Supplementary Material (ESI) for Chemical Communications
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Reversible shrinkage and expansion of a blue photofluorescene cadmium coordination polymer and *in situ* tetrazole ligand synthesis

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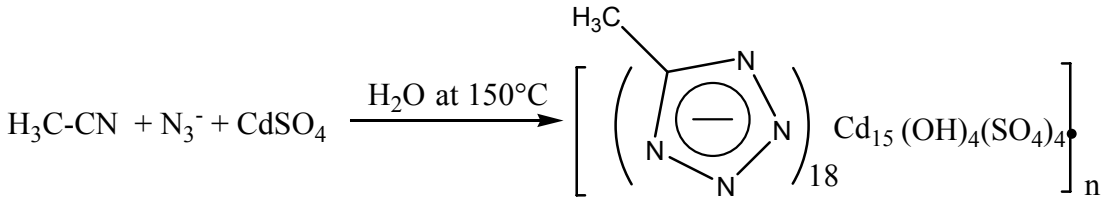
Experimental Section

Material and measurements.

All materials and reagents were obtained commercially and used without further purification. Elemental (C, H, N) analyses were performed on a Perkin–Elmer 2400 element analyzer. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400~4000cm-1 range using a Nicolet Avatar 360 FT-IR spectrophotometer. Powder XRD investigations were carried out on a Bruker AXS D8-Advanced diffractometer at 40 kV, 40 mA with Cu Kα (λ =1.5406 Å) radiation. The Fluorescence spectra were recorded with an F900 FL Spectrophotometer analyzer (EDINBURGH INSTRUMENTS). Single crystal X-ray diffraction data collections of **1-4** were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo Kα radiation (λ = 0.71073 Å) at 293 K. Data collection and reduction were performed using Bruker SMART APEX II CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) operated at 2000 W power (50 kV, 30 mA). A multi-scan absorption correction was applied using the APEX II program. All four structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to

carbon were placed in geometrically idealized positions and refined using a riding model. Hydrogen atoms on water molecules were located from difference Fourier maps and were refined using a riding model.



Scheme 1 In Situ Hydrothermal Synthesis of **1**

Preparation of Compound **1**: A mixture of $CdSO_4 \times 8H_2O$ (0.352 g; 1 mmol), NaN3 (0.065 g; 1 mmol), CH_3CN (3 mL) and H_2O (3 mL) was sealed in a 15 mL Teflon-lined reactor, which was heated in an oven to 150 °C for 50 h, then cooled to room temperature at a rate of 5°C h^{-1}. Colourless cubic crystals were obtained in 35% yield, based on Cd. Elemental analysis (%) calcd for **1** ($C_{36}H_{75}Cd_{15}N_{72}O_{28.5}S_4$), C, 11.42; H, 2.00; N, 26.63; S, 3.39. Found: C, 11.50; H, 2.09, N, 26.56; S, 3.36. IR (KBr, cm^{-1}): 3462, 1643, 1579, 1487, 1436, 1373, 1263, 1182, 1166, 1058, 983, 694, 617, 457.

Preparation of Compound **2**: The single crystals were obtained from heating the single crystals of **1** at 200°C under vacuum for 3h. Elemental analysis (%) calcd for **2** ($C_{36}H_{62.63}Cd_{15}N_{72}O_{22.32}S_4$), C, 11.76; H, 1.72; N, 27.44, S, 3.49. Found: C, 11.69; H, 1.82, N, 27.36, S, 3.45. IR (KBr, cm^{-1}): 3456, 1642, 1576, 1487, 1436, 1372, 1263, 1185, 1164, 1055, 981, 693, 615, 457.

Preparation of Compound **3**: The single crystals were obtained from heating the single crystals of **3** at 300°C under vacuum for 3h. Elemental analysis (%) calcd for **3**

($C_{36}H_{58}Cd_{15}N_{72}O_{20}S_4$), C, 11.90; H, 1.61; N, 27.75, S, 3.53. Found: C, 11.92; H, 1.68, N, 27.69, S, 3.50. IR (KBr, cm^{-1}): 3472, 1640, 1575, 1486, 1438, 1375, 1263, 1180, 1165, 1055, 981, 693, 615, 457.

Preparation of Compound **4**: The single crystals of **3** were immersed in water one day to obtain compound **4**. Elemental analysis (%) calcd for **1** ($C_{36}H_{73.98}Cd_{15}N_{72}O_{27.99}S_4$), C, 11.45; H, 1.97; N, 26.70, S, 3.40. Found: C, 11.50; H, 1.99, N, 26.79, S, 3.44. IR (KBr, cm^{-1}): 3473, 1641, 1574, 1485, 1438, 1374, 1264, 1183, 1164, 1053, 982, 695, 615, 457.

Crystal data, data collection parameters, and refinement statistics for 1-4 are listed in Table S1. Comparison of the unit cell parameters of 1-4 are given Table S2. Complete CIFs of 1-4 are deposited with the CCDC as 674092 – 674095.

Table S1

Crystallographic data and structure refinement summary for complexes **1–4**

complex	**1**	**2**	**3**	**4**
Formula	$C_{36}H_{75}Cd_{15}N_{72}O_{28.5}S_4$	$C_{36}H_{62.63}Cd_{15}N_{72}O_{22.32}S_4$	$C_{36}H_{58}Cd_{15}N_{72}O_{20}S_4$	$C_{36}H_{73.08}Cd_{15}N_{72}O_{27.56}S_4$
Mr	3787.04	3675.57	3633.78	3777.73
Crystal system	cubic	cubic	cubic	cubic
Space group	*I-43d*	*I-43d*	*I-43d*	*I-43d*
a/Å	21.4983(1)	21.4035(1)	21.3359(2)	21.5140(1)
V /Å^3	9936.02(8)	9805.15(8)	9712.54(16)	9957.80(8)
Z	4	4	4	4
D_Cg/cm^3	2.532	2.490	2.485	2.520
μ/mm^{-1}	3.326	3.362	3.391	3.318
Parameters	147	136	127	146
Goodness-of-fit	1.214	1.096	1.066	0.977
$R1$ [$I > 2\sigma(I)$][a]	0.0144, 0.0144	0.0141, 0.0142	0.0146, 0.0150	0.0193, 0.0203
$wR2$ [b]	0.0366, 0.0366	0.0318, 0.0318	0.0328, 0.0329	0.0382, 0.0383

[a] $R_1=\sum||F_0|-|F_c||/\sum|F_0|$. [b] $wR_2=\{\sum[w(F_0^2-F_c^2)^2]/\sum(F_0^2)^2\}$

Table S2

	Compound 1	Compound 2	Compound 3	Compound 4 (regenerated 1)
a (Å)	21.4983(1)	21.4035(1)	21.3359(2)	21.5140(1)
V ($Å^3$)	9936.02(8)	9805.15(8)	9712.54(16)	9957.80
Δ	130.8	88.7	245.3	

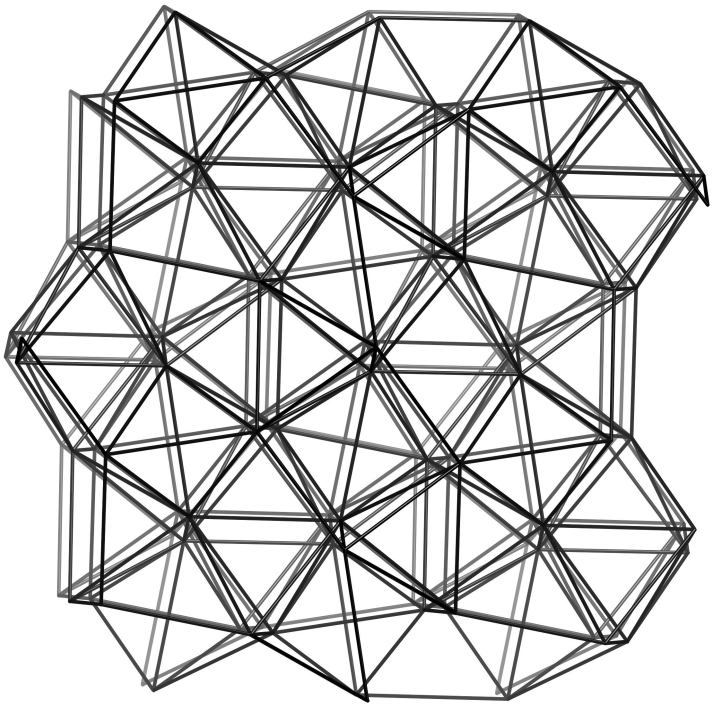


Fig. S1. Schematic representation of the nine-connected network.

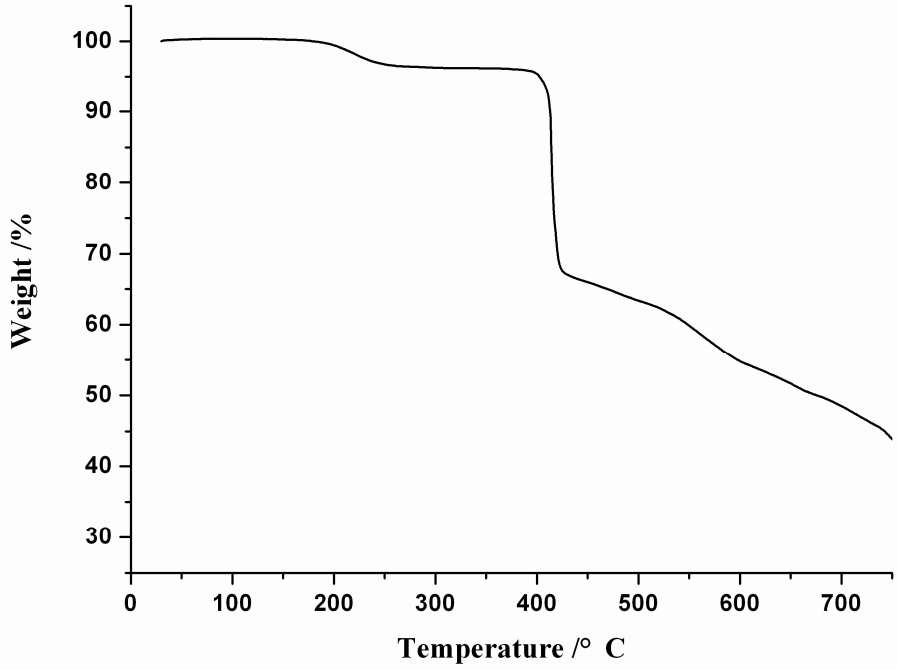


Fig. S2. The TGA plot of compound $[Cd_{15}(5MT)_{18}(OH)_4(SO_4)_4.8.5H_2O]$

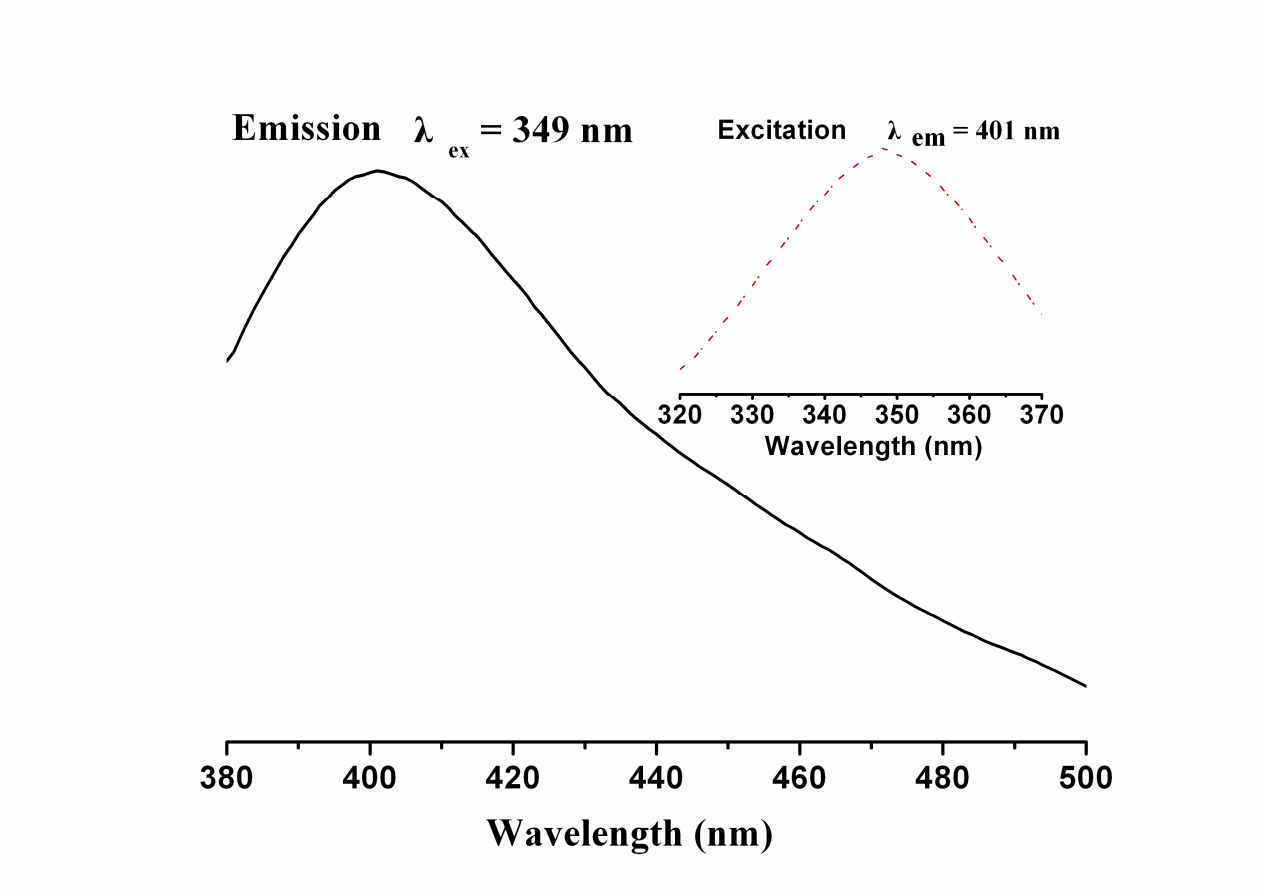


Fig. S3. Solid-state excitation and emission spectrum of **1** at room temperature.

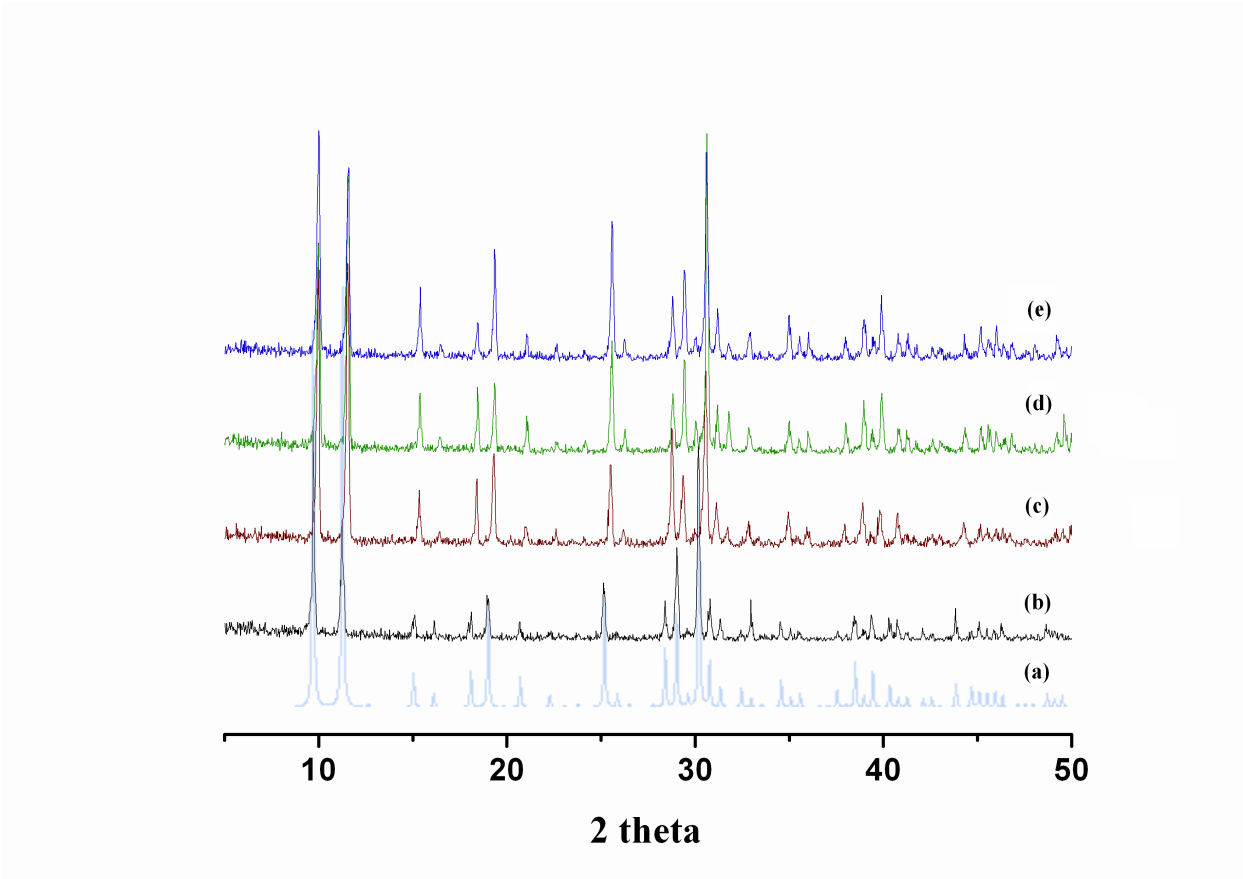


Fig. S4. XRD patterns: (a) simulated from single-crystal X-ray data; (b) as-synthesized compound $[Cd_{15}(5MT)_{18}(OH)_4(SO_4)_4.8.5H_2O]$**;** (c) compound $[Cd_{15}(5MT)_{18}(OH)_4(SO_4)_4.2.32H_2O]$; (d) compound $[Cd_{15}(5MT)_{18}(OH)_4(SO_4)_4]$; (e) restored compound $[Cd_{15}(5MT)_{18}(OH)_4(SO_4)_4.7.99H_2O]$ from compound $[Cd_{15}(5MT)_{18}(OH)_4(SO_4)_4]$

Powder X-ray diffraction results (Fig. 4S) indicate that the chemical composition of the power is $Cd_{15}(5\text{-}MT)_{18}(OH)_4(SO_4)_4$.