

*Supporting Information*

## Trigonal Antiprismatic Mononuclear Cr(II) Spin-Crossover Complexes

Shihao Liu,<sup>a,b</sup> Qi Liu,<sup>a</sup> Yi-Fei Deng,<sup>\*a</sup> and Yuan-Zhu Zhang<sup>\*a</sup>

<sup>a</sup> Department of Chemistry, Southern University of Science and Technology (SUSTech), Shenzhen 518055, China.

<sup>b</sup> Department of Chemistry, National University of Singapore, 117597 Singapore, Singapore.

### Materials and Syntheses

Tris(pyrazol-1-yl)methane (Tpm) and Tris(3,5-dimethylpyrazol-1-yl)methane (Tpm<sup>\*</sup>) were prepared according to the literature.<sup>1</sup> All other chemicals were commercially available and used without further purification. The solvents were dehydrated and deoxygenated by Solvent Purification Systems prior to use. All manipulations were performed under a dry and oxygen-free argon atmosphere using a glovebox.

Caution: Although no such issues were observed during the present work, perchlorate salts are potentially explosive and should be handled in small quantities and with great care.

**Synthesis of [Cr(Tpm)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (1).** A MeCN solution (5 mL) containing Tpm (42.8 mg, 0.20 mmol) was added to the aqueous solution (3 mL) of CrCl<sub>2</sub> (12.0 mg, 0.10 mmol), the resulting mixture was stirred vigorously for 12 h before filtered. NaBF<sub>4</sub> (43.9 mg, 0.40 mmol) in 2 mL H<sub>2</sub>O was subsequently added into the filtrate, and the resulting solution was left to evaporate slowly to yield the yellow crystals of **1** in three days. The product was collected by filtration and washed with water. Yield 35.2 mg (53%). Anal. Calcd for C<sub>20</sub>H<sub>20</sub>B<sub>2</sub>CrF<sub>8</sub>N<sub>12</sub> C, 36.73; H, 3.08; N 25.70. Found: C, 36.78; H, 2.99; N, 25.61.

**Synthesis of [Cr(Tpm)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (2).** Complex **2** was obtained with a procedure similar to **1**, by replacing NaBF<sub>4</sub> with Li(ClO<sub>4</sub>)·3H<sub>2</sub>O (64.2 mg, 0.40 mmol). The yellow crystals were collected in a week. Yield 49.6 mg (73%). Anal. Calcd for C<sub>20</sub>H<sub>20</sub>Cl<sub>2</sub>CrN<sub>12</sub>O<sub>8</sub> C, 35.36; H, 2.97; N 24.74. Found: C, 35.88; H, 2.79; N, 24.68.

**Synthesis of [Cr(Tpm<sup>\*</sup>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (3).** Complex **3** was obtained with a procedure similar to **1**, by replacing Tpm with Tpm<sup>\*</sup> (59.9 mg, 0.20 mmol). The yellow crystals were collected after one week. Yield 55.1 mg (67%). Anal. Calcd for C<sub>32</sub>H<sub>44</sub>B<sub>2</sub>CrF<sub>8</sub>N<sub>12</sub> C, 46.74; H, 5.39; N 20.44. Found: C, 46.84; H, 5.26; N, 20.28.

**Synthesis of [Cr(Tpm<sup>\*</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (4).** Complex **4** was obtained with a procedure similar to **3**, by replacing NaBF<sub>4</sub> with Li(ClO<sub>4</sub>)·3H<sub>2</sub>O (64.2 mg, 0.40 mmol). The yellow crystals were collected

after one week. Yield 70.5 mg (83%). Anal. Calcd for C<sub>32</sub>H<sub>44</sub>Cl<sub>2</sub>CrN<sub>12</sub>O<sub>8</sub> C, 45.34; H, 5.23; N 19.83. Found: C, 45.88; H, 5.20; N, 19.74.

### Physical Measurements

Single crystal X-ray crystallographic diffraction measurements for **1** - **4** were performed using a Bruker D8 VENTURE diffractometer (Germany) with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The high-temperature and low-temperature data are collected with the same crystal. The sweeping rate is 2 K/min between the measurements at different temperatures. Lorentz/polarization corrections were applied during data reduction, and the structures were solved by the direct method (SHELXS-2014). Refinements were performed by full-matrix least-squares (SHELXL-2014) on F<sup>2</sup>, and empirical absorption corrections (SADABS) were applied.<sup>2,3</sup> Anisotropic thermal parameters were used for the nonhydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Weighted R factors ( $wR$ ) and all the goodness-of-fit (S) values are based on F<sup>2</sup>; conventional R factors (R) are based on F, with F set to zero for negative F<sup>2</sup>. Data collection and structural refinement parameters are given in Table S1 - 4, and selected bond lengths and angles are given in Tables S5 - 8. CCDC-2385013 (**1**<sup>100K</sup>), 2385014 (**1**<sup>340K</sup>), 2385015 (**2**<sup>100K</sup>), 2385016 (**2**<sup>360K</sup>), 2385017 (**3**<sup>100K</sup>), 2385018 (**3**<sup>298</sup>) and 2385019 (**4**<sup>100K</sup>) contain the crystallographic data that can be obtained via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). Elemental analyses (EA) (C, H, N, and S) were measured by a vario electro luminescence (EL) cube CHNOS Elemental Analyzer (Elementar Analysensysteme GmbH, Germany). DSC measurements were recorded using a TA Instruments Discovery DSC2500 with a temperature sweep rate of 10 K / min. Powder X-ray diffraction (PXRD) measurements were recorded at 298 K using a Rigaku SmartLab X-ray diffractometer with Cu K $\alpha$  radiation (45 kV, 200 mA) between 5° and 50° (2 $\theta$ ). The simulated patterns are calculated from the single-crystal data at 360 K (**1**), 360 K (**2**), 298 K (**3**) and 100 K (**4**). Thermogravimetric analysis (TGA) measurements were carried out on freshly filtered crystals using the METTLER TOLEDO TGA2 instrument in an argon atmosphere over a temperature range of 30 - 500 °C with a heating rate of 10 °C /min. Magnetic measurements were performed using a superconducting quantum interference device (SQUID) MPMS3 magnetometer. Specifically, the freshly prepared crystals were slightly ground and then placed into a capsule for SQUID brass holder. In the sweeping mode, the magnetic data were recorded in the temperature range of 2 - 300 K with a rate of 3 K/min. Solutions of **2** and **4** for magnetic measurements were prepared by dissolving the fresh crystals in MeCN solvents in NMR tubes under Ar atmosphere. Magnetic data were corrected for the diamagnetism of the sample holder and for the diamagnetism of the sample using Pascal's constants.<sup>4</sup> Cyclic voltammetry (CV) measurements were carried out in an N<sub>2</sub> atmosphere at room temperature, using a three-electrode system equipped with a platinum-wire counter electrode, an Ag/Ag<sup>+</sup> reference electrode, and a glassy carbon (GC) working electrode. 0.1 M [n-Bu<sub>4</sub>N][PF<sub>6</sub>] in a MeCN solution was used as a supporting electrolyte. Potentials are given relative to the ferrocene/ferrocenium couple (0.40 V vs. SCE, E<sub>1/2</sub> = 0.90 ± 5 mV under the given conditions)

**Table S1** X-ray crystallographic data for complexes **1** and **2**.

Compound	<b>1</b> <sup>100K</sup>	<b>1</b> <sup>340K</sup>	<b>2</b> <sup>100K</sup>	<b>2</b> <sup>360K</sup>
Empirical formula	C <sub>20</sub> H <sub>20</sub> B <sub>2</sub> CrF <sub>8</sub> N <sub>12</sub>	C <sub>20</sub> H <sub>20</sub> B <sub>2</sub> CrF <sub>8</sub> N <sub>12</sub>	C <sub>20</sub> H <sub>20</sub> Cl <sub>2</sub> CrN <sub>12</sub> O <sub>8</sub>	C <sub>20</sub> H <sub>20</sub> Cl <sub>2</sub> CrN <sub>12</sub> O <sub>8</sub>
Mw / g mol <sup>-1</sup>	654.10	654.10	679.38	679.38
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	<i>P2</i> <sub>(1)</sub> / <i>n</i>	<i>P2</i> <sub>(1)</sub> / <i>n</i>	<i>P2</i> <sub>(1)</sub> / <i>n</i>	<i>P2</i> <sub>(1)</sub> / <i>n</i>
a, Å	10.2793(8)	10.515(3)	10.3906(6)	10.6790(15)
b, Å	7.7160(5)	8.032(3)	7.7653(5)	8.0181(15)
c, Å	17.0514(13)	17.068(5)	17.2161(12)	17.243(3)
α, deg	90	90	90	90
β, deg	102.226(3)	99.837(11)	104.759(3)	100.897(8)
γ, deg	90	90	90	90
V, Å <sup>3</sup>	1321.76(17)	1420.4(8)	1343.27(15)	1449.8(4)
Z	2	2	2	2
D <sub>cal</sub> / g cm <sup>-3</sup>	1.644	1.529	1.680	1.556
F(000)	660	660	692	692
Temperature, K	100(2)	340(2)	100(2)	360(2)
Radiation	MoKα	MoKα	MoKα	MoKα
Reflections collected	10281	10111	9253	9406
Unique reflections (R <sub>int</sub> )	3025(0.0450)	2861(0.0293)	3071(0.0411)	3071(0.0702)
Goodness-of-fit on F <sup>2</sup>	1.037	1.057	1.063	1.065
R <sub>1</sub> [I > 2σ(I)]	0.0470	0.0441	0.0365	0.0784
wR <sub>2</sub> [I > 2σ(I)]	0.1161	0.1266	0.0943	0.2440

**Table S2** X-ray crystallographic data for complexes **3** and **4**.

Compound	<b>3</b> <sup>100K</sup>	<b>3</b> <sup>298K</sup>	<b>4</b> <sup>100K</sup>
Empirical formula	C <sub>32</sub> H <sub>44</sub> B <sub>2</sub> CrF <sub>8</sub> N <sub>12</sub>	C <sub>32</sub> H <sub>44</sub> B <sub>2</sub> CrF <sub>8</sub> N <sub>12</sub>	C <sub>32</sub> H <sub>44</sub> Cl <sub>2</sub> CrN <sub>12</sub> O <sub>8</sub>
Mw / g mol <sup>-1</sup>	822.41	822.41	847.69
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	<i>C2/c</i>	<i>C2/c</i>	<i>P2<sub>(1)/n</sub></i>
a, Å	20.2546(14)	20.565(4)	8.3193(10)
b, Å	10.3004(7)	10.446(2)	10.3877(15)
c, Å	19.5000(15)	19.795(5)	21.848(3)
α, deg	90	90	90
β, deg	112.172(3)	112.059(9)	100.530(4)
γ, deg	90	90	90
V, Å <sup>3</sup>	3767.5(5)	3941.1(16)	1856.3(4)
Z	4	4	2
D <sub>cal</sub> / g cm <sup>-3</sup>	1.450	1.386	1.517
F(000)	1704	1704	884
Temperature, K	100(2)	298 (2)	100(2)
Radiation	MoKα	MoKα	MoKα
Reflections collected	15262	17523	13162
Unique reflections (R <sub>int</sub> )	3743(0.0602)	4408(0.0355)	3274(0.0478)
Goodness-of-fit on F <sup>2</sup>	1.125	1.032	1.137
R <sub>1</sub> [I > 2σ(I)]	0.1580	0.0529	0.0412
wR <sub>2</sub> [I > 2σ(I)]	0.3577	0.1612	0.1006

**Table S3.** Selected bond lengths [ $\text{\AA}$ ] and angles [deg] of **1** and **2**.

Compd.	<b>1</b>		<b>2</b>	
Temp.	100 K	340 K	100 K	360 K
Cr1-N1	2.068(2)	2.186(2)	2.066(2)	2.234(9)
Cr1-N2	2.063(2)	2.170(2)	2.063(2)	2.189(8)
Cr1-N3	2.064(2)	2.175(2)	2.067(2)	2.171(9)
Cr-N <sub>avrg.</sub>	2.065(2)	2.177(2)	2.065(2)	2.198(9)
N1-N2	2.815(4)	2.893(3)	2.817(2)	2.901(2)
N1-N3	2.812(3)	2.872(3)	2.818(2)	2.932(2)
N2-N3	2.773(3)	2.878(3)	2.771(2)	2.907(2)
N1-Cr1-N2	85.92(8)	83.25(8)	86.07(6)	83.5(3)
N1-Cr1-N3	85.79(8)	82.39(8)	85.97(6)	82.0(3)
N2-Cr1-N3	84.44(8)	82.97(8)	84.28(6)	83.6(3)
N1-Cr1-N1A	180.0	180.0	180.0	180.0
N1-Cr1-N2A	94.08(8)	96.75(8)	93.93(6)	98.0(3)
N1-Cr1-N3A	94.21(8)	97.61(8)	94.03(6)	96.5(3)
N2-Cr1-N3A	95.56(8)	97.03(8)	95.72(6)	96.4(3)
Cr...Cr	7.716(5)	8.032(2)	7.765(5)	8.018(2)

Symmetry transformations used to generate equivalent atoms. A  $1/2-x, 1/2+y, 1/2-z$ .

**Table S4.** Selected bond lengths [ $\text{\AA}$ ] and angles [deg] of **3** and **4**.

Compd.	<b>3</b>		<b>4</b>
Temp.	100 K	298 K	100 K
Cr1-N1	2.272(13)	2.304(2)	2.453(2)
Cr1-N2	2.094(11)	2.184(2)	2.115(2)
Cr1-N3	2.096(11)	2.115(2)	2.126(2)
Cr-N <sub>avrg.</sub>	2.154(13)	2.201(2)	2.231(2)
Cr1-N1*	2.188(13)		
Cr1-N2*	2.089(12)		
Cr1-N3*	2.090(12)		
Cr-N <sub>avrg.</sub> *	2.122(13)		
N1-N2	2.872(2)	2.979(4)	3.007(3)
N1-N3	3.015(2)	2.913(3)	2.977(4)
N2-N3	2.781(2)	2.852(3)	2.781(3)
N1*-N2*	2.882(2)		
N1*-N3*	2.850(3)		
N2*-N3*	2.868(2)		
N1-Cr1-N2	82.1(5)	83.15(8)	81.96(8)
N1-Cr1-N3	87.1(5)	82.36(8)	80.75(8)
N2-Cr1-N3	83.2(5)	83.09(7)	81.96(8)
N1-Cr1-N1A	180.0	180.0	180.0
N1-Cr1-N2A	97.9(5)	96.85(8)	98.04(8)
N1-Cr1-N3A	92.9(5)	97.64(8)	99.24(8)
N2-Cr1-N3A	96.8(5)	96.91(7)	98.04(9)
Cr...Cr	9.749(1)	9.898(2)	8.319(1)
N1*-Cr1-N2*	84.7(5)		
N1*-Cr1-N3*	83.6(6)		
N2*-Cr1-N3*	86.6(6)		
N1*-Cr1-N1*A	180.0		
N1*-Cr1-N2*A	95.3(5)		
N1*-Cr1-N3*A	96.4(6)		
N2*-Cr1-N3*A	93.4(6)		

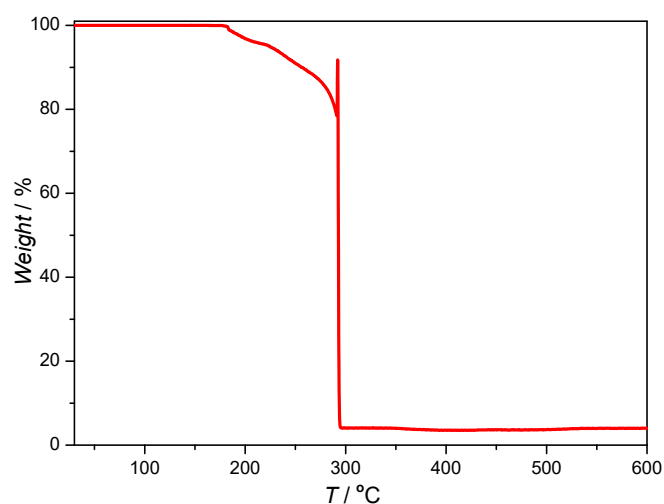
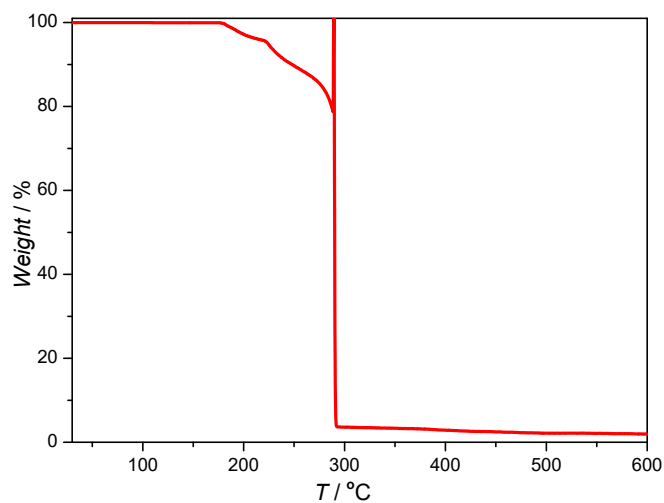
Symmetry transformations used to generate equivalent atoms. **3**: A -x, y, 1/2-z; **4**: A 1/2-x, 1/2+y, 1/2-z.

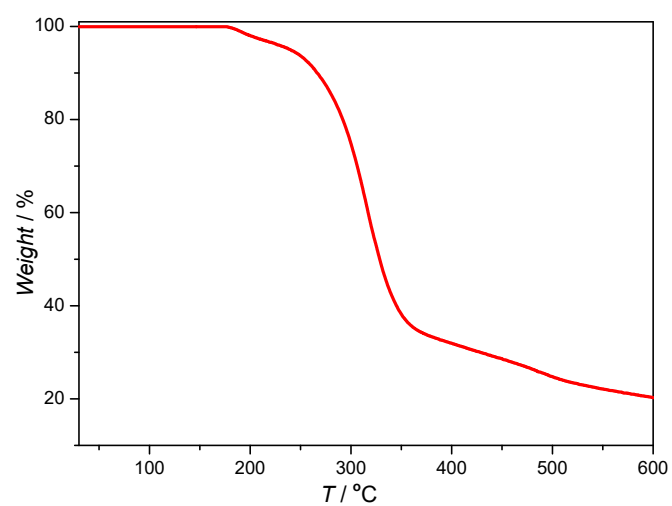
The asterisks (\*) correspond to the disordered atoms.

**Table S5.** Selected structural parameters for **1 - 4**.

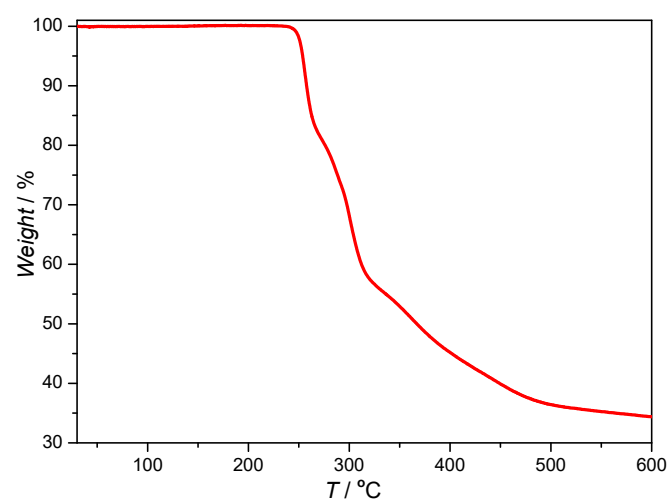
Compd.	Octahedron ( $O_h$ ) <sup>a</sup>	Bailar twist angle <sup>b</sup>	Intra cis N-Co-N <sup>c</sup>	Inter cis N-Co-N <sup>d</sup>	
<b>1</b>	340 K	0.732	60.29(12)°	82.39(8) – 83.25(8)°	96.75(8)° - 97.61(8)°
	100 K	0.321	59.51(11)°	84.44(8) – 85.92(8)°	94.08(8)° - 95.56(8)°
<b>2</b>	360 K	0.728	60.49(16)°	82.0(3) – 83.6(3)°	96.94(13) - 97.32(12)°
	100 K	0.314	61.09(8)	84.28(6) – 86.07(6)°	93.96(6) – 95.72(6)°
<b>3</b>	298 K	0.858	60.16(10)	82.36(8) – 83.15(8)°	96.85(8) – 97.64(8)°
	100 K	0.722	60.49(68)	82.1(5) – 87.1(5)°	92.9(5) – 97.9(5)°
<b>4</b>	100 K	1.506	58.27(11)	80.75(8) – 81.96(8)°	98.04(8) – 99.25(8)°

a: Continuous shape measures (CShM) using SHAPE software<sup>5</sup>; b: Rotation angles between two staggered triangles; c: N-atoms from the same chelate ligand; d: N-atoms from the different chelate ligand

**Figure S1.** TGA plot of **1** measured under an argon atmosphere with a heating rate of 10 °C /min.**Figure S2.** TGA plot of **2** measured under an argon atmosphere with a heating rate of 10 °C /min.

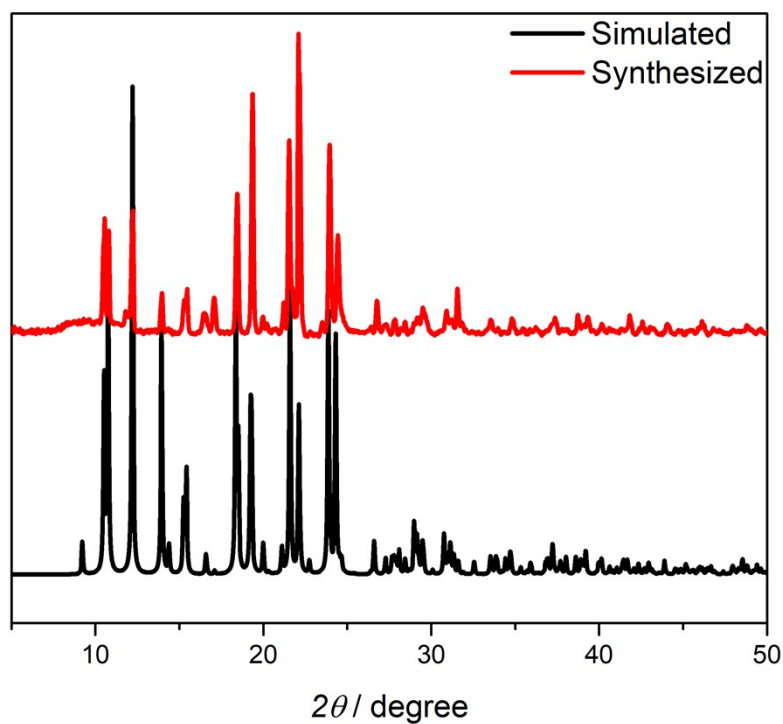


**Figure S3.** TGA plot of **3** measured under an argon atmosphere with a heating rate of 10 °C /min.

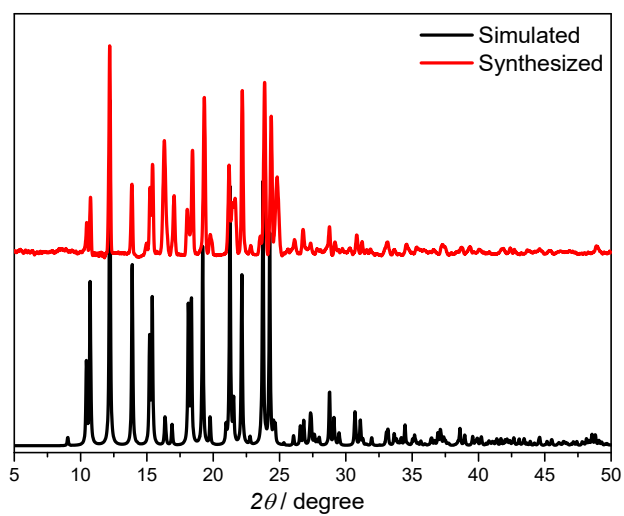


**Figure S4.** TGA plot of **4** measured under an argon atmosphere with a heating rate of 10 °C /min.

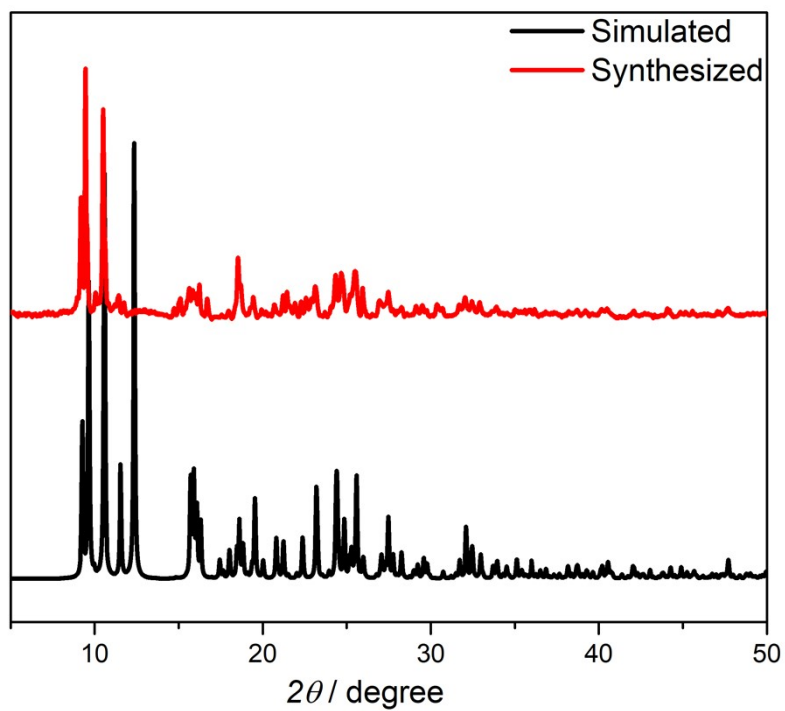




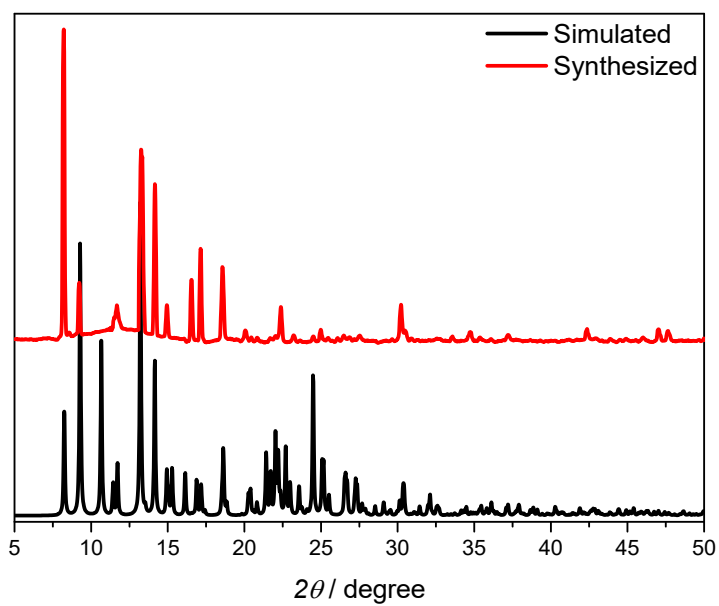
**Figure S5.** The PXRD pattern of **1** at 298 K. The simulated spectra are calculated from single crystal data of **1** at 340 K.



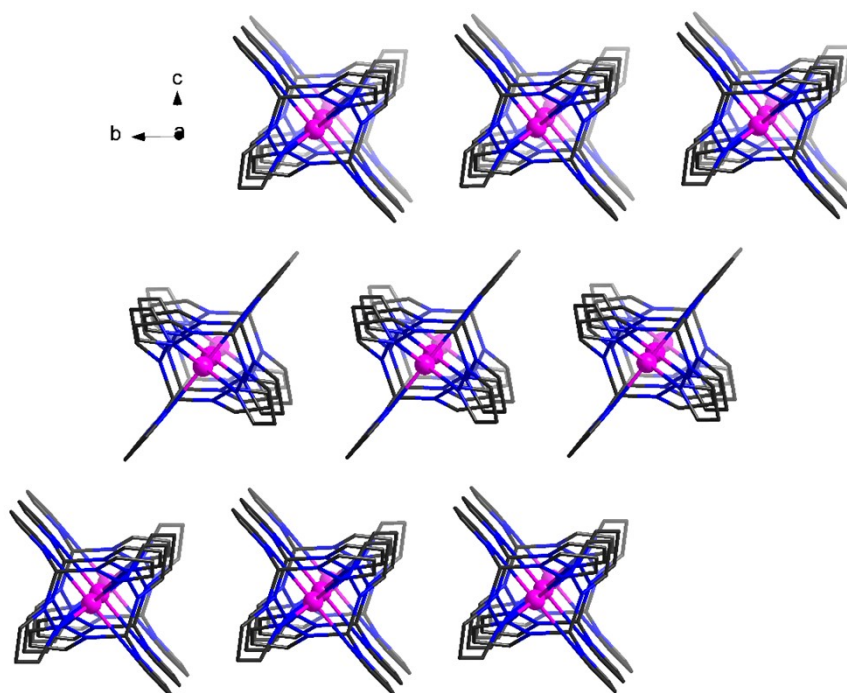
**Figure S6.** The PXRD pattern of **2** at 298 K. The simulated spectra are calculated from single crystal data of **2** at 360 K.



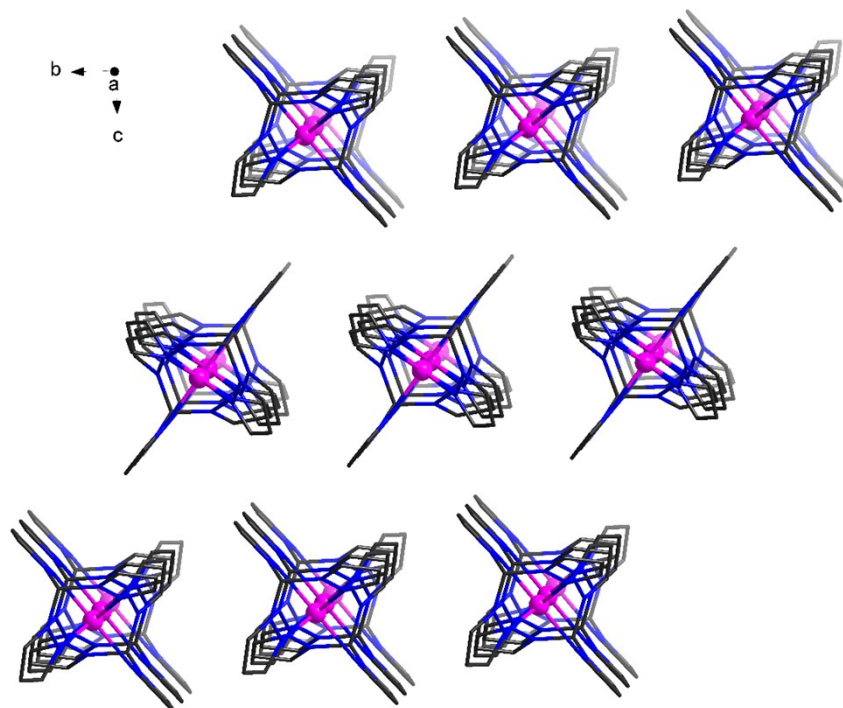
**Figure S7.** The PXRD pattern of **3** at 298 K. The simulated spectra are calculated from single crystal data of **3** at 298 K.



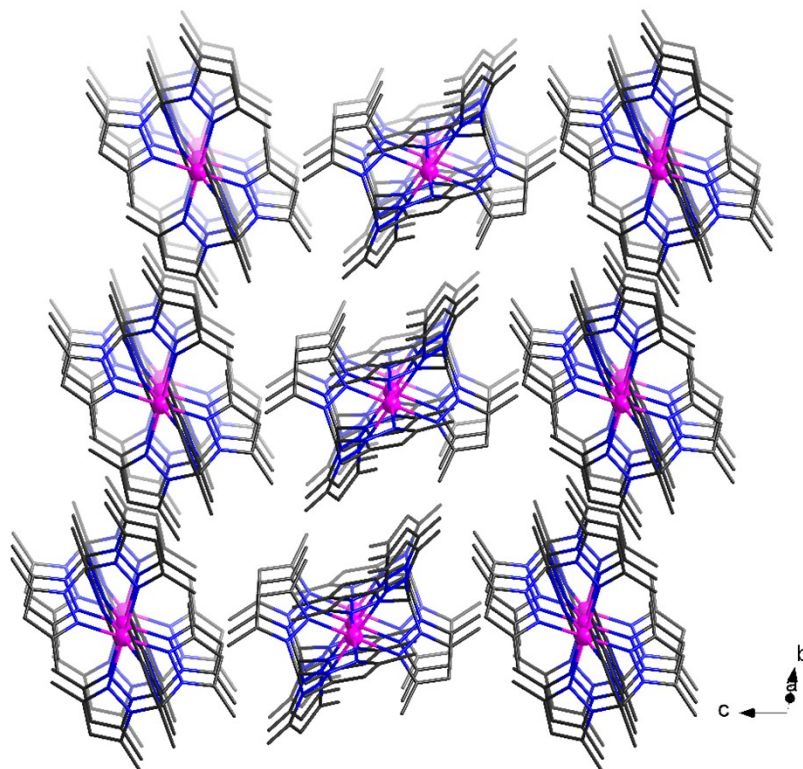
**Figure S8.** The PXRD pattern of **4** at 298 K. The simulated spectra are calculated from single crystal data of **4** at 100 K.



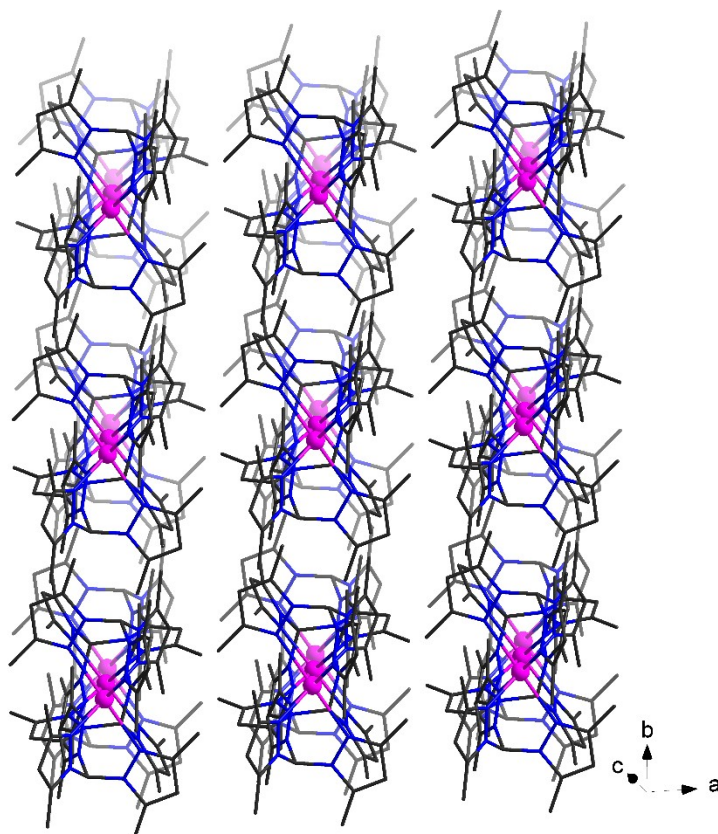
**Figure S9.** The packing structure of **1** at 340 K. Hydrogen atoms and counterions are omitted for clarity.



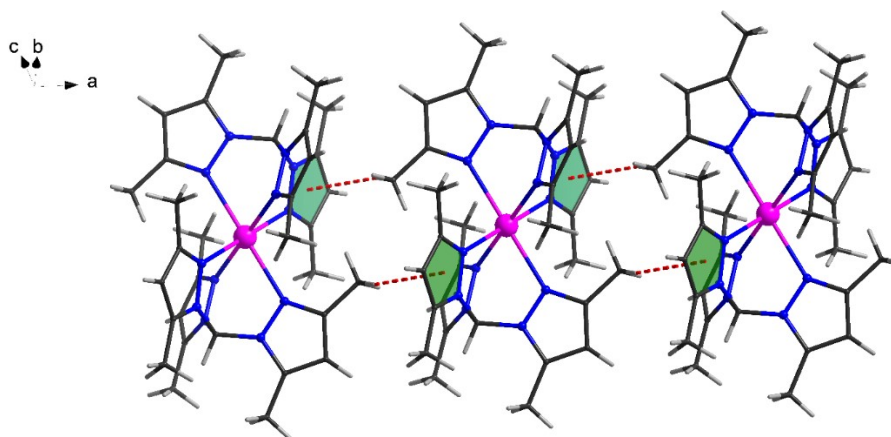
**Figure S10.** The packing structure of **2** at 360 K. Hydrogen atoms and counterions are omitted for clarity.



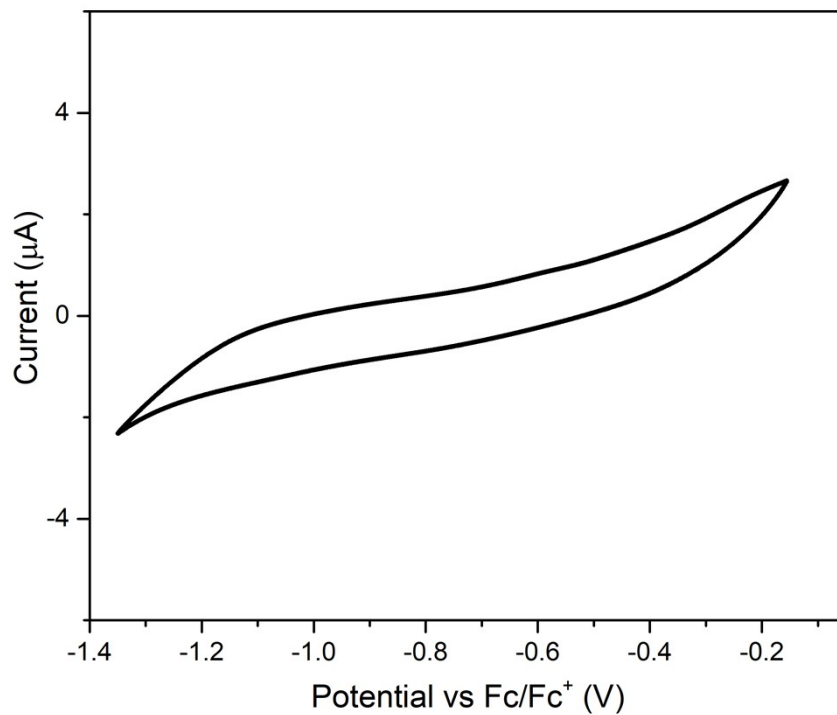
**Figure S11.** The packing structure of **3** at 298 K. Hydrogen atoms and counterions are omitted for clarity.



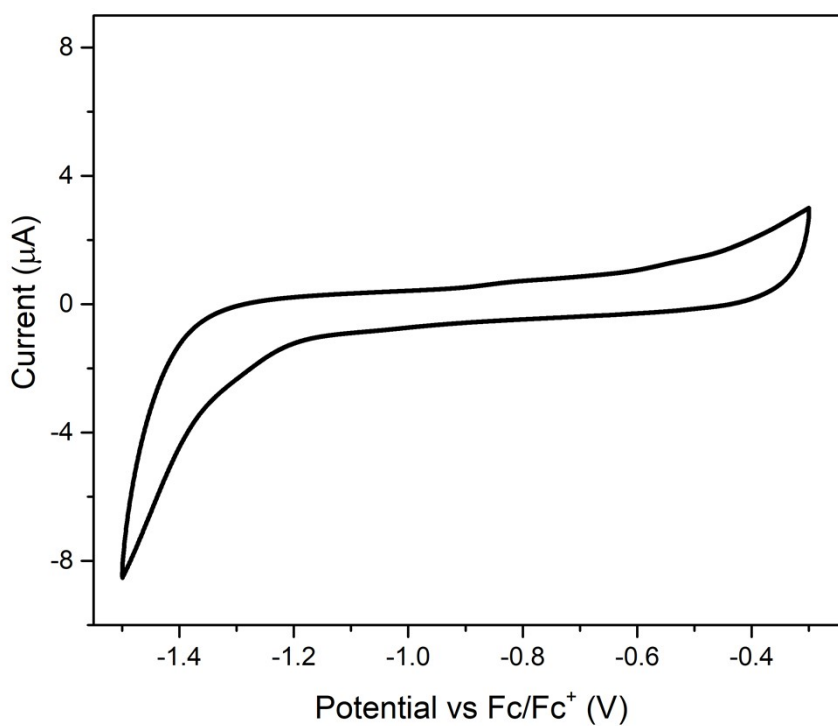
**Figure S12.** The packing structure of **4** at 100 K. Hydrogen atoms and counterions are omitted for clarity.



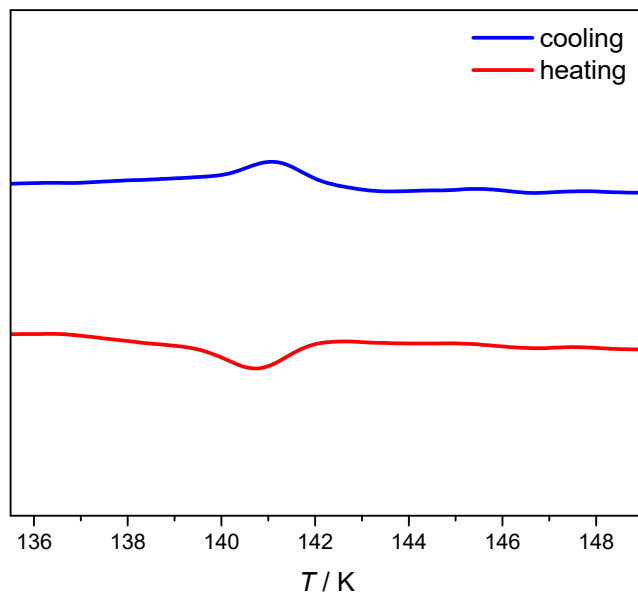
**Figure S13.** View of C-H... $\pi$  interactions (3.58 Å) between adjacent  $[\text{Cr}(\text{Tpm}^*)_2]^{2+}$  cations in **4** at 100 K.



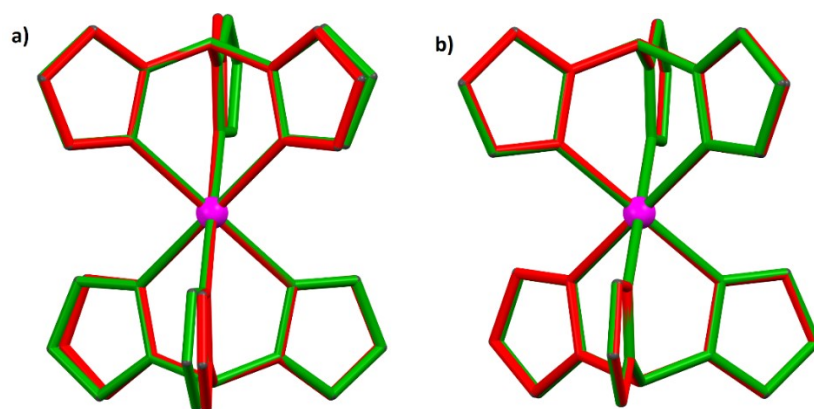
**Figure S14.** Cyclic voltammograms of Tpm in MeCN solution at room temperature.



**Figure S15.** Cyclic voltammograms of Tpm\* in MeCN solution at room temperature.

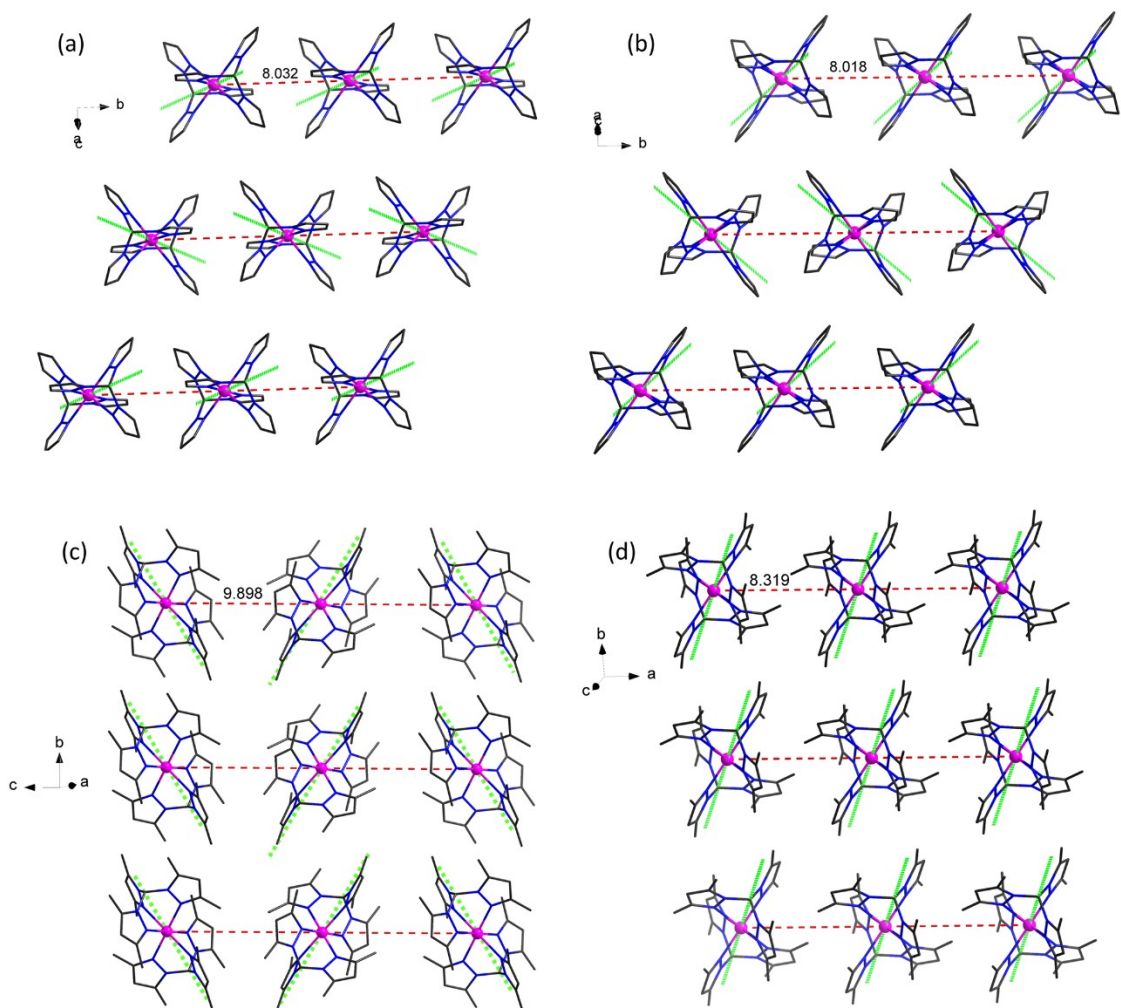


**Figure S16.** DSC plots of **3** at heating (red) and cooling (black) modes.

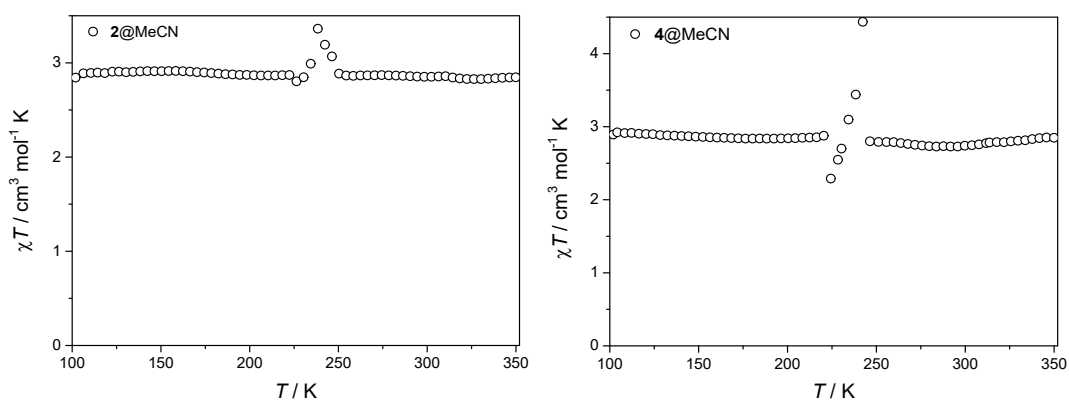


**Figure S17.** The minimized overlay of  $[\text{Cr}(\text{Tpm})_2]^{2+}$  of **1** (green) and **2** (red) at 360 (a) and 100 K (b).



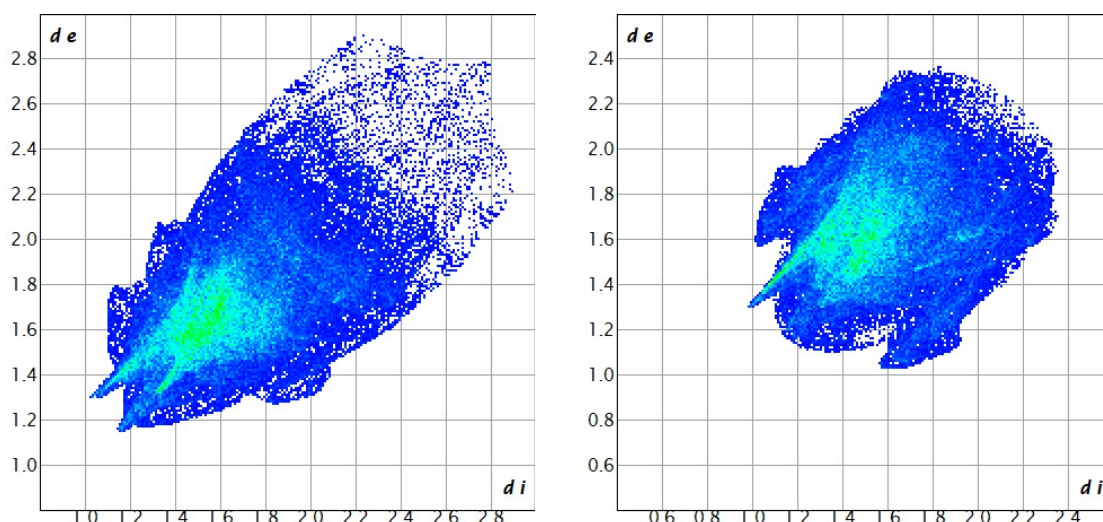


**Figure S18.** The orientations ( $C_3$  axis) of  $[\text{Cr}(\text{Tpm})_2]^{2+}$  cations in **1** (a), **2** (b), **3** (c) and **4** (d) along the nearest intermolecular packing arrangement. The  $C_3$  axis direction is indicated by the dashed green lines.



**Figure S19.** Variable-temperature magnetic susceptibility data of **2** (left) and **4** (right) in MeCN solution.





**Figure S20.** Hirshfeld surfaces associated with the fingerprint plots for the  $[\text{Cr}(\text{Tpm}^*)]^{2+}$  cations of **3** (left) at 298 K and **4** (right) at 100 K.

**Table S6.** Selected parameters for Cr(II) spin-crossover complexes.

Compd.	Coordination environment	Transition type	$T_{1/2}$ / K	reference
$[\text{Cr}^{\text{II}}(\text{depe})_2\text{I}_2]$	$\text{P}_4\text{I}_2$	Abrupt	174	6
$[\text{Cr}^{\text{II}}_2(\mu^2\text{:}\eta^5\text{-P}_5)(\eta^5\text{-Cp}^*)_2][\text{PF}_6]$	$\text{C}_5\text{P}_5$	Hysteretic	33; 31	7
$[\text{Cr}^{\text{II}}_2(\mu^2\text{:}\eta^5\text{-P}_5)(\eta^5\text{-Cp}^*)_2][\text{SbF}_6]$	$\text{C}_5\text{P}_5$	Hysteretic	23; 21	7
$[\text{Cr}^{\text{II}}(\text{1Me-indenyl})_2]$	$\text{C}_{10}$	Gradual	130	8
$[\text{Cr}^{\text{II}}(\text{1,2,3-Me-indenyl})_2]$	$\text{C}_{10}$	Gradual, incomplete	150	9
$[\text{Cr}^{\text{II}}(\text{4,7-Me-indenyl})_2]$	$\text{C}_{10}$	Gradual	250	9
$[\text{Cr}^{\text{II}}(\text{2,4,5,6,7-Me-indenyl})_2]$	$\text{C}_{10}$	Gradual	>350	9
$[\text{Cr}(\text{Tpm})_2][\text{BF}_4]$	$\text{N}_6$	Gradual	190	This work
$[\text{Cr}(\text{Tpm})_2][\text{ClO}_4]$	$\text{N}_6$	Gradual	194	This work
$[\text{Cr}(\text{Tpm}^*)_2][\text{BF}_4]$	$\text{N}_6$	Abrupt, 50 % transition	142	This work

## Reference

1. D. L. Reger, T. C. Grattan, K. J. Brown, C. A. Little, J. J. S. Lamba, A. L. Rheingold and R. D. Sommer, *J. Organomet. Chem.*, 2000, **607**, 120-128.
2. G. M. Sheldrick, SHELXL-2014, Program for the solution of crystal structures. *University of Göttingen, Göttingen, Germany* 2014.
3. G. M. Sheldrick, SADABS, v.2.01, Bruker/Siemens Area Detector Absorption Correction Program. Bruker AXS: Madison. *Wisconsin* 1998.
4. G. A. Bain, J. F. Berry, Diamagnetic Corrections and Pascal's Constants. *J. Chem. Educ.* 2008, **85**, 532-536.
5. SHAPE: continuous shape measures calculation, version 2.0; Electronic Structure Group, Universitat de Barcelona: Barcelona, Spain, 2010.
6. D. M. Halepoto, D. G. Holt, L. F. Larkworthy, G. J. Leigh, D. C. Povey and G. W. Smith, *J. Chem. Soc., Chem.*

*Commun.*, 1989, 1322-1323.

7. A. K. Hughes, V. J. Murphy and D. O'Hare, *J. Chem. Soc., Chem. Commun.*, 1994, 163-164.

8. M. B. Meredith, J. A. Crisp, E. D. Brady, T. P. Hanusa, G. T. Yee, N. R. Brooks, B. E. Kucera and V. G. Young, *Organometallics*, 2006, **25**, 4945-4952.

9. M. B. Meredith, J. A. Crisp, E. D. Brady, T. P. Hanusa, G. T. Yee, M. Pink, W. W. Brennessel and V. G. Young Jr, *Organometallics*, 2008, **27**, 5464-5473.