

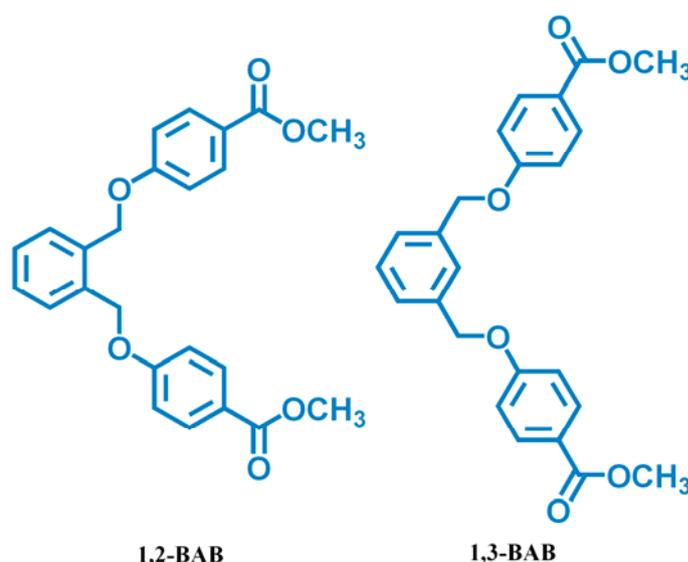
Trapping In Situ Scission Products of C–O Ester Bonds by Unique Coordination Supramolecular Architectures

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Reagents were purchased commercially and were used without further purification excepted acetone. Elemental analyses of C, H, and N were performed on an EA1110 CHNS-0 CE elemental analyzer. IR (KBr pellet) spectra were recorded on a Nicolet Magna 750FT-IR spectrometer. ¹H NMR spectra were recorded on a AMX-400 (400 MHz) supported by an Aspect 3000 data system. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CHCl₃: δ 7.27 ppm). Data are reported as follows: chemical shift; multiplicity (s = singlet, d = doublet, t = triplet, q = quaternity, m = multiplet). X-ray intensities of complexes **1**, **2**, **3** and **4** were collected on a Saturn 70 CCD diffractometer equipped with graphite monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 113.15 or 293(2) K. Empirical absorption corrections were applied to the data using the SADABS program.¹ The structures were solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXTL-97 program.² All of the non-hydrogen atoms were refined anisotropically. Crystallographic data and other pertinent information for **1**, **2**, **3** and **4** are summarized in CIFs.

Syntheses of 1,2-BAB and 1,3-BAB.



Scheme S1

A mixture of methyl 4-hydroxybenzoate (6.09 g 40mmol), o-xylylene dibromide or m-xylylene dibromide (5.28 g 20mmol), 18-crown-6 (0.13g 0.5mmol) and K_2CO_3 (6.08 g 44mmol) in 100 mL of acetone was refluxed for 20 hours. The mixture was allowed to cool to room temperature and 60 mL CH_2Cl_2 was added. Then the resulting mixture was stirred for 30 minutes and filtered. The solvents of the filtrate were removed under reduced pressure, and the residue was dissolved in 200 mL of CH_3OH at $70^\circ C$, and 100 mL of H_2O was added, then cooled to room temperature. The precipitate was collected, washed with CH_3OH/H_2O (2:1) and dried at $80^\circ C$ for 10 hours to give 7.56 g (93%) of **1,2-BAB** or 7.64 g (94%) of **1,3-BAB** as white solids.

Analytical found for organic compound **1,2-BAB**: C, 70.32; H, 5.64. Calculate: C, 70.92; H, 5.46. 1H NMR ($CDCl_3$): δ 3.884 (6H, s), 5.221 (4H, s), 6.969 (4H, d), 7.400 (2H, m), 7.513 (2H, m), 7.981 (4H, d). IR (KBr, cm^{-1}): 3078 (w), 3007 (w), 2949 (w), 2928 (w), 2875 (w), 2839 (w), 2081 (w), 1906 (w), 1718 (vs), 1606 (vs), 1510 (s), 1434(s), 1383(m), 1317 (m), 1281 (m), 1244(m), 1168(s), 1111 (s), 1044(vs), 1003 (m), 848 (s), 769 (s), 696

(m).

Analytical found for organic compound **1,3-BAB**: C, 70.28; H, 6.71. Calculate: C, 70.92; H, 5.46. ^1H NMR (CDCl_3): δ 3.855 (6H, s), 5.105 (4H, s), 6.956 (4H, d), 7.382 (3H, s), 7.474 (1H, s), 7.968 (4H, d). IR (KBr, cm^{-1}): 3077 (w), 3014 (w), 2958 (m), 2921 (w), 2893 (w), 1925 (w), 1722 (vs), 1606 (vs), 1508 (vs), 1433 (vs), 1363 (s), 1288 (s), 1250 (s), 1171 (s), 1111 (s), 1059 (m), 1013 (m), 954 (m), 850 (s), 768 (s), 698 (m).

Synthesis of complex $[\text{Zn}_4(1,2\text{-BAB})_4(\text{Phen})_4](\text{G-I})_2(\text{H}_2\text{O})$ (1). A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.089 g 0.30 mmol), 1,2-BAB (0.061 g 0.15 mmol), $\text{Phen} \cdot \text{H}_2\text{O}$ (0.042 g 0.21mmol) and H_2O 15 mL was placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated to 160°C for 60 h. Then the reactant mixture was cooled at a rate of $0.5^\circ\text{C}/\text{min}$ to lead to the formation of crystal **1**. Analytical found for complex **1**: C, 66.07; H, 3.99; N, 3.59. Calculate: C, 65.97; H, 4.20; N, 3.71. IR (KBr, cm^{-1}): 3425 (s), 3067 (w), 2935 (w), 2887 (w), 1686 (m), 1605 (vs), 1549 (m), 1512 (s), 1421(m), 1390 (vs), 1299 (m), 1241 (s), 1172 (m), 1103(m), 1008(s), 848 (m), 785 (s), 725 (m).

Synthesis of complex $[\text{Cd}_2(1,2\text{-BAB})_2(\text{Phen})_2](\text{G-II})_2(\text{H}_2\text{O})$ (2). A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.113 g 0.37 mmol), 1,2-BAB (0.084 g 0.21mol), $\text{Phen} \cdot \text{H}_2\text{O}$ (0.041 g 0.2mmol) and H_2O 15 mL was placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated to 170°C for 60 h. Then the reactant mixture was cooled at a rate of $0.5^\circ\text{C}/\text{min}$ to lead to the formation of crystal **2**. Analytical found for complex **2**: C, 61.79; H, 3.61; N, 3.62. Calculate: C, 61.16; H, 3.66; N, 3.57. IR (KBr, cm^{-1}): 3172 (w), 3063 (w), 3017 (w), 2952 (w), 2918 (w), 2870 (w), 1703 (w), 1603 (vs), 1592 (vs), 1541(vs), 1474 (m), 1341 (m), 1244 (vs), 1228 (s), 1172(vs), 1140(vs), 851 (m), 787(m),

728 (m), 699 (m).

Synthesis of complex [Zn(1,3-BAB)(Phen)]·(G-III) (3). A mixture of ZnSO₄·7H₂O (0.103 g 0.36 mmol), 1,3-BAB (0.066 g 0.16 mmol), Phen·H₂O (0.042 g 0.2mmol) and H₂O 15 mL was placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated to 170°C for 60 h. Then the reactant mixture was cooled at a rate of 0.5 °C/min to lead to the formation of crystal **3**. Analytical found for complex **3**: C, 64.38; H, 3.89; N, 3.73. Calculate: C, 64.79; H, 3.98; N, 3.69. IR (KBr, cm⁻¹): 3405 (w), 3063 (w), 2926 (w), 2875 (w), 1689 (m), 1605 (vs), 1592 (m), 1535 (m), 1513 (m), 1421 (s), 1396 (vs), 1299 (s), 1246 (vs), 1170 (m), 1104 (m), 1010 (m), 867 (m), 847 (m), 786 (m), 726(m), 662(m).

Synthesis of complex [Zn₄(1,2-BAB)₄(Phen)₄]·(G-I)₂(H₂O) (4). A mixture of Zn(NO₃)₂·6H₂O (0.012 g 0.40 mmol), 1,2-BAB (0.061 g 0.15 mmol), Phen·H₂O (0.042 g 0.21mmol) and H₂O 13 mL was placed in a Parr Teflon-lined stainless steel vessel (23 mL). The vessel was sealed and heated to 170°C for 60 h. Then the reactant mixture was cooled at a rate of 0.5 °C/min to lead to the formation of crystal **4**.

References

- (1) G. M. Sheldrick, SADABS; University of Göttingen: Göttingen, Germany, 1996.
- (2) SHELXTL (version 5.05); Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

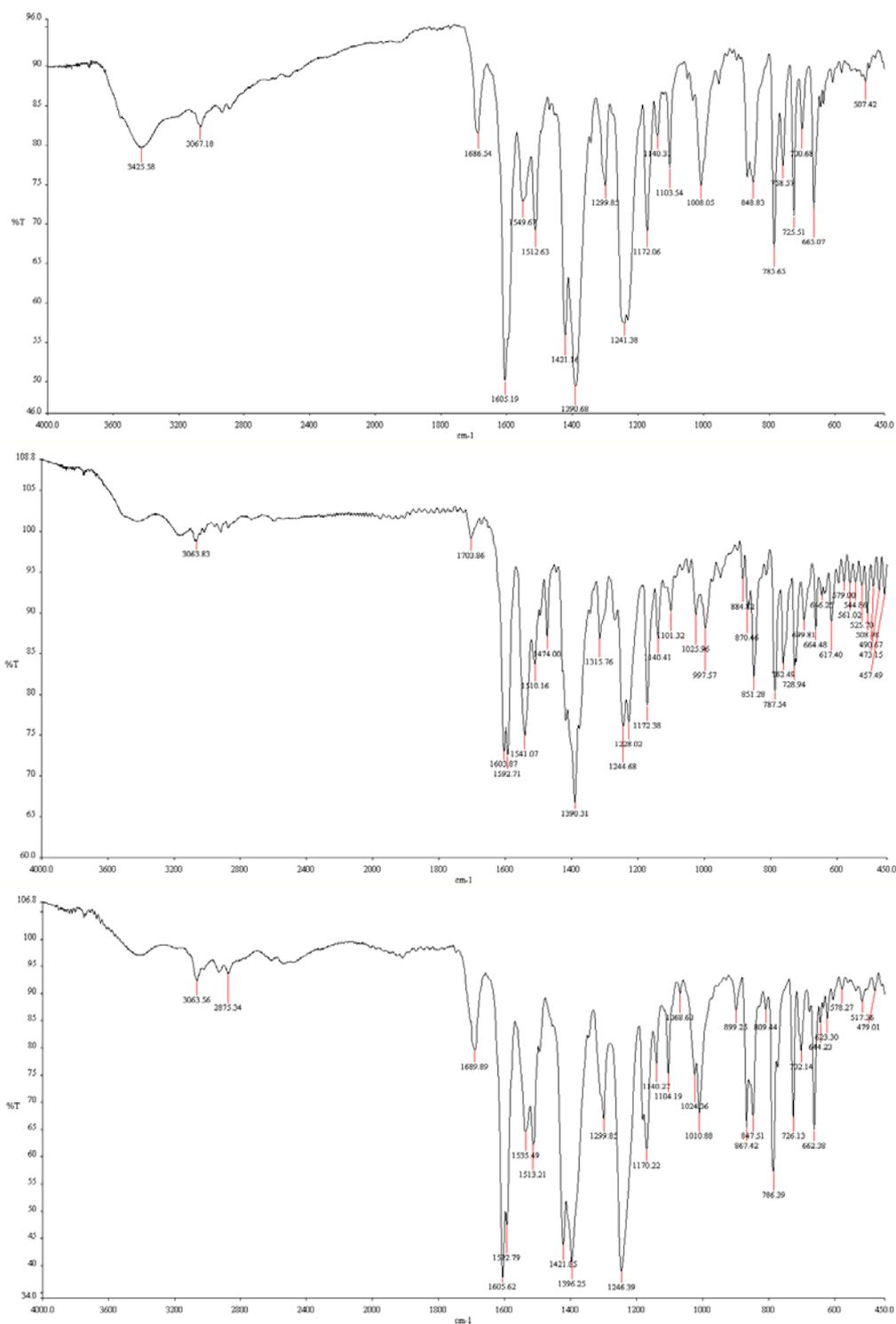


Fig. S1 IR spectrum for complexes **1** (upper), **2** (middle) and **3** (down).

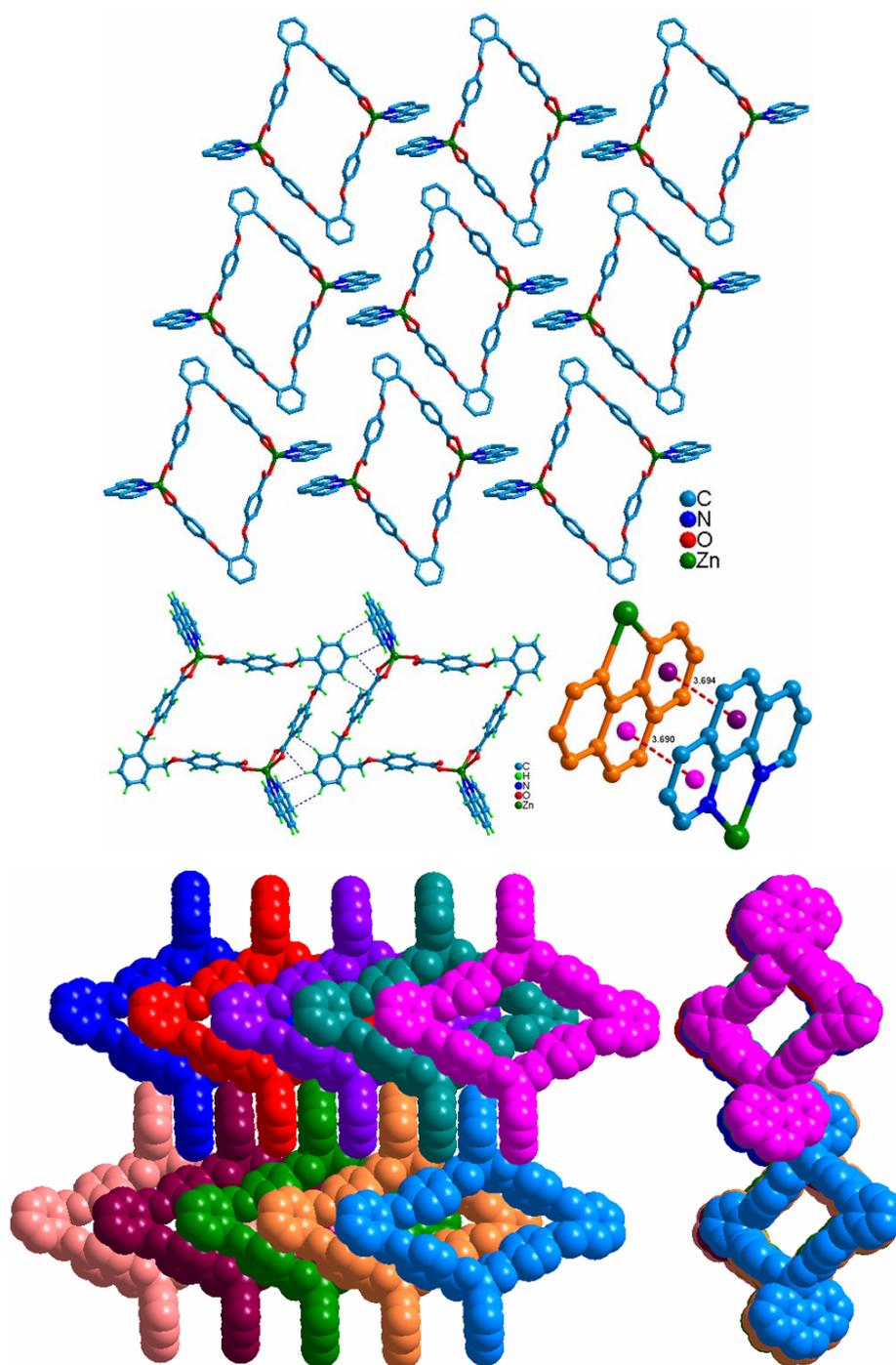


Fig. S2 View of the 2D structure in **1** showing the aromatic π - π and C-H... π interactions between the [Zn₂(1,2-BAB)₂(Phen)₂] nanoscale metallacycles (up); Two views of the 2D structure in **1** showing the aromatic face-to-face π - π interactions between the phen groups of the nanoscale metallacycles (down).

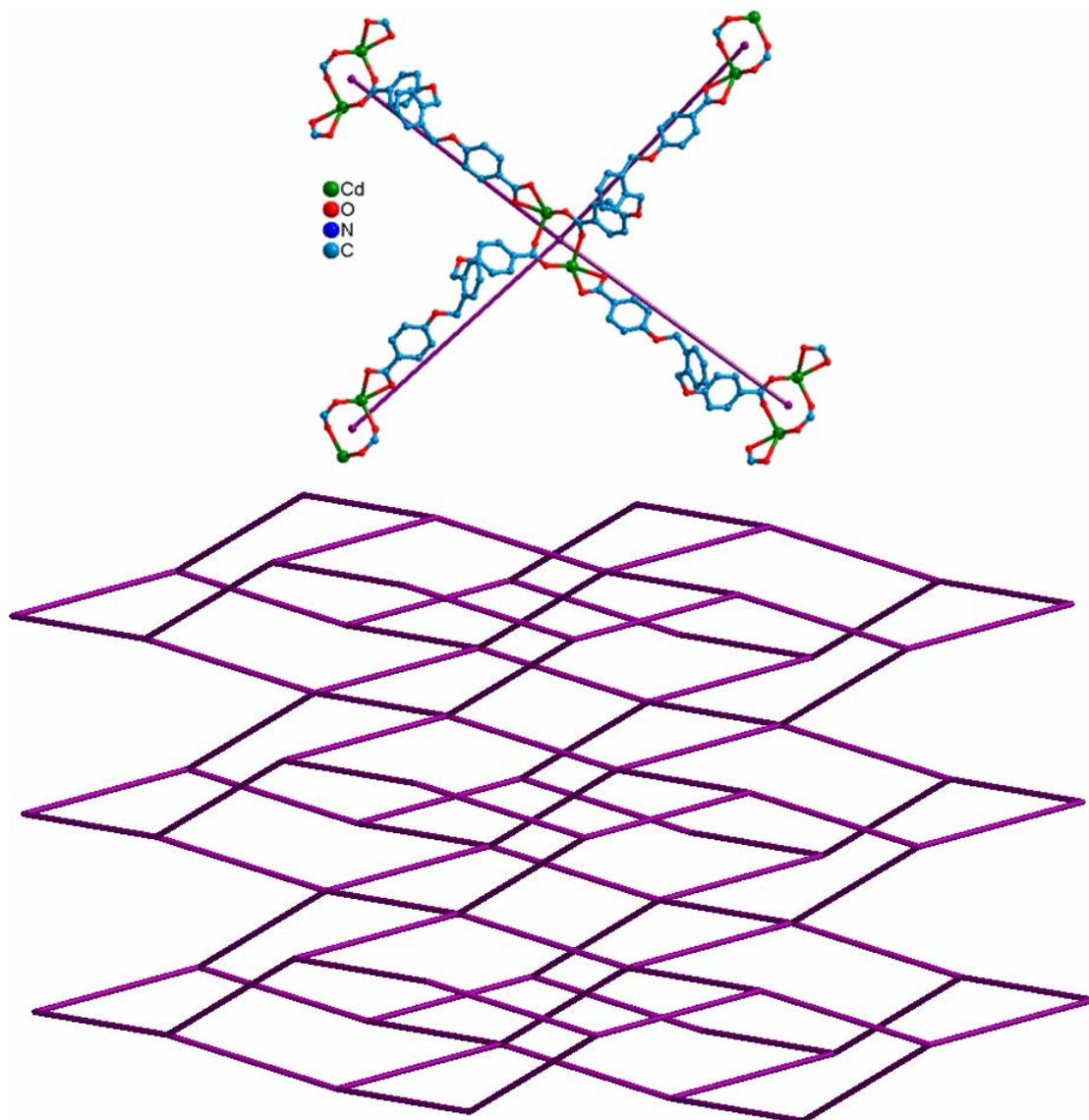


Fig. S3 View of the SBU as a four-connected node and the schematic representation of the diamondoid topology of **2**.

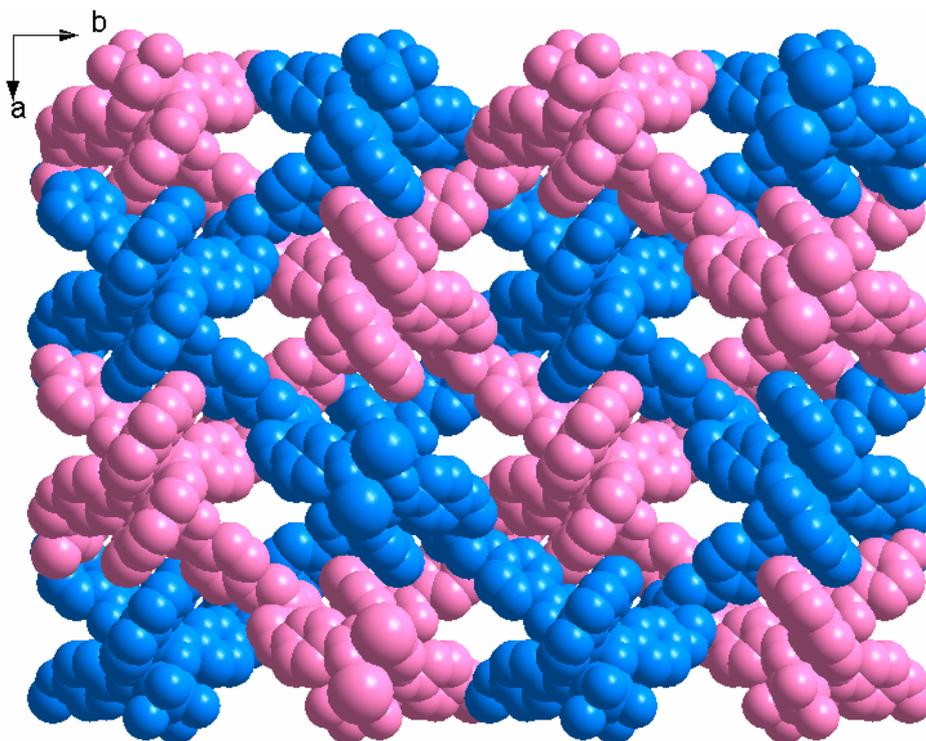


Fig. S4 Space-filling plot of the two-fold interpenetrating framework in **2** with 1D channels along the c axis. Template *o*-xylene molecules are omitted.

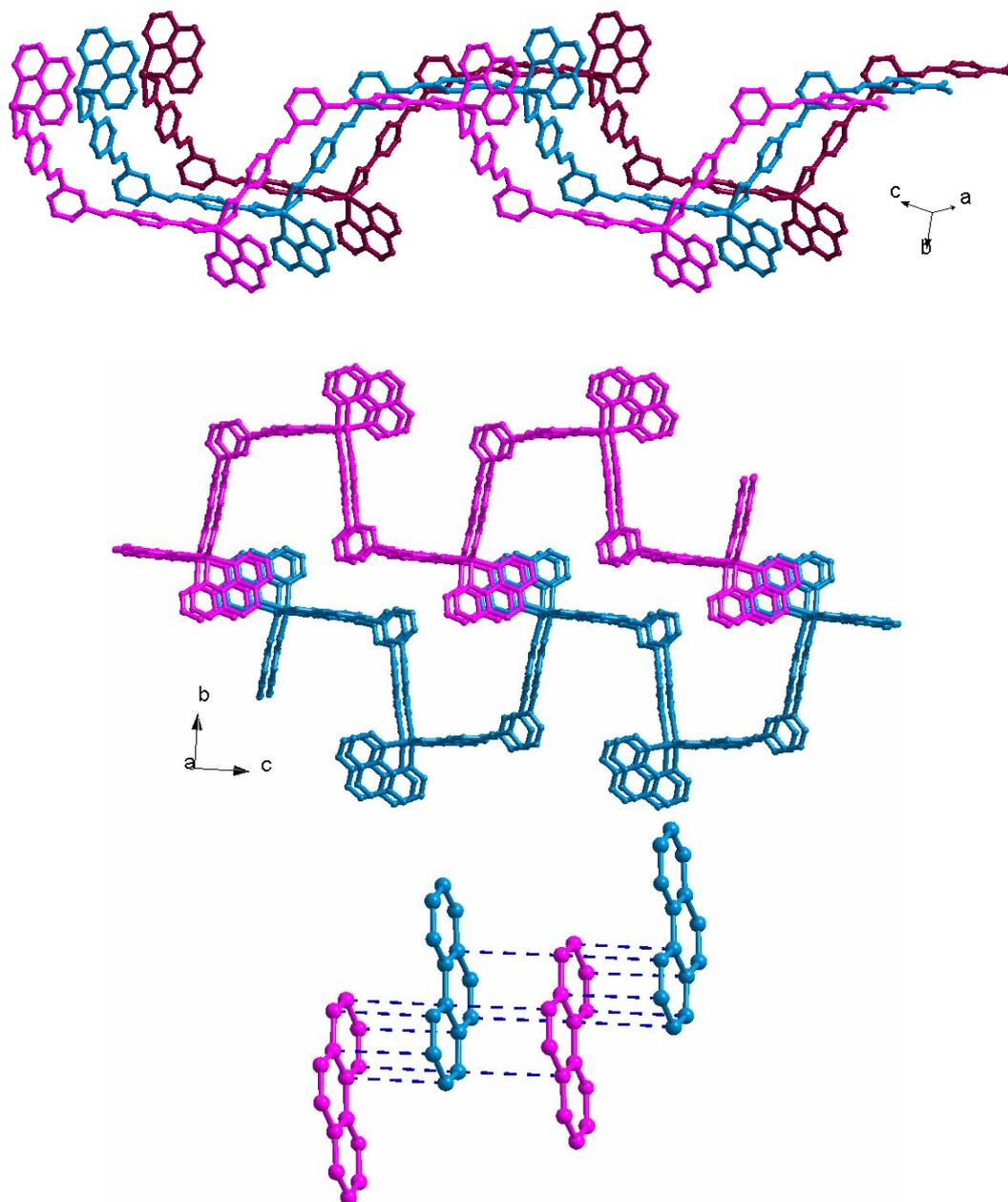


Fig. S5 A view of the 2D waved structure in **3** (up); A view of the 3D structure in **3**, showing π - π stacking interactions the phen groups (down).

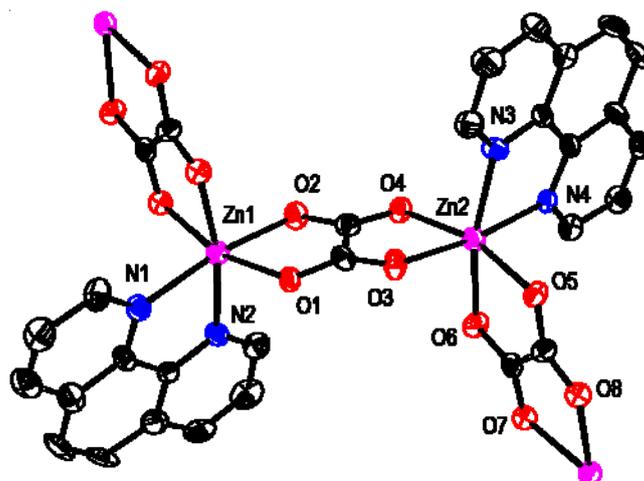


Fig. S6 The asymmetric unit structure of **4**, showing the atom-numbering scheme. The displacement ellipsoids are plotted at the 20% probability level. H atoms have been omitted for clarity.

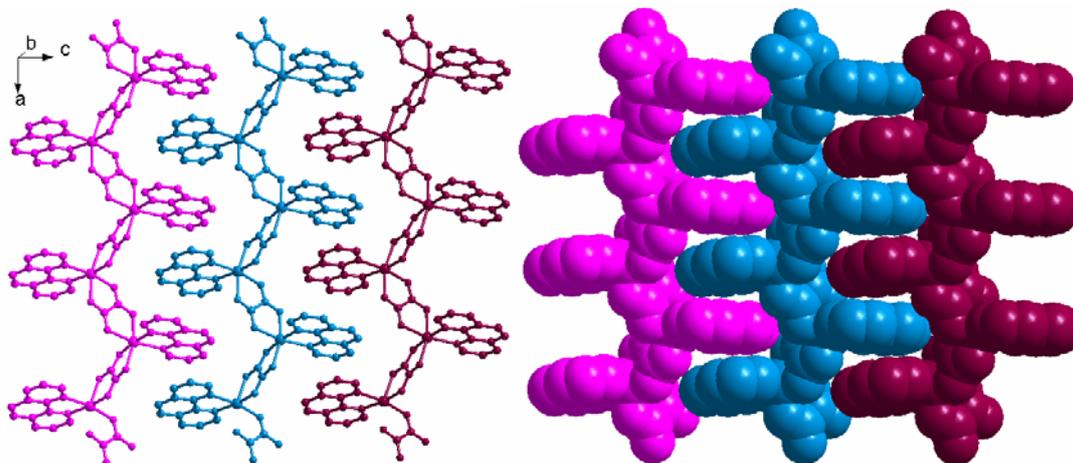


Fig. S7 Two views of the 2D structure in **4** showing the aromatic face-to-face π - π interactions between the phen groups of the different chains.