

## Electronic supplementary information

### Controlled assembly of an unprecedented 2D + 3D interpenetrated array of (4,4)-connected and pcu topologies

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**General information.** All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried with standard procedures. Starting chemicals were purchased from commercial source and used as received.  $^1\text{H}$ , and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded at 300.13 and 75.48 MHz, respectively, on a Bruker AV-300 spectrometer. The chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}$  spectra were referenced by the residual solvent signals relative to tetramethylsilane at 0 ppm. Infra-red spectra were acquired from a Bio-Rad FTS-185 infra-red spectrophotometer. Elemental analyses were performed on a Thermo Flash 2000 CHN-O elemental analyzer. High Resolution Mass Spectroscopy (HRMS) was measured on a Finnigan/Thermo Quest (MAT) mass spectrometer at National Chung Hsing University (Taiwan).

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 6 Thermogravimetric Analyzer under flowing N<sub>2</sub> gas (40 mL/min), and the heating rate was 20 °C/min. Powder X-ray diffraction (PXRD) measurements were recorded on Shimadzu Lab-X XRD-6000 diffractometer with Cu K $\alpha$ ,  $\lambda = 1.54060 \text{ \AA}$ .

**Synthesis of dia.** To a 50 mL flask fitted with magnetic stirrer 9,10-dibromoanthracene (0.500 g, 1.49 mmol), imidazole (0.507 g, 7.45 mmol), 1,10-phenanthrene (0.0402 g, 0.223 mmol), Cu<sub>2</sub>O (0.0402 g, 0.223 mmol), cesium carbonate (1.358 g, 4.17 mmol), and polyethylene glycol (0.3 g) were placed under nitrogen, followed by DMF (10 mL). The reaction mixture was allowed to stir at 110 °C for 48 hrs. The solvent of the reaction mixture was removed under reduced pressure. The residue was diluted with water (10 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL). The organic layer was separated and dried over anhydrous MgSO<sub>4</sub>. Removal of solvent resulted in a brownish gummy mass which was purified by column chromatography over silica gel using *n*-hexane and an increasing proportion of ethyl acetate as eluent. Ultimately, ethyl acetate as eluent gave the desired light yellow solid. Yield: 0.290 g, 63%. m.p.: 349 °C. Anal. Calcd for C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>: C, 77.40; H, 4.54; N, 18.05. Found: C, 77.08; H, 4.76; N, 18.11. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.31 (s, 2H, imi *H*), 7.47–7.56 (m, 10H, anthracene *H*), 7.83 (s, 2H, imi *H*). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  122.7 (CH), 128.1 (CH), 128.7

(quaternary C), 130.0 (CH), 130.5 (quaternary C), 139.5 (CH). HRMS (EI): calcd  $C_{12}H_{12}N_4$ : 310.1218; found: 310.1216.

**Synthesis of 1.** A samples of dia (0.0500 g, 0.161 mmol) in dichloromethane (1 mL) was placed inside a glass tube (diameter = 0.4 cm, length = 15 cm).  $Co(NO_3)_2 \cdot 6H_2O$  (0.0938 g, 0.322 mmol) was dissolved in methanol (1 mL). The methanol solution was carefully placed on top of the dichloromethane solution. The interfacial region became turbid. The glass tube was then sealed with parafilm and left undisturbed for few weeks. The light red crystals formed were filtered, washed with dichloromethane and water, and dried in the air. Yield: 0.0502, 64% (based on dia). Anal. Calcd for  $C_{40}H_{28}CoN_{10}O_6 \cdot 2CH_2Cl_2$ : C, 51.81; H, 3.31; N, 14.38. Found: C, 51.99; H, 3.60; N, 14.55. IR (KBr/pellet,  $cm^{-1}$ ): 4743.2 (w), 4462.1 (w), 3126.3 (w), 2925.2 (w), 2367.9 (w, sh), 2050.0 (w), 1508.4 (vs), 1330.6 (vs), 1088.4 (m), 1033.3 (m), 935.7 (m), 766.1 (vs), 658.1 (vs), 506.8 (w, sh).

**Synthesis of 2.** A mixture of dia (0.0500 g, 0.161 mmol) and  $Co(NO_3)_2 \cdot 6H_2O$  (0.0938 g, 0.322 mmol) in water (5 mL) was placed in a 50 mL Teflon-lined autoclave, which was heated according to the following temperature program: heated to 140 °C and maintained at this temperature for 5 h, cooled down to 110 °C in 30 min, maintained at this temperature for 3 h, cooled down to 90 °C in 20 min, maintained at this temperature

for 4 h, then allowed to cool to RT slowly. The colorless crystals were filtered under suction, washed with water and dichloromethane, and dried in air. Yield: 0.034 g, 54% (based on dia). Anal. Calcd for  $C_{50}H_{35}CoN_{12}O_6 \cdot H_2O$ : C, 61.48; H, 3.82; N, 17.21. Found: C, 61.38; H, 3.85; N, 16.92. IR (KBr/pellet,  $cm^{-1}$ ): 3107.0 (w, sh), 2966.3 (w), 1503.2 (s), 1439.7 (m), 1410.9 (m), 1303.0 (w), 1246.3 (w), 1216.4 (m), 1157.8 (m), 1082.5 (s), 1030.4 (s), 930.5 (s), 832.8 (m), 768.6 (s), 728.3 (m), 658.0 (vs), 416.1 (vs).

**Synthesis of 3.** A mixture of dia (0.025 g, 0.080 mmol), terephthalic acid (0.0134 g, 0.080 mmol),  $Co(NO_3)_2 \cdot 6H_2O$  (0.046 g, 0.161 mmol), and  $NEt_3$  (0.0266 g, 0.189 mmol) in water (5 mL) was placed in a 50 mL Teflon-lined autoclave, which was heated to 170 °C in 1 h. It was hold at the temperature for 12 h and then allowed to cool down to room temperature in 12 h. Colorless crystals were separated by filtration, washed with deionized water and dichloromethane, and dried in air. Yield: 0.0349 g, 46 % (based on dia). Anal. Calcd for  $C_{76}H_{54}Co_2N_{12}O_{10} \cdot H_2O$ : C, 63.78; H, 3.94; N, 11.74. Found: C, 63.80; H, 3.94; N, 11.92. IR (KBr/pellet,  $cm^{-1}$ ): 3131.6 (w, sh), 3069.7 (w), 2923.5 (w, sh), 2852.6 (w), 2371.9 (w), 2345.8 (w), 1582.6 (s, sh), 1498.6 (m), 1363.6 (s, sh), 1328.6 (w, sh), 1247.8 (w), 1219.7 (w), 1151.7 (w, sh), 1104.2 (vs), 1078.2 (vs), 1029.1 (m, sh), 920.4 (m), 913.2 (m), 806.3 (s, sh), 753.1 (vs), 702.6 (m), 662.8 (s, sh), 519.6 (m), 459.7 (m).

**X-ray diffraction studies.** Reflection data were collected on a Bruker APEX II

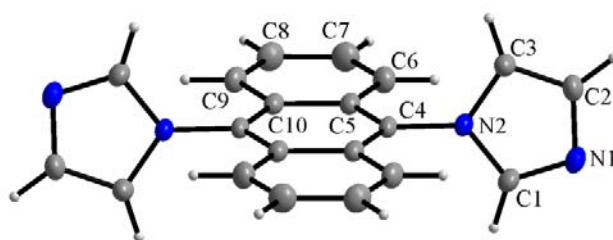
equipped with a CCD area detector and a graphite monochromator utilizing MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 150(2) K. The unit cell parameters were obtained by least-squares refinement. The data were integrated via SAINT.<sup>1</sup> Lorentz and polarization effect and multiscan absorption corrections were applied with SADABS.<sup>2</sup> The structures were solved by direct methods and refined by full-matrix least squares methods against  $F^2$  with SHELXTL.<sup>3</sup> All non-H atoms were refined anisotropically. All H-atoms, except those of water, were fixed at calculated positions and refined with the use of a riding model. H-atoms of the water molecules were located from difference electron density map and not refined. Crystallographic data are listed in Table 1S. CCDC-800198 (dia), 800199 (**1**), -800200 (**2**), and -800201 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S1.** Crystallographic data of dia and **1–3**.

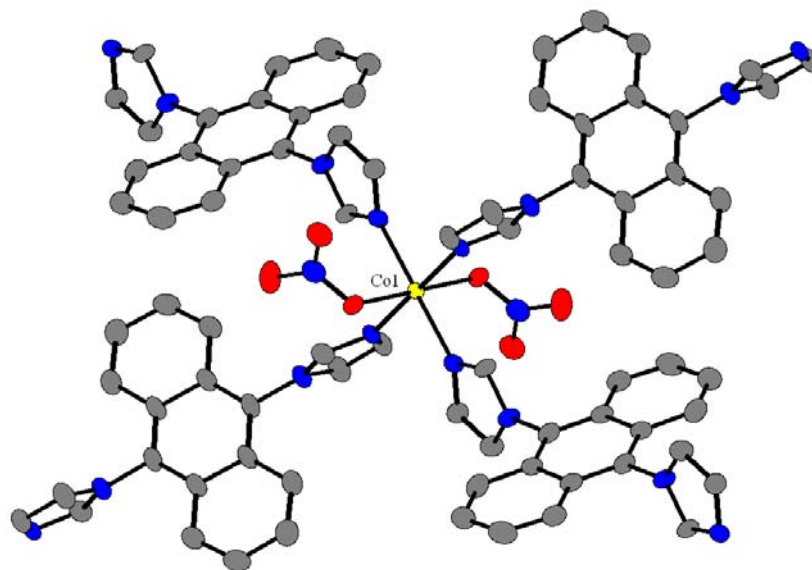
	<b>dia</b>	<b>1</b>	<b>2</b>	<b>3</b>
empirical formula	C <sub>20</sub> H <sub>14</sub> N <sub>4</sub>	C <sub>40</sub> H <sub>28</sub> CoN <sub>10</sub> O <sub>6</sub> · 2CH <sub>2</sub> Cl <sub>2</sub>	C <sub>50</sub> H <sub>35</sub> CoN <sub>12</sub> O <sub>6</sub> · H <sub>2</sub> O	C <sub>76</sub> H <sub>54</sub> Co <sub>2</sub> N <sub>12</sub> O <sub>10</sub> · H <sub>2</sub> O
formula weight	310.35	973.51	976.85	1431.19
crystal size (mm)	0.38x0.28x0.07	0.1x0.07x0.06	0.27x0.21x0.11	0.25x0.15x0.10
crystal system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a$ , (Å)	5.6711(11)	8.587(2)	10.1791(5)	11.2647(13)

<i>b</i> , (Å)	8.1633(16)	10.268(3)	13.7563(6)	13.3120(17)
<i>c</i> , (Å)	8.5872(17)	11.825(3)	16.5846(8)	13.6154(17)
$\alpha$ (deg)	93.010(4)	93.996(6)	66.855(2)	61.920(4)
$\beta$ (deg)	103.997(4)	98.019(6)	87.383(3)	71.986(4)
$\gamma$ (deg)	93.971(4)	92.232(6)	86.095(3)	75.482(4)
<i>V</i> (Å <sup>3</sup> )	383.83(13)	1028.7(4)	2129.97(17)	1699.6(4)
<i>T</i> , K	150(2)	150(2)	150(2)	150(2)
<i>Z</i>	1	1	2	1
reflections collected	4614	12181	32065	19933
independent reflections	1968	5263	10957	8673
params refined	109	286	634	463
goodness-of-fit on <i>F</i> <sup>2</sup>	1.277	0.808	1.052	0.914
<i>R</i> <sub>1</sub> <sup><i>a</i></sup> [ <i>I</i> > 2σ <i>I</i> ]	0.0408	0.0663	0.0555	0.0536
<i>wR</i> <sub>2</sub> <sup><i>b</i></sup> (all data)	0.1209	0.1745	0.1463	0.1346

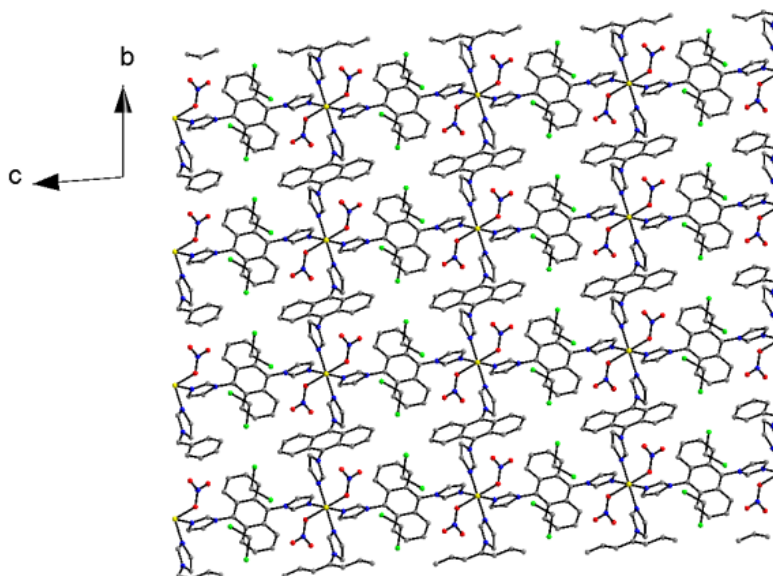
<sup>*a*</sup>  $R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|$ . <sup>*b*</sup>  $wR_2 = [\sum(|F_o|^2 - |F_c|^2)^2 / \sum (F_o^2)]^{1/2}$



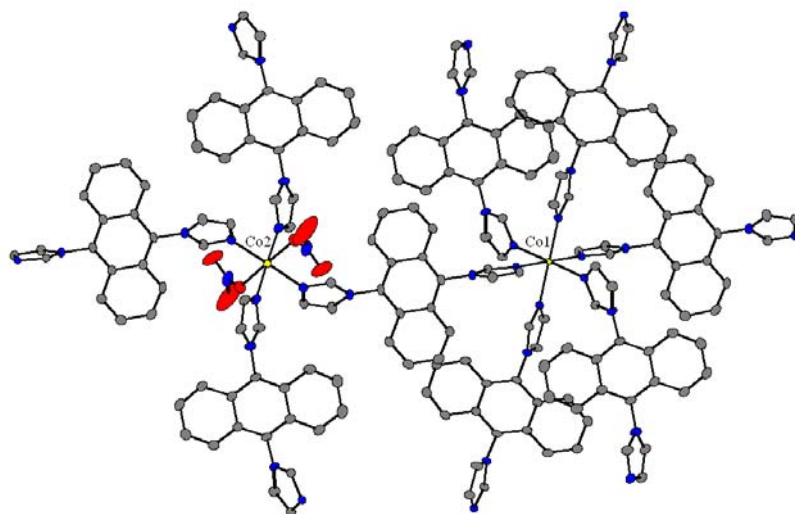
**Fig. S1** Thermal ellipsoid plot of dia.



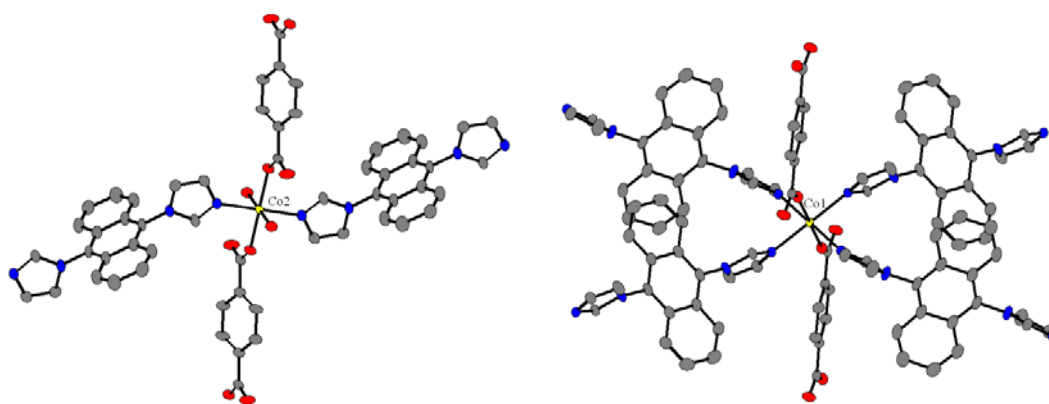
**Fig. S2** The coordination environment in **1**.



**Fig. S3** View of the (4,4) net in **1** along the a-axis. Color code: grey, C; blue, N; red, O;  
green, Cl; yellow, Co.

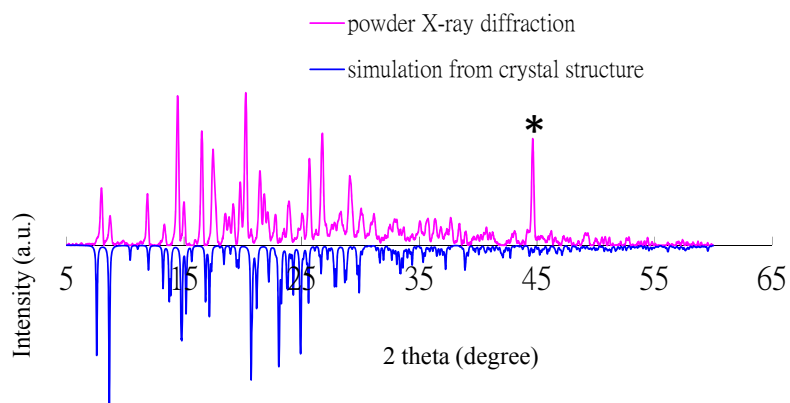


**Fig. S4** The coordination environment in **2**.

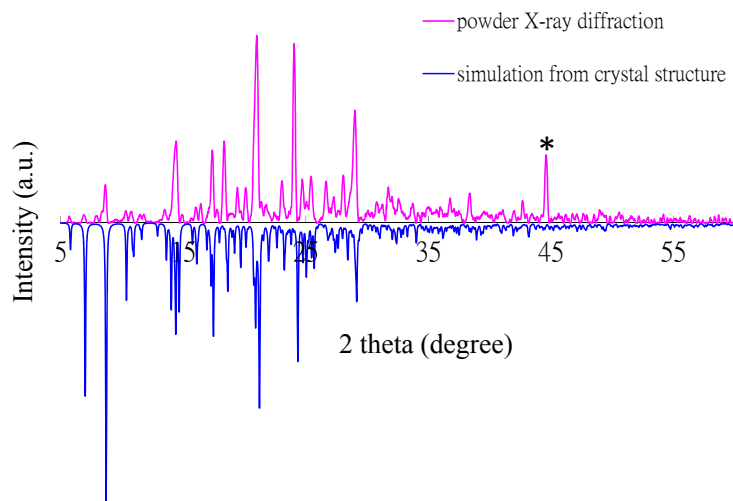


**Fig. S5** The coordination environment of the four-connected (left) and six-connected nodes (right) in **3**.

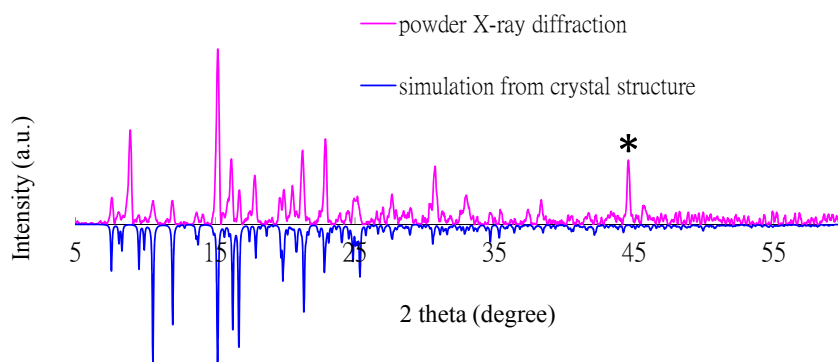




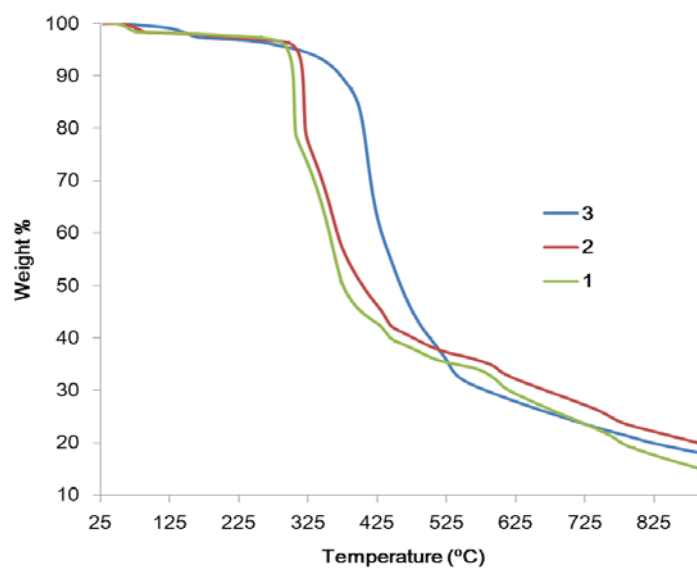
**Fig. S6** XPRD patterns of **1**. The peak attributable to the sample holder is marked.



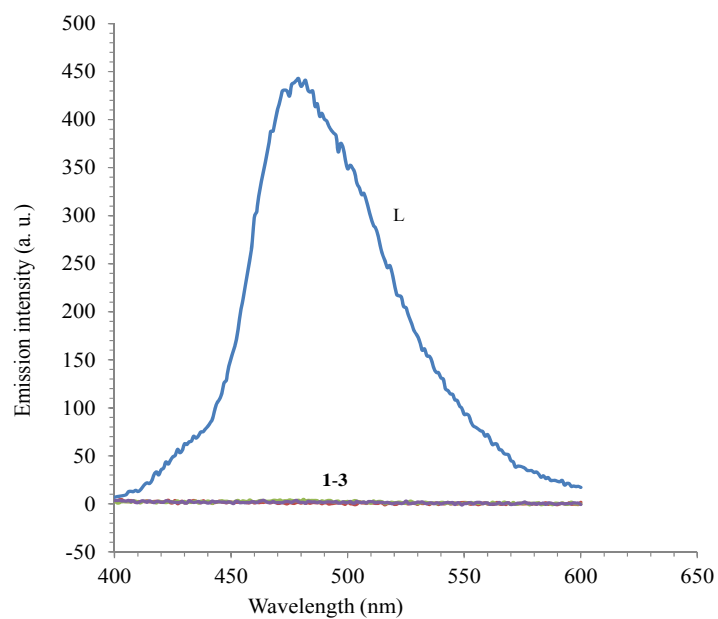
**Fig. S7** XPRD patterns of **2**. The peak attributable to the sample holder is marked.



**Fig. S8** XPRD patterns of **3**. The peak attributable to the sample holder is marked.



**Fig. S9** The TGA curves of **1-3**.



**Fig. S10** The emission spectra of dia and complexes **1–3** in solid state at room temperature.

## References

1. *SAINT*, Bruker AXS Inc.:Madison, Wisconsin, USA., 2007.
2. Sheldrick, G. M. *SADABS*, University of Göttingen, Germany, 1996.
3. Sheldrick, G. *Acta Crystallogr.* **2008**, *A64*, 112.