$ (No. 14), $a = 36.351(2)$ Å, $b = 17.1037(10)$ Å, $c = 19.3682(11)$ Å, $\beta = 93.364(2)$ °, $V = 12021(1)$ Å³, $M = 1476.35$, $T = 120(2)$ K, $Z = 8$, $D_{\text{calc}} = 1.631$ g cm⁻³, $\mu = 0.531$ mm⁻¹, $F(000) = 5888$. A total of 53416 reflections were collected, of which 14586 were unique, with $R_{\text{int}} = 0.072$. Final R_1 (wR_2) = 0.059 (0.160) with GOF = 1.00. The final difference Fourier extrema were 0.64 and -0.59 e/Å³. Crystallographic data for **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 792549. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Encapsulation of complex 2 into carbon nanotubes:

Purified SWNT (3 mg) (NanoCarbLab, average diameter = 1.39 nm) were annealed in air at 520 °C for 15 minutes. A three-fold excess of the fullerene complex (9 mg) was dispersed in chloroform (1 mL) using ultrasonic waves forming a supersaturated solution; the resultant solution was dropped slowly onto the freshly annealed nanotubes in an agate mortar, allowing the solvent in each drop to evaporate before adding a further drop. The resultant black solid was allowed to dry thoroughly in air, ground using a mortar and pestle for 5 minutes then suspended in *n*-hexane (5 mL) and treated with ultrasonic waves for 3 hours. The solid was then filtered off and first washed with carbon disulphide (20 mL) and then methanol (20 mL) to remove any unencapsulated fullerenes.

TEM conditions and image analysis.

HRTEM analysis was performed using a JEOL2100 field-emission gun microscope. The imaging conditions were carefully tuned by lowering the accelerating voltage of the microscope to 100 kV and reducing the beam current density to a minimum. Nanotube samples (2–3 mg) were dispersed in methanol (2 mL) using an ultrasonic bath and deposited onto lacey carbon film coated TEM copper grids. The filling rates were determined by taking micrographs of 100 nm² areas from different regions of the specimen, estimating the proportion of filled nanotubes for each area and averaging the filling factors over 50–70 areas. TEM image simulation was carried out using spherical aberration coefficient (C_s) = 1 mm, defocus (Δf) = -5.5 nm, and the defocus spread (d_s) = 5 nm.

References

1. G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112.
2. A. L. Spek, *Acta Crystallogr. Sect. D*, 2009, **65**, 148.