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 400–4000 cm⁻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 F² 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.

\[
\text{H}_3\text{C-CN} + \text{N}_3^- + \text{CdSO}_4 \rightarrow \text{H}_2\text{O} \text{ at } 150^\circ\text{C}
\]

\[
\begin{array}{c}
\text{Cd}_{15} (\text{OH})_4 (\text{SO}_4)_4 \n\end{array}
\]

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

Preparation of Compound 1: A mixture of CdSO\(_4\)×8H\(_2\)O (0.352 g; 1 mmol), NaN\(_3\) (0.065 g; 1 mmol), CH\(_3\)CN (3 mL) and H\(_2\)O (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
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\textsubscript{36}H\textsubscript{73.98}Cd\textsubscript{15}N\textsubscript{72}O\textsubscript{27.99}S\textsubscript{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\textsuperscript{-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 S2

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>V (Å³)</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 1</td>
<td>21.4983(1)</td>
<td>9936.02(8)</td>
<td>130.8</td>
</tr>
<tr>
<td>Compound 2</td>
<td>21.4035(1)</td>
<td>9850.15(8)</td>
<td>88.7</td>
</tr>
<tr>
<td>Compound 3</td>
<td>21.3359(2)</td>
<td>9712.54(16)</td>
<td>245.3</td>
</tr>
<tr>
<td>Compound 4 (regenerated 1)</td>
<td>21.5140(1)</td>
<td>9957.80</td>
<td></td>
</tr>
</tbody>
</table>

Fig. S1. Schematic representation of the nine-connected network.
Fig. S2. The TGA plot of compound $[\text{Cd}_{15}(5\text{MT})_{18}(\text{OH})_4(\text{SO}_4)_4\cdot8.5\text{H}_2\text{O}]$
Fig. S3. Solid-state excitation and emission spectrum of 1 at room temperature.
Powder X-ray diffraction results (Fig. 4S) indicate that the chemical composition of the power is $\text{Cd}_{15}(5\text{-MT})_{18}(\text{OH})_4(\text{SO}_4)_4$. 