Electronic Supplementary Information

An infinite catenane self-assembled by π···π interactions

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Experimental:

Chemicals were obtained from Sigma Aldrich and used without further purification.

Ligand Synthesis

Precursor (P) 2,7-bis(bromomethyl)-9,10-dihydrophenanthrene[1]

The synthesis of **P** followed the same procedure as that in the literature.[1] 9,10-dihydrophenanthrene (29 mmol, 5.27 g), paraformaldehyde (128 mmol, 3.86 g), hydrogen bromide (48%), phosphoric acid (85%) and hydrogen bromide (33% in HOAc) were placed in a round-bottom flask and heated to 80 °C under an inert atmosphere. The mixture was stirred for approximately 24 hours after which the temperature was increased to 120 °C for a further 12 hours (monitoring with TLC). Once the solution had cooled, the solid was filtered, washed with acetone and recrystallised from benzene to yield fine white needle-shaped crystals (4.7 g, 45%); δ_H (400 MHz; $CDCl_3$) 2.88 (s, 4 H) 4.53 (s, 4 H) 7.28 (d, *J*=1.75 Hz, 2 H) 7.34 (dd, *J*=7.99, 1.95 Hz, 1 H) 7.71 (d, *J*=7.99 Hz, 2 H); δ_C (400 MHz; $CDCl_3$) 28.74, 33.56, 124.22, 127.74, 128.86, 134.17, 137.03, 137.91.

Intermediate (I) 2,7-bis(bromomethyl)phenanthrene[2]

The dehydrogenation of **P** was accomplished by modification of a known synthetic procedure.[1,2] 2,7-Bis(bromomethyl)-9,10-dihydrophenanthrene was added to a mixture of dichloro dicyano quinone (DDQ) (15 mmol, 3.42 g) and dry benzene (freshly distilled, 22 ml). The orange mixture was heated under reflux for 3 days (monitored by TLC). The dark solid that formed was dissolved in benzene (200 ml) and filtered through a pad of neutral alumina leaving a clear solution. The solvent was removed under reduced pressure affording a semi-crystalline white solid. Recrystallisation from a chloroform/hexane mixture resulted in crystals suitable for structure determination. The single-crystal structure of the precursor has not been reported in the literature. (1.06 g, 25%); δ_H (300 MHz, $CDCl_3$) 4.72 (s, 4 H) 7.70

(ddd, *J*=8.47, 1.72, 1.54 Hz, 4 H) 7.73 (s, 2 H) 7.90 (d, *J*=1.91 Hz, 2 H) 8.64 (d, *J*=8.51 Hz, 2 H) δ_C (300 MHz, $CDCl_3$) 33.44, 46.17, 123.49, 123.58, 127.04, 127.29, 127.58, 128.33, 128.70, 129.82, 132.21, 136.20.

Crystal data for **I**: $C_{16}H_{12}Br_2$, M = 364.08, Colourless Plate, 0.24 × 0.22 × 0.08 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 14.073(3), b = 8.4828(15), c = 11.281(2) Å, β = 101.917(2)°, V = 1317.7(4) $Å^3$, Z = 4, D_c = 1.835 g/cm^3, F_{000} = 712, Bruker APEX CCD area-detector, MoKα radiation, λ = 0.71073 Å, T = 100(2) K, $2\theta_{max}$ = 52.6°, 7323 reflections collected, 2666 unique (R_{int} = 0.0383). Final *GooF* = 1.025, *R1* = 0.0347, *wR2* = 0.0859, *R* indices based on 2104 reflections with I >2σ(I) (refinement on F^2), 163 parameters, 0 restraints. Lp and absorption corrections applied, μ = 6.129 mm^{-1}.

Ligand (L) 1,1'-(phenanthrene-2,7-diyldimethanediyl)bis(1*H*-imidazole)
The synthesis of **L** was adapted from literature procedures.[3,4] Imidazole (6.4 mmol, 0.44 g), sodium hydroxide (6.4 mmol, 0.26 g) and DMSO were stirred at 60 °C. After 1 hr. 2,7-bis(bromomethyl)phenanthrene (**I**) (2.9 mmol, 1.06 g) was added. The reaction mixture was monitored (by TLC) over 7 days until all reaction precursors were consumed. The reaction mixture was quenched with water (200 ml) and the light yellow precipitate filtered, dissolved in chloroform and washed again with water. The organic layer was extracted and solvent removed under reduced pressure to afford a light yellow powder. Single crystals were grown by the dropwise addition of a chloroform solution in *n*-hexane. The crystal data was subsequently collected and the structure solved and refined as a non-merohedral twin (0.71 g, 71%); δ_H (300 MHz, *DMSO-d*$_6$) 5.41 (s, 4 H) 6.95 (s, 2 H) 7.26 (t, *J*=1.17 Hz, 2 H) 7.56 (dd, *J*=8.51, 1.76 Hz, 2 H) 7.80 (s, 2 H) 7.83 (d, *J*=1.76 Hz, 2 H) 7.85 (s, 2 H) 8.78 (d, *J*=8.66 Hz, 2 H); δ_C (300 MHz, *DMSO-d*$_6$) 49.37, 119.66, 123.60, 126.31, 126.93, 127.11, 128.81, 128.92, 131.55, 136.38, 137.54.

Crystal data for **L**: $C_{22}H_{16}N_4$, M = 336.39, Colourless shard, 0.28 × 0.20 × 0.06 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 6.3522(14), b = 5.5996(13), c = 23.548(5) Å, β = 94.630(3)°, V = 834.9(3) $Å^3$, Z = 2, D_c = 1.338 g/cm^3, F_{000} = 352, Bruker APEX CCD area -detector, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 50.3°, 2799 reflections collected, 1495 unique (R_{int} = 0.0674). Final *GooF* = 1.066, *R1* = 0.0641, *wR2* = 0.1606, *R* indices based on 1061 reflections with I >2σ(I) (refinement on F^2), 128 parameters, |0 restraints. Lp and absorption corrections applied, μ = 0.082 mm^{-1}.

References

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