

## Electronic Supplementary Information

### Renaissance of the coordination chemistry of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT).

#### Part I: First crystal structure of a TPymT complex with a *d*-metal cation

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**Physical measurements.** Infrared spectra were recorded with a Varian 640 FTIR spectrometer equipped with an ATR in the 500–4000 cm<sup>-1</sup> range. <sup>1</sup>H NMR spectra in DMSO-*d*<sub>6</sub> were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. Chemical shifts are reported with respect to SiMe<sub>4</sub>. The <sup>113</sup>Cd solid-state cross-polarization magic angle spinning (CP MAS) NMR spectrum of powdered [Cd<sub>2</sub>(TPymT)(H<sub>2</sub>O)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>] $\cdot$ H<sub>2</sub>O (**1**) was recorded with a Bruker Avance III 400 MHz (9.4 T) spectrometer at 25 °C. The chemical shift is reported with respect to Cd(ClO<sub>4</sub>)<sub>2</sub> (1 M (aq)) at 0 ppm using Cd(NO<sub>3</sub>)<sub>2</sub> $\cdot$ 4H<sub>2</sub>O as a secondary reference at -100 ppm.<sup>1</sup> The MAS frequency was 5 kHz, the contact time was 2 ms, and the recycle delay was 6 s. Diffuse reflectance spectra were obtained with a Varian Cary 100 spectrometer using polytetrafluoroethylene (PTFE) as a reference. Solid-state emission spectra were obtained with a Perkin Elmer LS 50 luminescence spectrometer. Kubelka-Munk and emission spectra were normalized to allow meaningful comparisons. Thermogravimetric analysis (TGA) data were recorded using a Q5000 IR TGA instrument at a heating rate of 10 °C/min between room temperature and 800 °C, under a constant flow of air (100 mL/min). Elemental analyses were performed on a Perkin Elmer 2400 CHN analyzer.

**Synthesis of TPymT.** TPymT was obtained using the synthetic procedure described by Lerner and Lippard.<sup>2</sup> However, the yield of TPymT was much less regardless of the reaction time. 2-Cyanopyrimidine (52 mmol, 5.5 g) was heated with stirring in a stoppered flask at 160 °C for 72 h. The resulting product was washed with diethyl ether (5  $\times$  20 mL) to remove unreacted starting material. Yield: 0.962 g (17.6%). <sup>1</sup>H NMR,  $\delta$ : 7.82 (t, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz, 3H, *p*-CH, pyrimidine), 9.16 (d, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz, 6H, *m*-CH, pyrimidine) ppm.

**Synthesis of 1.** A hot aqueous (5 mL) solution of 3CdSO<sub>4</sub> $\cdot$ 8H<sub>2</sub>O (0.165 mmol, 0.127 g) was added to a suspension of TPymT (0.15 mmol, 0.047 g) in the same solvent (3 mL). The mixture was refluxed until all of the reactants dissolved. The resulting yellow solution was cooled yielding pale orange block-like crystals. Yield: 0.124 g (96.3%). <sup>113</sup>Cd CP MAS NMR,  $\delta$ : -12.6 ppm.

**X-ray powder diffraction.** X-ray powder diffraction for bulk samples of **TPymT** and **1** was carried out using a Rigaku Ultima IV X-ray powder diffractometer. The Parallel Beam mode was used to collect the data ( $\lambda = 1.541836 \text{ \AA}$ ).

**Single crystal X-ray diffraction.** The X-ray data for **1** were collected at 200(2) K on a Bruker AXS SMART single crystal diffractometer with a sealed Mo tube APEX II CCD detector. The Mo radiation wavelength,  $0.71073 \text{ \AA}$ , was used. Data collection and processing were performed with APEX software from Bruker AXS.<sup>3</sup> The crystal structures were solved by direct methods and refined using the SHELX program.<sup>4</sup> All non-hydrogen atoms were refined anisotropically and the positions of all hydrogen atoms were obtained from the Fourier map analysis. Figures were generated using the Mercury program.<sup>5</sup>  $\text{C}_{15}\text{H}_{23}\text{Cd}_2\text{N}_9\text{O}_{15}\text{S}_2$ ,  $M_r = 858.34 \text{ g mol}^{-1}$ , orthorhombic, space group *Pbcn*,  $a = 23.8424(5)$ ,  $b = 14.7858(3)$ ,  $c = 7.6296(2) \text{ \AA}$ ,  $V = 2689.66(11) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho = 2.120 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 1.825 \text{ mm}^{-1}$ , reflections: 31679 collected, 3302 unique,  $R_{\text{int}} = 0.026$ ,  $R_1(\text{all}) = 0.0219$ ,  $wR_2(\text{all}) = 0.0594$ .

CCDC 955952 (**1**) contains the supplementary crystallographic data. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

## References

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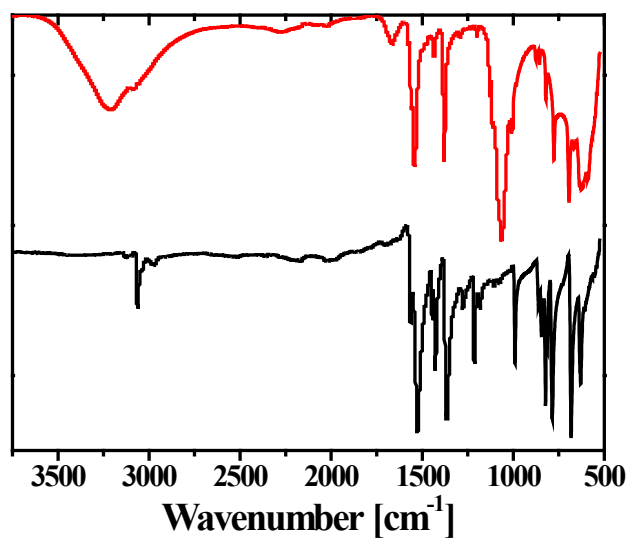


Fig. S1 IR spectra of TPymT (black) and 1 (red) at 298 K.

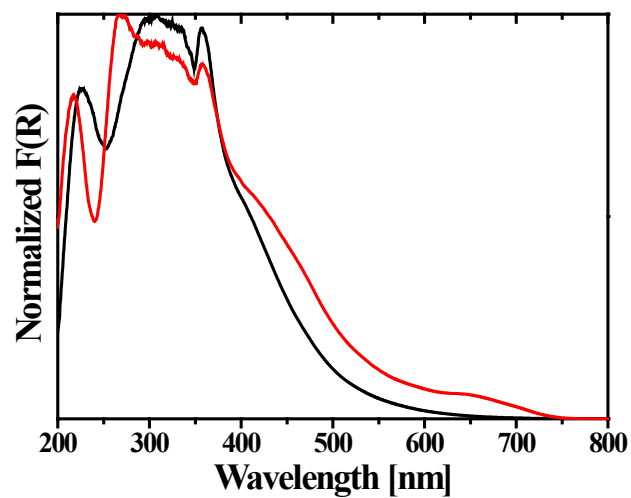
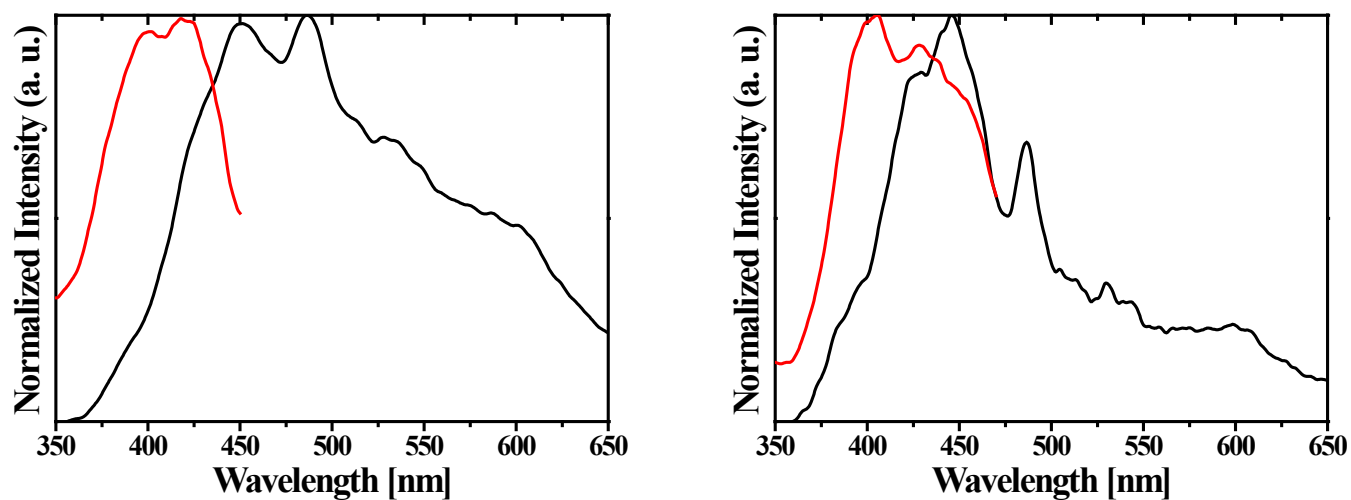
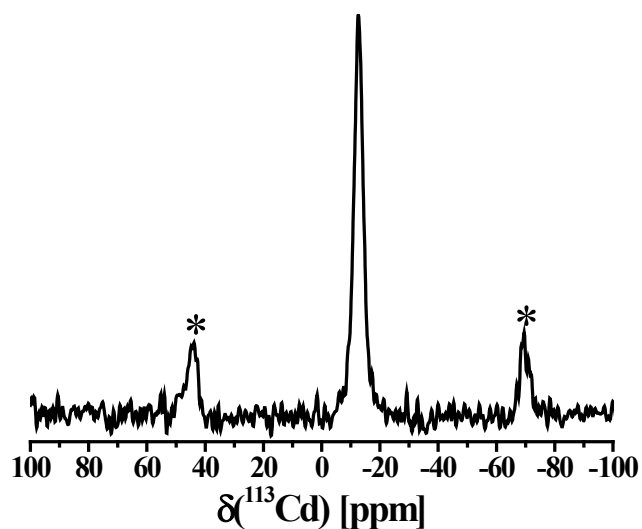


Fig. S2 Normalized Kubelka-Munk spectra of TPymT (black) and 1 (red) at 298 K.



**Fig. S3** Normalized solid-state emission (black,  $\lambda_{\text{exc}} = 350$  nm) and excitation (red,  $\lambda_{\text{em}} = 480$  nm) spectra of TPymT (left) and **1** (right) at 298 K.



**Fig. S4** The  $^{113}\text{Cd}$  solid-state CP MAS NMR spectrum of powdered **1** at 298 K. Spinning sidebands are labeled with asterisks.

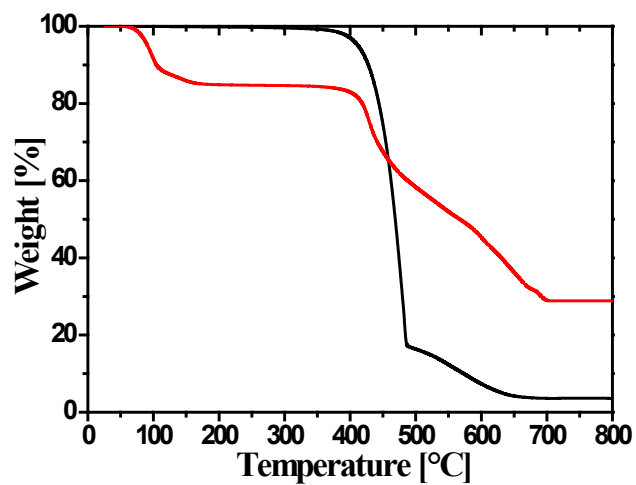


Fig. S5 TG analyses of TPymT (black) and 1 (red) performed in a dynamic air atmosphere.

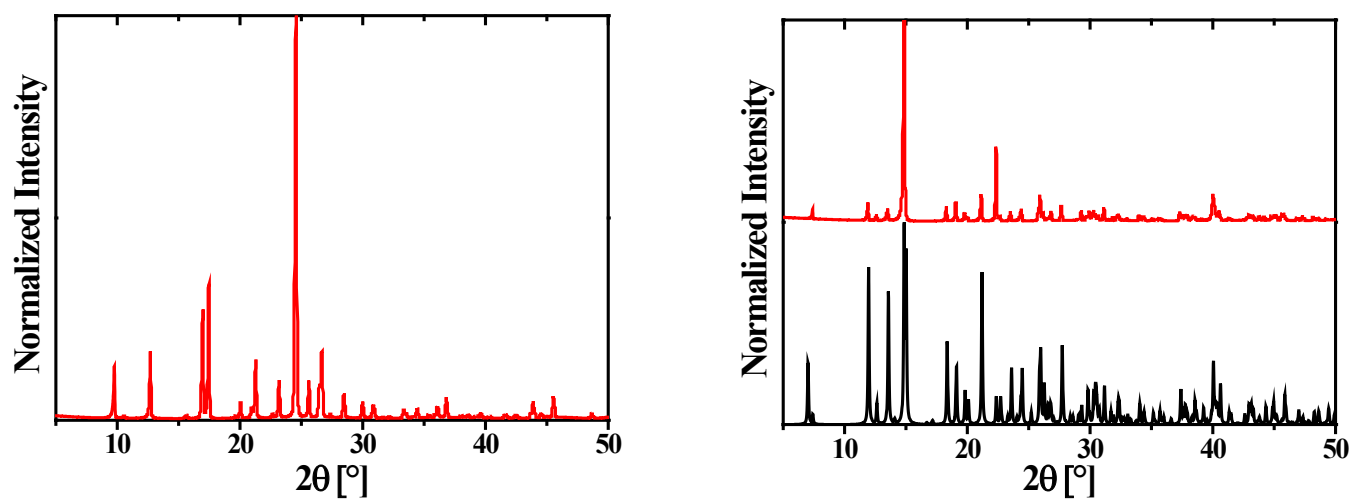


Fig. S6 Calculated (black) and experimental (red) X-ray powder diffraction patterns of TPymT (left) and 1 (right).

**Table S1** Selected bond lengths (Å) and bond angles (°) for **1**

<i>Bond lengths</i>					
Cd(1)–N(1)	2.4436(16)	N(2)–C(1)	1.335(2)	C(3)–C(4)	1.373(4)
Cd(1)–N(3)	2.5202(16)	N(3)–C(7)	1.330(2)	C(4)–C(5)	1.374(4)
Cd(1)–N(4)	2.6670(19)	N(3)–C(8)	1.341(3)	C(6)–C(7)	1.494(4)
Cd(1)–O(4)	2.2041(15)	N(4)–C(2)	1.323(3)	C(8)–C(9)	1.384(3)
Cd(1)–O(5)	2.2916(16)	N(4)–C(3)	1.340(3)	S(1)–O(1)	1.4785(17)
Cd(1)–O(6)	2.2904(19)	N(5)–C(2)	1.333(3)	S(1)–O(2)	1.4766(17)
Cd(1)–O(7)	2.3090(17)	N(5)–C(5)	1.344(3)	S(1)–O(3)	1.4678(18)
N(1)–C(1)	1.336(3)	C(1)–C(2)	1.488(3)	S(1)–O(4)	1.4787(15)
N(1)–C(6)	1.330(2)				
<i>Bond angles</i>					
Cd(1)–N(1)–C(1)	123.81(13)	O(7)–Cd(1)–N(1)	140.91(6)	N(4)–C(3)–C(4)	122.0(2)
Cd(1)–N(1)–C(6)	120.87(14)	O(7)–Cd(1)–N(3)	79.59(6)	N(5)–C(2)–C(1)	117.05(19)
Cd(1)–N(3)–C(7)	119.05(14)	O(7)–Cd(1)–N(4)	153.32(6)	N(5)–C(5)–C(4)	121.9(2)
Cd(1)–N(3)–C(8)	125.09(13)	O(4)–Cd(1)–O(5)	175.33(6)	C(1)–N(1)–C(6)	115.26(18)
Cd(1)–N(4)–C(2)	116.02(14)	O(4)–Cd(1)–O(6)	93.75(6)	C(1)–N(2)–C(1) <sub>a</sub>	114.7(2)
Cd(1)–N(4)–C(3)	126.26(17)	O(4)–Cd(1)–O(7)	91.42(6)	C(2)–N(4)–C(3)	115.9(2)
Cd(1)–O(4)–S(1)	125.98(9)	O(5)–Cd(1)–O(6)	86.62(6)	C(2)–N(5)–C(5)	115.6(2)
N(1)–Cd(1)–N(3)	65.91(5)	O(5)–Cd(1)–O(7)	84.04(6)	C(7)–N(3)–C(8)	115.67(18)
N(1)–Cd(1)–N(4)	62.92(6)	O(6)–Cd(1)–O(7)	80.77(7)	C(6)–C(7)–N(3) <sub>a</sub>	116.14(12)
N(3)–Cd(1)–N(4)	126.98(6)	N(1)–C(1)–N(2)	124.89(19)	C(7)–C(6)–N(1) <sub>a</sub>	117.68(12)
O(4)–Cd(1)–N(1)	105.59(5)	N(1)–C(6)–N(1) <sub>a</sub>	124.6(2)	C(3)–C(4)–C(5)	117.4(2)
O(4)–Cd(1)–N(3)	89.61(5)	N(3)–C(7)–N(3) <sub>a</sub>	127.7(2)	C(8)–C(9)–C(8) <sub>a</sub>	117.4(2)
O(4)–Cd(1)–N(4)	91.19(6)	N(4)–C(2)–N(5)	127.1(2)	O(1)–S(1)–O(2)	108.56(9)
O(5)–Cd(1)–N(1)	77.49(6)	N(1)–C(1)–C(2)	116.99(17)	O(1)–S(1)–O(3)	110.19(10)
O(5)–Cd(1)–N(3)	88.49(6)	N(1)–C(6)–C(7)	117.68(12)	O(1)–S(1)–O(4)	108.27(9)
O(5)–Cd(1)–N(4)	93.36(6)	N(2)–C(1)–C(2)	118.09(18)	O(2)–S(1)–O(3)	110.01(10)
O(6)–Cd(1)–N(1)	131.26(7)	N(3)–C(7)–C(6)	116.14(12)	O(2)–S(1)–O(4)	109.21(9)
O(6)–Cd(1)–N(3)	160.14(7)	N(3)–C(8)–C(9)	121.74(19)	O(3)–S(1)–O(4)	110.56(9)
O(6)–Cd(1)–N(4)	72.57(7)	N(4)–C(2)–C(1)	115.77(18)		

**Table S2.** Hydrogen bond lengths (Å) and angles (°) for **1**<sup>a</sup>

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠(DHA)
O(5)–H(5B)···O(3) <sup>#1</sup>	0.96	1.71	2.662(2)	176
O(5)–H(5C)···O(8)	1.00	1.76	2.741(2)	165
O(6)–H(6A)···O(2) <sup>#1</sup>	0.95	1.77	2.725(2)	174
O(6)–H(6B)···O(2) <sup>#2</sup>	1.00	1.71	2.698(2)	168
O(7)–H(7A)···O(1) <sup>#3</sup>	0.96	1.74	2.695(2)	173
O(7)–H(7B)···O(1) <sup>#1</sup>	1.00	1.74	2.745(2)	173
O(8)–H(8B)···N(2) <sup>#4</sup>	0.99	2.39	2.922(3)	113
O(8)–H(8B)···N(5) <sup>#4</sup>	0.99	1.88	2.862(2)	169

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1 *x*, *y*,  $-1 + z$ ; #2  $1/2 - x$ ,  $3/2 - y$ ,  $-1/2 + z$ ; #3 *x*,  $1 - y$ ,  $-1/2 + z$ ; #4  $1 - x$ ,  $2 - y$ ,  $-z$ .

**Table S3.**  $\pi$ ··· $\pi$  bond lengths (Å) and angles (°) for **1**<sup>a</sup>

Cg( <i>I</i> )	Cg( <i>J</i> ) <sup>b</sup>	<i>d</i> [Cg( <i>I</i> )–Cg( <i>J</i> )]	$\alpha$	$\beta$
Cg(1)	Cg(3) <sup>#1</sup>	5.4325(13)	13.32	42.59
Cg(1)	Cg(3) <sup>#2</sup>	5.4325(13)	13.32	42.59
Cg(2)	Cg(2) <sup>#3</sup>	4.1796(10)	0.00	36.83
Cg(2)	Cg(2) <sup>#4</sup>	4.1796(10)	0.00	36.83
Cg(2)	Cg(2) <sup>#5</sup>	4.1796(10)	0.00	36.83
Cg(2)	Cg(2) <sup>#6</sup>	4.1796(10)	0.00	36.83
Cg(3)	Cg(1) <sup>#1</sup>	5.4326(13)	13.32	52.24
Cg(3)	Cg(1) <sup>#7</sup>	5.4326(13)	13.32	52.24
Cg(3)	Cg(3) <sup>#7</sup>	3.9341(18)	2.38	16.81
Cg(3)	Cg(3) <sup>#2</sup>	3.9342(18)	2.38	14.67

<sup>a</sup> Cg(*I*)–Cg(*J*): distance between ring centroids;  $\alpha$ : dihedral angle between planes Cg(*I*) and Cg(*J*);  $\beta$ : angle Cg(*I*) → Cg(*J*) vector and normal to plane *I*.

<sup>b</sup> Symmetry transformations used to generate equivalent atoms: #1  $1 - x$ ,  $2 - y$ ,  $-z$ ; #2 *x*,  $2 - y$ ,  $1/2 + z$ ; #3  $1 - x$ ,  $1 - y$ ,  $-z$ ; #4  $1 - x$ ,  $1 - y$ ,  $1 - z$ ; #5 *x*,  $1 - y$ ,  $-1/2 + z$ ; #6 *x*,  $1 - y$ ,  $1/2 + z$ ; #7 *x*,  $2 - y$ ,  $-1/2 + z$ . Cg(1): N(1)–C(1)–N(2)–C(1)a–N(1)a–C(6), Cg(2): N(3)–C(7)–N(3)a–C(8)a–C(9)–C(8), Cg(3): N(4)–C(2)–N(5)–C(5)–C(4)–C(3).