ESI to accompany:

2D → 2D Parallel interpenetration of (4,4) sheets expedited by a ditopic bis(4,2':6',4''-terpyridine)

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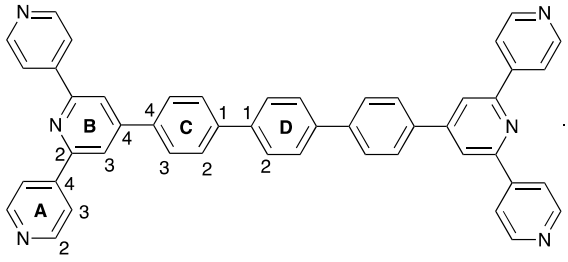
Experimental details

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.

4-Acetylpyridine, 2,5-bis(octyloxy)benzene-1,4-dicarbaldehyde and aqueous NH_3 (25%) were purchased from Sigma-Aldrich and used without further purification. [1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde was prepared based by Suzuki cross-coupling as reported by Chand and coworker.[1]

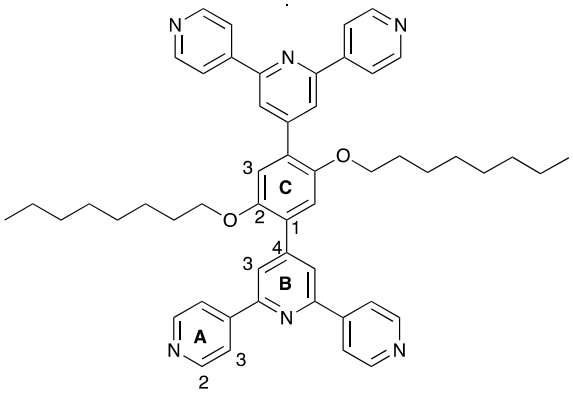
4,4''-Di((4,2':6',4''-terpyridin)-4'-yl)-1,1':4',1''-terphenyl



4-Acetylpyridine (1.24 g, 10.2 mmol) was added to a solution of [1,1':4',1''-

terphenyl]-4,4''-dicarbaldehyde (0.716 g, 2.50 mmol) in EtOH (250 mL). KOH pellets (0.56 g, 10 mmol) were added in one portion, followed by aqueous NH_3 (25%, 13 mL). The reaction mixture was stirred at room temperature for 20 h, during which time a precipitate formed. The product was collected by filtration, washed well with H_2O and EtOH, and dried in vacuo over P_2O_5. 4,4''-Di((4,2':6',4''-terpyridin)-4'-yl)-1,1':4',1''-terphenyl was isolated as a pale yellow solid (0.50 g, 0.72 mmol, 29%). Decomp. > 320 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm 8.82 (m, 8H, H^{A2}), 8.12 (s overlapping m, 12H, H^{A3+B3}), 7.89 (m, 8H, H^{C2+C3}), 7.83 (s, 4H, H^{D2}); ^{13}C NMR (126 MHz, $CDCl_3$) 155.4 (C^{B2}), 150.6 (C^{A2}), 146.1 (C^{A4}), 141.8 ($C^{C1/D1}$), 139.5 ($C^{C1/D1}$), 136.9 (C^{B4+C4}), 127.8 (C^{C2+C3}), 127.7 (C^{D2}), 121.3 (C^{A3}), 118.6 (C^{B3}). IR (solid / ν / cm^{-1}) 3974 (w), 3920 (w), 3027 (w), 2919 (w), 2849 (w), 1695 (w), 1592 (m), 1557 (w), 1533 (w), 1490 (w), 1432 (w), 1393 (w), 1386 (w), 1256 (w), 1217 (w), 1125 (w), 1064 (w), 1004 (w), 996 (w), 833 (w), 811 (s), 739 (w), 668 (w), 647 (m), 646 (m), 624 (m), 621 (m), 615 (w), 581 (m), 575 (m), 570 (m), 566 (m), 541 (s), 537 (s), 529 (m), 512 (s), 510 (m). ESI MS *m/z* 693.7 $[M + H]^+$ (base peak, calc. 693.28).

Synthesis of 1



4-Acetylpyridine (1.27 g, 10.2 mmol) was added to a solution of 2,5-bis(octyloxy)benzene-1,4-dicarbaldehyde (1.00 g, 2.56 mmol) in EtOH (15 cm^3). KOH pellets (0.575 g, 10.2 mmol) were added in one portion, followed by aqueous NH_3 (25%, 15 cm^3). The reaction mixture was stirred at room temperature for 20 h, during which time a precipitate formed. This solid was collected by filtration,

washed well with H_2O and EtOH, and dried in vacuo over P_2O_5. Compound 2 was recrystallized from EtOH/$CHCl_3$ and was isolated as bright yellow crystals (including single) (0.62 g, 30%). M.pt. = 255 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm 8.81 (m, 8H, H^{A2}), 8.11 (s, 4H, H^{B3}), 8.09 (m, 8H, H^{A3}), 7.16 (m, 2H, H^{C3}), 4.06 (t, *J* = 6.2 Hz, 4H, H^{OCH_2}), 1.74 (m, 4H, $H^{OCH_2CH_2}$), 1.37 (m, 4H, $H^{OCH_2CH_2CH_2}$), 1.28-1.06 (overlapping m, 16H, H^{CH_2}), 0.80 (t, *J* = 7.0 Hz, 6H, H^{CH_3}). ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm: 154.8 (C^{B2}), 150.7 (C^{A2}), 148.3 (C^{C2}), 146.3 (C^{B4}), 129.3 (C^{C1}), 121.6 (C^{B3}), 121.3 (C^{A3}), 115.3 (C^{C3}), 69.9 (C^{OCH_2}), 31.9 (C^{CH_2}), 29.6 ($C^{OCH_2CH_2}$), 29.5 (C^{CH_2}), 29.3 (C^{CH_2}), 26.5 ($C^{OCH_2CH_2CH_2}$), 22.7 (C^{CH_2}), 14.2 (C^{CH_3}). IR (solid, *ν*, cm^{-1}) 2920 (m), 2853 (m), 1591 (s), 1557 (m), 1538 (w), 1510 (m), 1469 (m), 1425 (m), 1412 (m), 1387 (m), 1209 (m), 1062 (m), 1053 (m), 1022 (m), 992 (m), 967 (m), 861 (m), 838 (m), 825 (s), 737 (m), 705 (m), 652 (s), 648 (m), 627 (s), 610 (m), 508 (s). ESI MS *m/z* 797.9 $[M + H]^+$ (base peak, calc. 797.5). UV-Vis λ / nm (ε / $dm^3\ mol^{-1}\ cm^{-1}$) (CH_2Cl_2, 2.5×10^{-5} mol dm^{-3}): 234 (52000), 259 (50500), 349 (11500). Found C 72.37, H 6.66, N 9.58; $C_{52}H_{56}N_6O_2 \cdot {}^1/_2CHCl_3 \cdot {}^1/_2H_2O$ requires C 72.84, H 6.69, N 9.71%.

[Zn_2Cl_4(1)]

A solution of **1** (19.9 mg, 0.025 mmol) in $CHCl_3$ (6.0 mL) was placed in a long test tube, and MeOH (3.0 mL) was layered on top, followed by a solution of $ZnCl_2$ (6.8 mg, 0.05 mmol) in MeOH (5.0 mL). The tube was sealed with parafilm and after a month at room temperature, yellow crystals had formed. Yield (11.3 mg, 0.011 mmol, 42.3%). Found C 57.77, H 5.64, N 7.21; $C_{52}H_{56}Cl_4N_6O_2Zn_2$ requires C 58.39, H 5.28, N 7.86.

Crystallography

General

Data were collected on a Bruker-Nonius Kappa APEX diffractometer; data reduction, solution and refinement used APEX2[2] and SHELX13.[3] The ORTEP plot was produced with Mercury v. 3.3[4,5] which was also used for structure analysis.

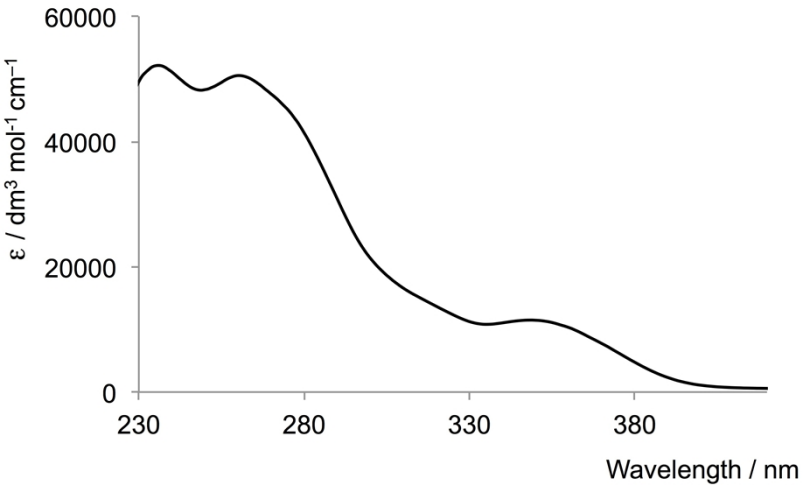


Fig. S1. Absorption spectrum of a CH_2Cl_2 solution of **1** (2.5×10^{-5} mol dm^{-3}).

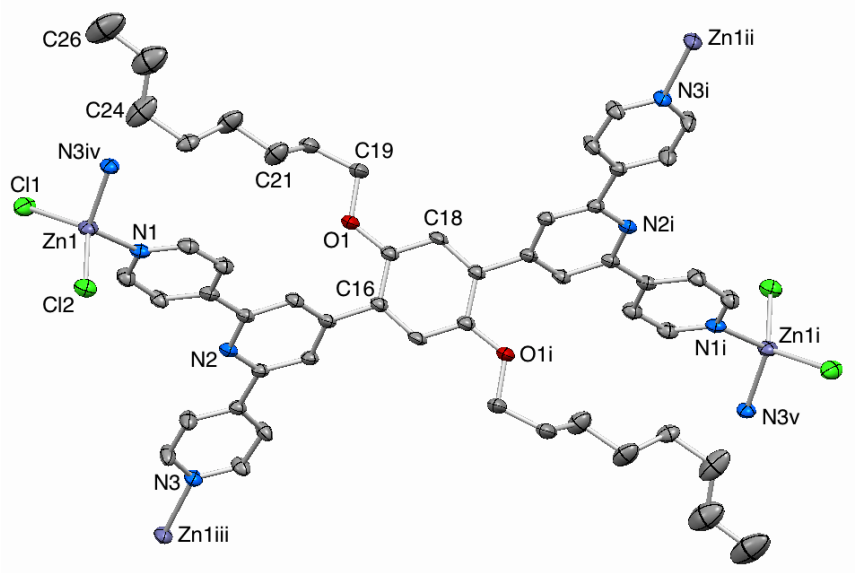


Fig. S2. ORTEP diagram of the 4-connecting node in $\{[Zn_2Cl_4(\mathbf{1})]\cdot 4H_2O\}_n$ with ellipsoids plotted at 50% probability level; H atoms are omitted for clarity. Symmetry codes: i = 1–*x*, 2–*y*, 1–*z*; ii = 1–*x*, 1+*y*, $^1/_2$–*z*; iii = *x*, 1–*y*, $^1/_2$+*z*; iv = *x*, 1–*y*, –$^1/_2$+*z*; v = 1–*x*, 1+*y*, $^3/_2$–*z*. Selected bond parameters: Zn1–N1 = 2.037(3), Zn1–N3^{iv} = 2.036(3), Zn1–Cl1 = 2.2182(12), Zn1–Cl2 = 2.2315(11)Å; N3^{iv}–Zn1–N1 = 111.69(13), N3^{iv}–Zn1–Cl1 = 106.61(10), N1–Zn1–Cl1 = 104.28(10), N3^{iv}–Zn1–Cl2 = 106.27(10), N1–Zn1–Cl2 = 104.15(9), Cl1–Zn1–Cl2 = 123.77(5)°.

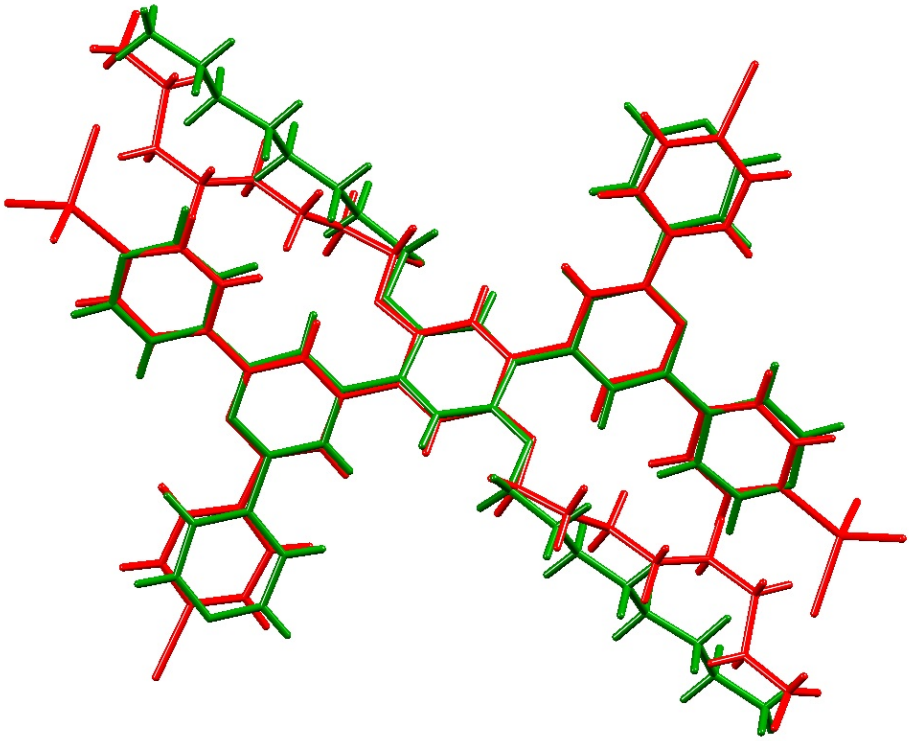


Fig. S3. Comparison of the conformations of **1** in the free ligand (green) and in $\{[Zn_2Cl_4(\mathbf{1})]\cdot 4H_2O\}_n$ (red) by structure overlay.

1 P. K. Mandali and D. K. Chand, *Catal. Commun.*, 2013, **31**, 16.

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

3 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.

4 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.

5 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.