Electronic Supplementary Information

An unprecedented 2D→3D metal-organic polyrotaxane framework constructed from cadmium and flexible star-like ligand

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Materials. All reagents and solvents for syntheses were purchased from commercial sources and used as received.

General Characterization and Physical Measurements. The C, H, and N elemental analysis was conducted on a Perkin-Elmer 240C elemental analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from 50 to 800 °C under nitrogen. The powder X-ray diffraction (PXRD) data was collected on a Rigaku RINT2000 diffractometer at room temperature with Cu Kα radiation in a flat plate geometry. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. The photoluminescent properties of the Tipa and compound **1** were measured on a Perkin-Elmer LS55 spectrometer.

Experimental data for tri(4-imidazolylphenyl)amine: tris-(4-iodophenyl)amine was synthesized by procedures reported earlier.[1] A mixture of tris-(4-iodophenyl)amine (3.12 g, 5 mmol)], imidazole (1.02 g, 15 mmol), potassium carbonate (5.52 g, 40 mmol) and CuO (0.16 g, 2 mmol) were heated while stirring in 20 mL of DMSO at 150 ºC for 48h. The resulting slurry was cooled to room temperature, and solids were removed by filtration. DMSO of the filtrate was removed by distillation under reduced pressure. Methylene chloride was added to the remaining filtrate, and the mixture was then washed with water and dried over sodium sulfate. The methylene choride was then removed. The tri(4-imidazolylphenyl)amine was crystallized in methanol and water, and pale yellow solid was obtained.

Experimental data for compound 1: A mixture of $CdCl_2{\cdot}2.5H_2O$ (0.068 g, 0.3 mmol), Tipa (0.044 g, 0.1 mmol), CH_3OH (8 mL) and water (2 mL) was placed in a 23-ml Teflon reactor and kept under autogenous pressure at 150 ºC for three days. Then the mixture was cooled to room temperature, and pink crystals of 1 were obtained in 54% yield based Cd(II). $C_{27}H_{23.14}O_{1.07}N_7CdCl_2$: Calc.: C 50.19, H 3.61, N 15.18. Found: C 50.28, H 3.50, N 15.29. FTIR (KBr pellet, cm^{-1}): 3425 (m), 3120 (m), 2951 (m), 1546 (s), 1515 (s), 1419 (m), 1342 (m), 1214 (w), 1061 (w), 873 (w), 769 (m), 657 (w), 528 (w).

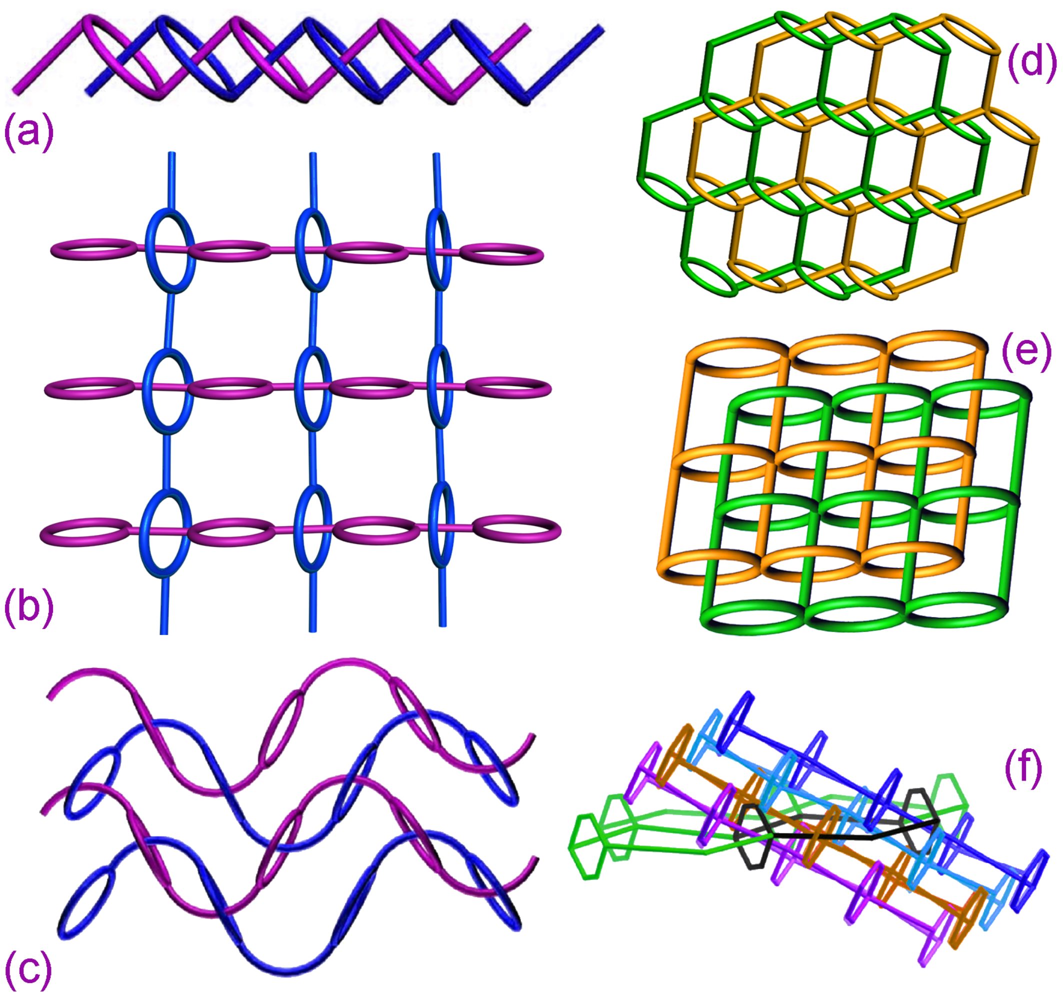
Crystal data for 1 ($C_{27}H_{23.14}O_{1.07}N_7CdCl_2$): monoclinic, space group $P2_1/n$, Mr = 646.09, a = 12.2544(3), b = 14.7363(3), c = 15.4417(4) Å, β = 107.644(3)º, V = 2657.35(11) Å^3, Z = 4, μ = 1.059 mm^{-1}, D_c = 1.615 Mgm^{-3}, F(000) = 1299, T = 293(2) K, 11828 reflections collected, 6110 unique with R_{int} = 0.0187, $R1$ = 0.0310, $wR2$ = 0.0808 ($I>2\sigma(I)$) and GOF = 1.012.

Single-crystal X-ray diffraction data for complex 1 was recorded at a temperature of 293(2) K on a Oxford Diffraction Gemini R Ultra diffractometer, using a ω scan technique with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by Direct Method of SHELXS-97[2] and refined by full-matrix least-squares techniques using the SHELXL-97 program[3] Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of the ligands were refined as rigid groups. The hydrogen atoms associated with the water molecules were not located from the difference Fourier maps.

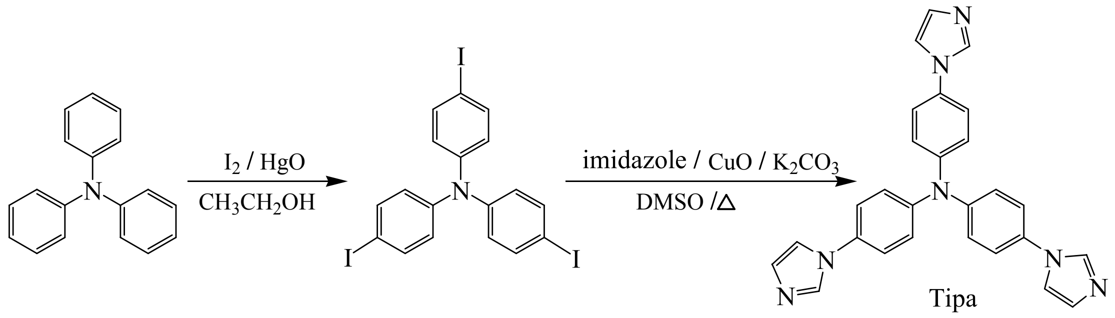
1 (*a*) O. P. Varnavski, J. C. Ostrowski, L. Sukhomlinova, R. J. Twieg, G. C. Bazan and T. Goodson, *J. Am. Chem. Soc.*, 2002, 124, 1736; (*b*) S. P. McIlroy, E. Cló, L. Nikolajsen, P. K. Frederiksen, C. B. Nielsen, K. V. Mikkelsen, K. V. Gothelf and P. R. Ogilby, *J. Org. Chem.*, 2005, 70, 1134.

2 G. M. Sheldrick, *SHELXS-97*, *Program for Solution of Crystal Structures, University of Göttingen*, Germany, 1997.

3 G. M. Sheldrick, *SHELXL-97, Program for Refinement of Crystal Structures*, *University of Göttingen*, Germany, 1997.



Scheme S1. Schematic representations of the known (a) 1D → 1D, (b) inclined 1D → 2D, (c) parallel 1D → 2D, (d) and (e) parallel 2D → 2D, and (f) inclined 2D → 3D polyrotaxane networks.



Scheme S2. Synthesis of the ligand Tipa.

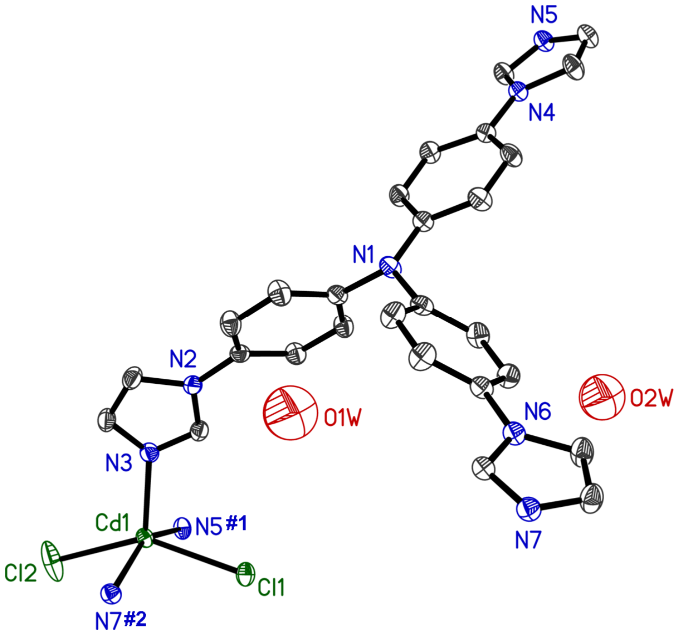


Fig. S1. The ORTEP figure of **1** (Displacement ellipsoids drawn at the 30% probability level). [Symmetry codes: #1 -x+2, y+1/2, -z+3/2; #2 -x+1, -y+2, -z+2.]

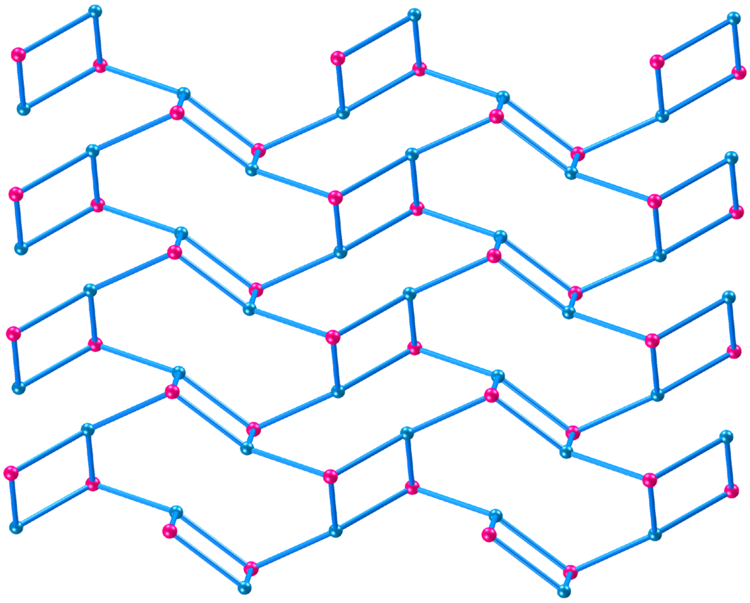


Fig. S2. The $4 \cdot 8^2$ topology of the sheet in **1**.

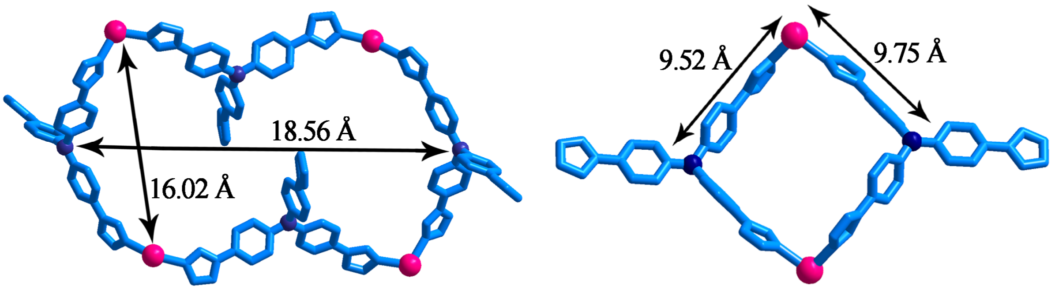


Fig. S3. Two kinds of windows within one layer.

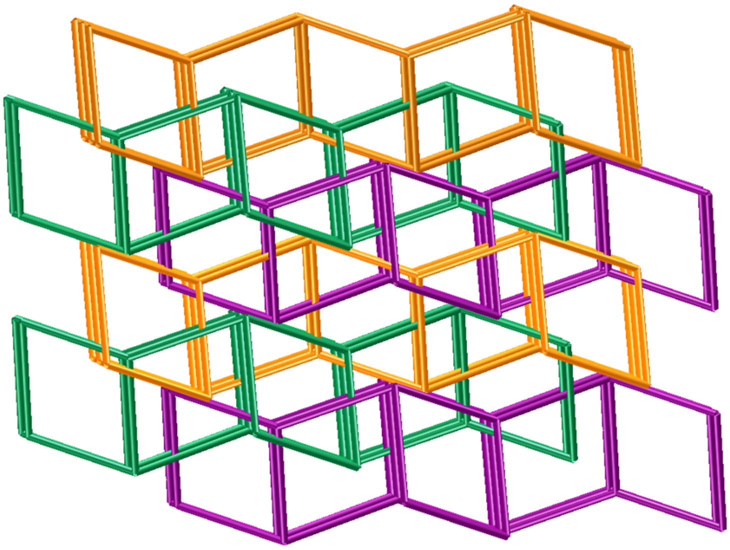


Fig. S4. Schematic view of the ABC packing of the sheets.

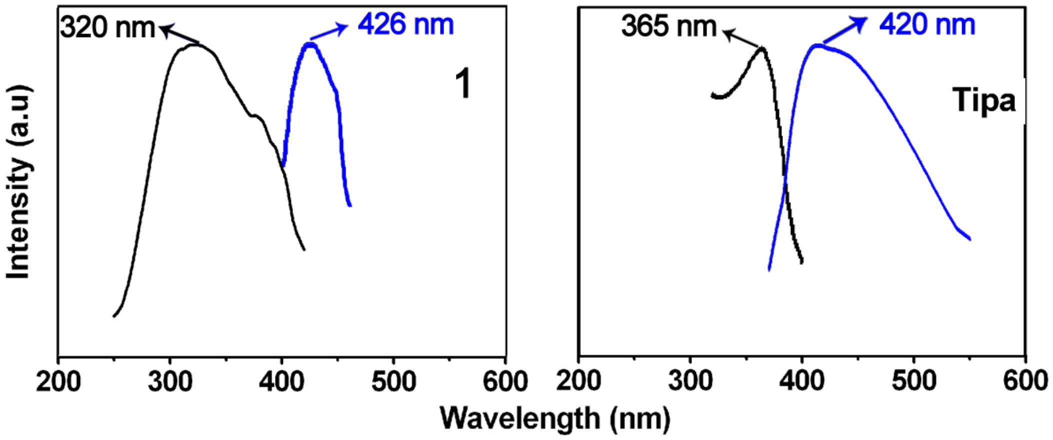


Fig. S5. Emission spectra of free tri(4-imidazolylphenyl)amine and **1** at room temperature.

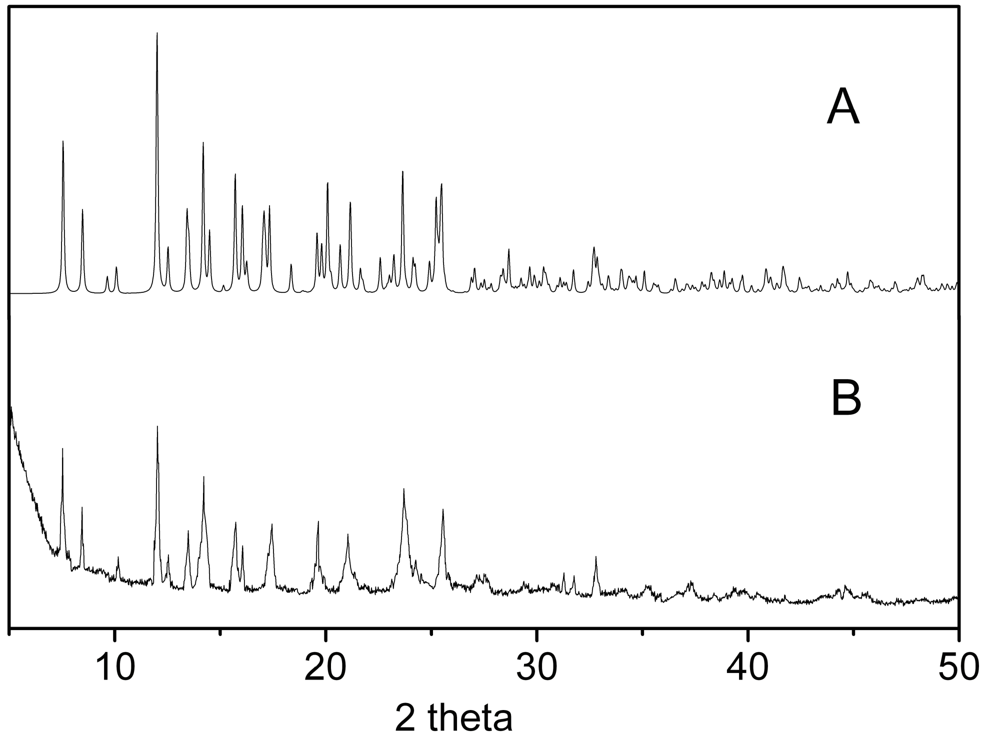


Fig. S6. Simulated (A) and measured (B) PXRD patterns of **1**.

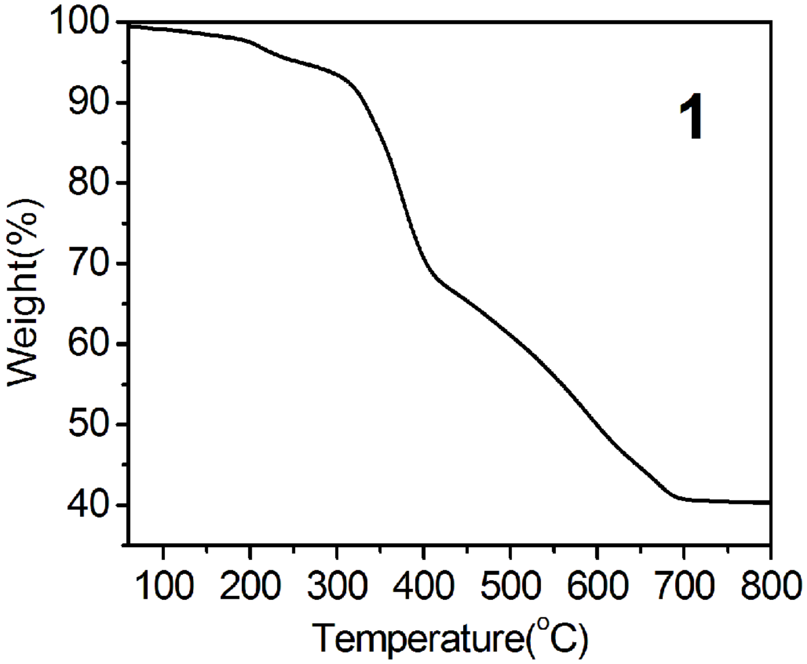


Fig. S7. The TGA curve of compound **1**.

To estimate the stability of compound **1**, the thermogravimetric analysis (TGA) was carried out in flowing N_2 atmosphere with a heating rate of 10 °C/min^{-1} in the temperature range 50-800 °C. From the TGA curve of **1**, the first weight loss occurs from 55 to 220 °C, corresponding to the loss of the water molecules. The removal of the organic components occurs in the temperature range of 220–695 °C, indicating the collapse of the polyrotaxane framework.