ESI to accompany:

A 3-dimensional {$4^2.8^4$} lvt net built on a ditopic bis(3,2':6',3''-terpyridine) tecton bearing long alkyl tails

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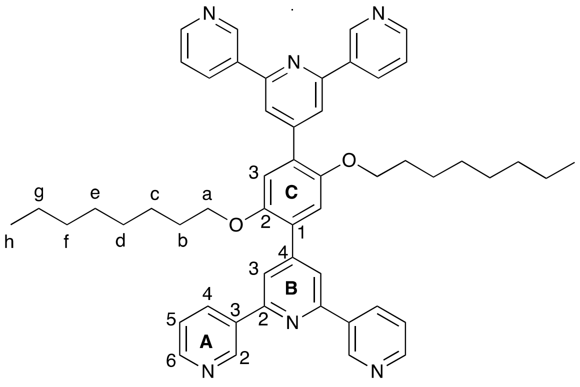
Experimental details

General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 NMR spectrometer with chemical shifts referenced to residual solvent peaks (TMS = ∂ 0 ppm). The FT IR spectra were recorded on a Shimadzu FTIR 8400S spectrophotometer with a solid sample (Golden Gate ATR) accessory. Electrospray ionisation (ESI) mass spectra were measured on a Bruker esquire 3000plus spectrometer. Solution electronic absorption spectra were recorded on a Agilent 8453 spectrophotometer.

3-Acetylpyridine, 2,5-bis(octoxy)benzene-1,4-dicarbaldehyde and aqueous NH_3 (25%) were purchased from Sigma-Aldrich and used without further purification.

Synthesis of 1



2,5-Bis(octoxy)terephthalaldehyde (0.25 g, 0.64 mmol) was dissolved in EtOH (40 mL), then 3-acetylpyridine (0.36 g, 3.0 mmol) and KOH (0.84 g, 15.0 mmol) were added to the solution and a change from colourless to yellow and then dark red was observed. Aqueous NH_3 (32%, 6.3 mL) was slowly added to the reaction mixture and this was then stirred at room temperature overnight. The solid that formed was collected by filtration, washed with EtOH (3 × 20 mL) and H_2O (3 × 20 mL) and dried in vacuo. Compound **1** was isolated as a pale yellow powder (0.21 g, 0.26 mmol, 41%). M.p. = 174.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm 9.39 (d, *J* = 1.5 Hz, 4H, H^{A2}), 8.71 (m, 4H, H^{A6}), 8.53 (m, 4H, H^{A4}), 8.03 (s, 4H, H^{B3}), 7.47 (m, 4H, H^{A5}), 7.17 (s, 2H, H^{C3}), 4.06 (t, *J* = 6.3 Hz, 4H, H^a), 1.75 (m, 4H, H^b), 1.36 (m, 4H, H^c), 1.25 –1.13 overlapping with 1.13–1.01 (m, 16H, $H^{d/e/f/g}$), 0.79 (t, *J* = 7.1 Hz, 6H, H^h). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ / ppm 154.8 (C^{B2}), 150.7 (C^{C2}), 150.3 (C^{A6}), 148.6 (C^{A2}), 148.1 (C^{C1}), 134.9 (C^{A3}), 134.6 (C^{A4}), 129.4 (C^{B4}), 123.8 (C^{A5}), 120.3 (C^{B3}), 115.4 (C^{C3}), 69.9 (C^a), 31.8 (C^f), 29.5 (C^b), 29.4 ($C^{d/e}$), 29.3 ($C^{d/e}$), 26.4 (C^c), 22.7 (C^g), 14.2 (C^h). IR (solid, ν / cm^{-1}) 3057 (w), 3037 (w), 2923 (s), 2853 (m), 1904 (w), 1600 (s), 1576 (m), 1545 (s), 1515 (m), 1479 (m), 1467 (m), 1439 (m), 1414 (m), 1383 (s), 1339 (m), 1327 (m), 1282 (m), 1264 (m), 1212 (s), 1142 (m), 1129 (m), 1080 (m), 1058 (m), 1031 (m), 1017 (s), 990 (m), 972 (m), 960 (m), 922 (w), 899 (w), 873 (s), 839 (m), 805 (s), 778 (m), 747 (m), 723 (m), 712 (s), 701 (s), 678 (s), 661 (m), 619 (s), 556 (m), 489 (m), 475 (w), 460 (w). UV-VIS (CH_2Cl_2, 1.25×10^{-5} M) λ/nm (ε/ $dm^3 \times mol^{-1} \times cm^{-1}$) 241 (51500), 258 sh (47200), 277 sh (42600), 320 (17400), 354 sh (10300). ESI-MS *m/z* 797.8 $[M+H]^+$ (calc. 797.5). Found C 76.75, H 6.98, N 10.52; required for $C_{52}H_{56}N_6O_2 \cdot H_2O$ C 76.63, H 7.17, N 10.31.

$[Co(NCS)_2(\mathbf{1}) \cdot 4CHCl_3]_n$

A solution of $Co(NCS)_2$ (5.25 mg, 0.03 mmol) in MeOH (8 mL) was layered over a solution of **1** (12.0 mg, 0.015 mmol) in $CHCl_3$ (5 mL). Pink crystals of $[Co(NCS)_2(\mathbf{1}) \cdot 4CHCl_3]_n$ were obtained after 2–4 weeks (3.00 mg, 0.002 mmol, 13%). Inadequate material was obtained for bulk elemental analysis.

Crystallography

General

Single crystal data were collected on a Bruker APEX-II diffractometer with data reduction, solution and refinement using the programs APEX[1] and CRYSTALS.[2] The crystal was a racemic twin. Structural analysis and diagrams used Mercury v. 3.3[3,4] and TOPOS.[5]

$[Co(NCS)_2(\mathbf{1})\cdot 4CHCl_3]_n$

$C_{58}H_{60}Cl_{12}CoN_8O_2S_2$, M = 1449.66, pink block, orthorhombic, space group $Pna2_1$, a = 17.8916(15), b = 19.6745(17), c = 19.088(2) Å, U = 6719.1(8) Å^3, Z = 4, D_c = 1.433 Mg m^{-3}, μ(Cu-Kα) = 7.350 mm^{-1}, T = 123 K. Total 64379 reflections, 11789 unique, R_{int} = 0.090. Refinement of 11763 reflections (704 parameters) with $I > 2\sigma(I)$ converged at final R_1 = 0.1343 (R_1 all data = 0.1464), wR_2 = 0.3170 (wR_2 all data = 0.3268), gof = 1.0827. Flack parameter = 0.480(10). CCDC 1035825.

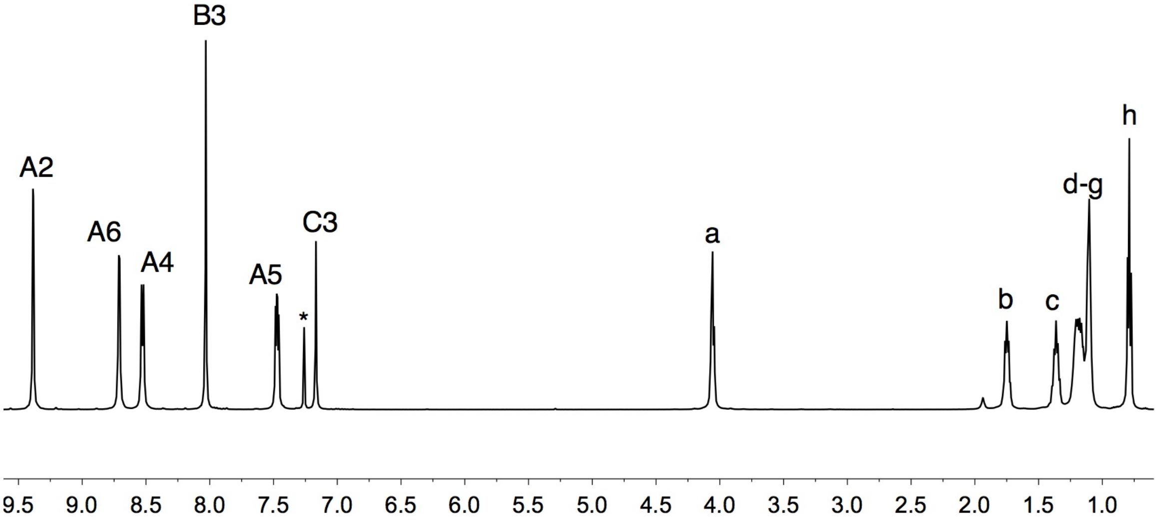


Fig. S1. 500 MHz ^1H NMR spectrum (295 K) of ligand **1**. The peak labelled with an asterisk is residual $CHCl_3$ in the $CDCl_3$ solvent

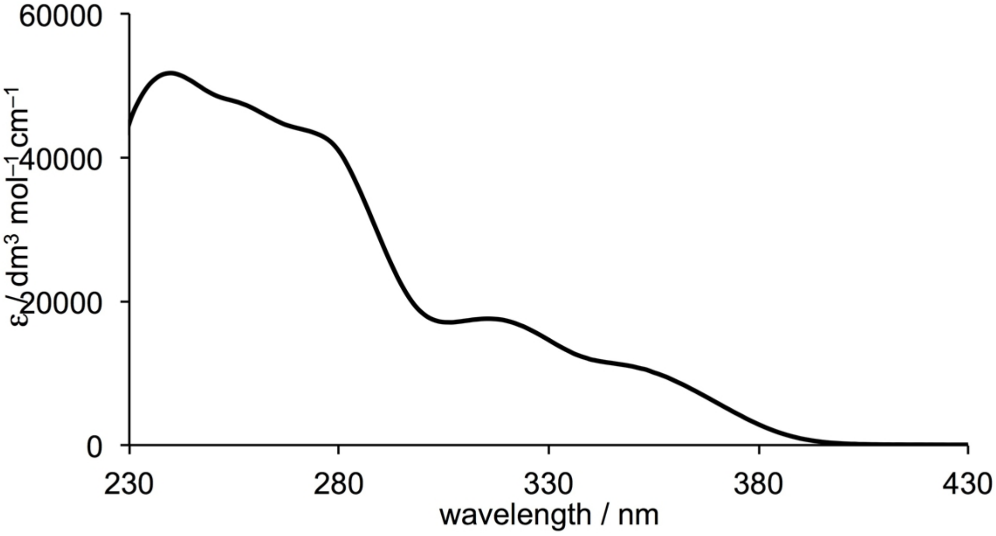


Fig. S2. Absorption spectrum of a CH_2Cl_2 solution of **1** (2.5×10^{-5} mol dm^{-3}).

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[1] Bruker Analytical X-ray Systems, Inc., 2006, APEX2, version 2 User Manual, M86-E01078, Madison, WI.

[2] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487.

[3] I. J. Bruno, J. C. Cole, P. R. Edgington, M. K. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr., Sect. B*, 2002, **58**, 389.

[4] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.* 2008, **41**, 466.

[5] V. A. Blatov and A. P. Shevchenko, TOPOS Professional v. 4.0, Samara State University, Russia.