

## Supplementary Information

### **Fine-Tuning of Thermally Induced SCO Behaviors of Trinuclear Cyanido-Bridged Complexes by Regulating the Electron Donating Ability of C<sub>CN</sub>-Terminal Fragment**

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## Results and Discussion

### Thermo-gravimetric curve of complexes

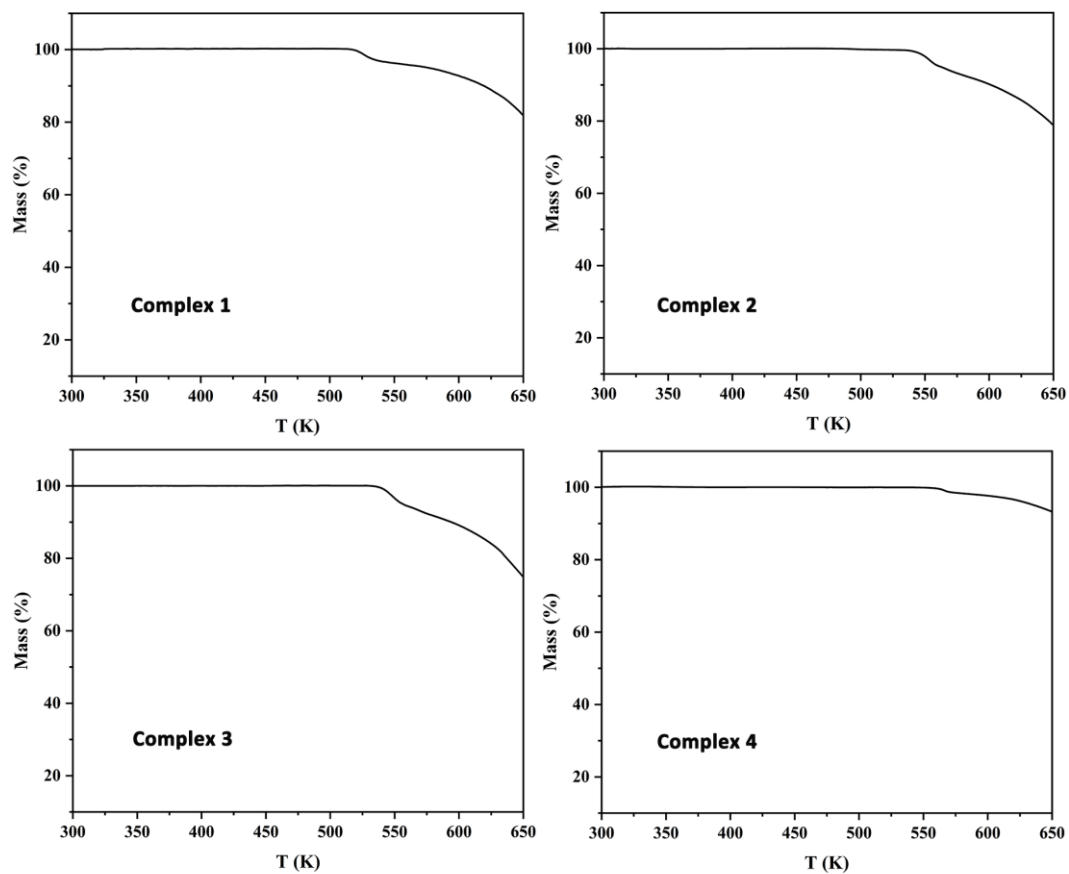


Fig. S1 Thermo-gravimetric curve of 1-4 in flowing nitrogen atmosphere.

## Crystallographic data

**Table S1** Crystallographic data of **0**, **1** and **2** at 293 K

	<b>0</b>	<b>1</b>	<b>2</b>
Empirical formula	C <sub>28</sub> H <sub>28</sub> F <sub>6</sub> FeN <sub>12</sub> O <sub>8</sub> S <sub>2</sub>	C <sub>92</sub> H <sub>82</sub> F <sub>6</sub> Fe <sub>3</sub> N <sub>14</sub> O <sub>6</sub> P <sub>4</sub> S <sub>2</sub>	C <sub>98</sub> H <sub>94</sub> F <sub>6</sub> Fe <sub>3</sub> N <sub>14</sub> O <sub>6</sub> P <sub>4</sub> S <sub>2</sub>
Color and Habit	Faint yellow block	Black-red block	Dark red block
Crystal Size (mm)	0.425'0.353'0.272	0.417'0.335'0.237	0.385'0.327'0.216
Temperature(K)	293	293	293
Crystal system	Triclinic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
a (Å)	10.898(2)	12.8808(3)	12.2516(2)
b (Å)	11.798(3)	20.5335(5)	20.5089(3)
c (Å)	15.055(4)	17.2688(4)	19.4786(3)
alpha (deg.)	87.208(7)	90	90
beta (deg.)	75.799(5)	97.894(2)	101.0760(10)
gamma (deg.)	78.617(7)	90	90
Volume (Å <sup>3</sup> )	1839.6(7)	4524.11(19)	4803.16(13)
Z	2	2	2
Formula weight	894.59	1949.26	2033.42
Density(cal.)(g·cm <sup>-3</sup> )	1.615	1.431	1.406
μ(mm <sup>-1</sup> )	0.619	3.762	3.558
F(000)	912.0	2008.0	2104.0
Theta range (deg.)	2.79 to 52.744	5.846 to 109.642	5.494 to 109.642
Reflections collected	19461	33051	41673
Independent reflections	7432 [R <sub>int</sub> = 0.0472]	8573 [R <sub>int</sub> = 0.0929]	9106 [R <sub>int</sub> = 0.0288]
Index range	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18	-14 ≤ h ≤ 15, -19 ≤ k ≤ 25, -21 ≤ l ≤ 21	-14 ≤ h ≤ 11, -24 ≤ k ≤ 25, -23 ≤ l ≤ 23
Data/restraints/parameters	7432/7/527	8573/13/575	9106/2/605
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0709, wR <sub>2</sub> = 0.1807	R <sub>1</sub> = 0.0869, wR <sub>2</sub> = 0.2035	R <sub>1</sub> = 0.0444, wR <sub>2</sub> = 0.1210
Final R indexes [all data]	R <sub>1</sub> = 0.0900, wR <sub>2</sub> = 0.2105	R <sub>1</sub> = 0.1303, wR <sub>2</sub> = 0.2251	R <sub>1</sub> = 0.0532, wR <sub>2</sub> = 0.1268
Goodness-of-fit	1.041	1.038	0.987

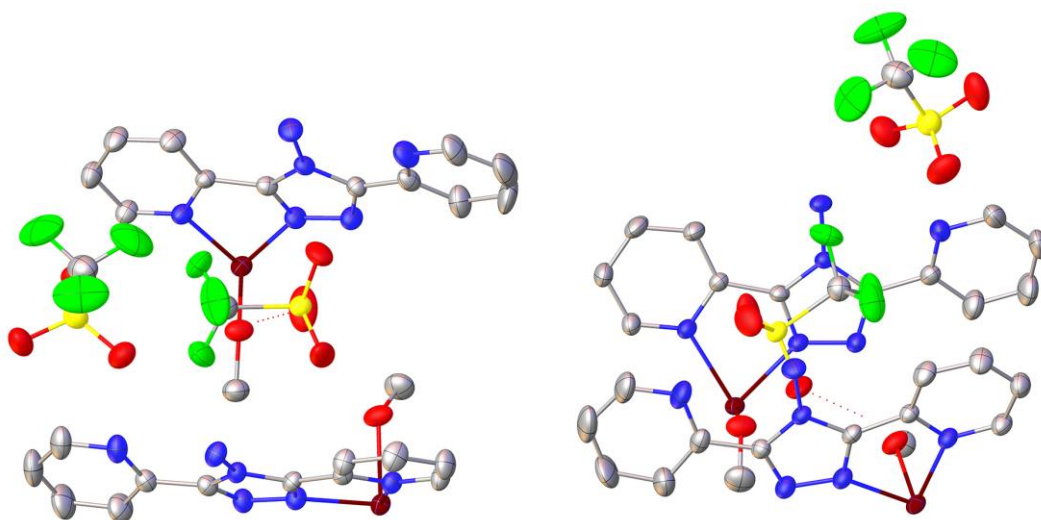
$$R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|; wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}$$

**Table S2** Crystallographic data of **3** for 100 K and 293 K and **4** for 293 K

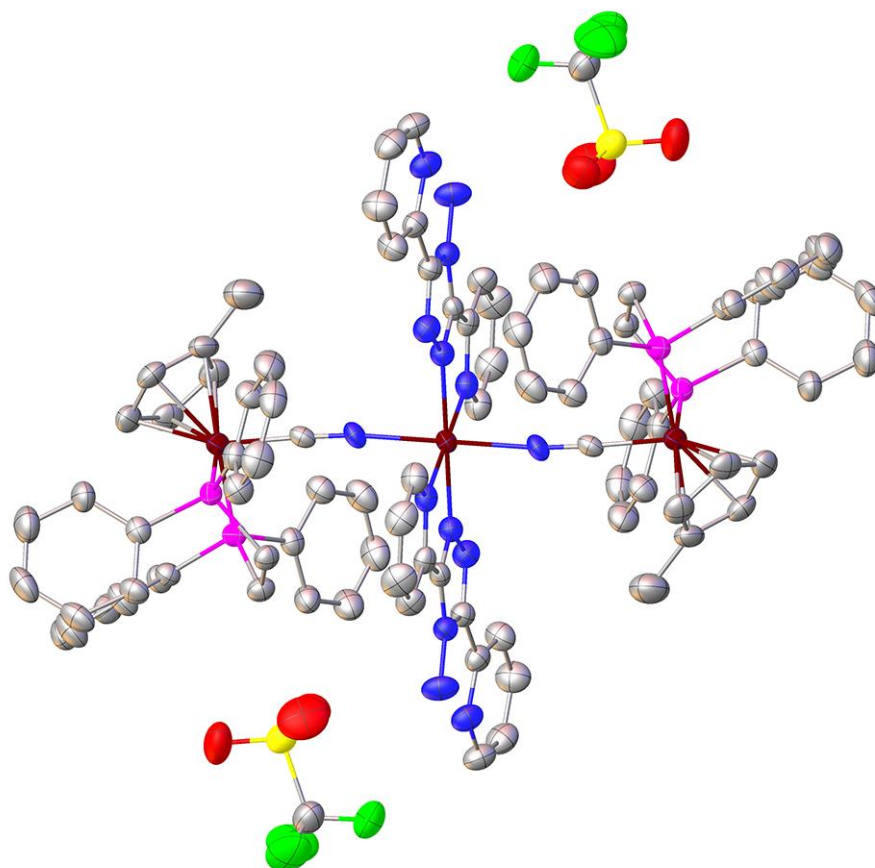
	<b>3 (100 K)</b>	<b>3(293 K)</b>	<b>4</b>
Empirical formula	C <sub>100</sub> H <sub>98</sub> F <sub>6</sub> Fe <sub>3</sub> N <sub>14</sub> O <sub>6</sub> P <sub>4</sub> S <sub>2</sub>	C <sub>100</sub> H <sub>98</sub> F <sub>6</sub> Fe <sub>3</sub> N <sub>14</sub> O <sub>6</sub> P <sub>4</sub> S <sub>2</sub>	C <sub>100</sub> H <sub>98</sub> F <sub>6</sub> FeN <sub>14</sub> O <sub>6</sub> P <sub>4</sub> Ru <sub>2</sub> S <sub>2</sub>
Color and Habit	Dark red block	Red block	Dark red block
Crystal Size (mm)	0.328'0.275'0.213	0.315'0.246'0.202	0.426'0.342'0.304
Temperature(K)	100	293	293
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
a (Å)	11.8086(2)	12.00670(10)	12.1314(2))
b (Å)	14.1394(3)	14.40640(10)	14.6758(3)
c (Å)	15.5340(4)	15.52430(10)	15.4174(3)
alpha (deg.)	70.707(2)	71.0090(10)	71.000(2)
beta (deg.)	84.123(2)	84.4960(10)	83.364(2))
gamma (deg.)	81.194(2)	81.4470(10)	79.993(2)
Volume (Å <sup>3</sup> )	2415.41(10)	2507.65(4)	2550.72(9)
Z	1	1	1
Formula weight	2061.47	2061.47	2151.91
Density(cal.)(g·cm <sup>-3</sup> )	1.417	1.365	1.401
μ(mm <sup>-1</sup> )	0.628	3.412	3.403
F(000)	1068.0	1068.0	1104.0
Theta range (deg.)	4.346 to 61.006	5.684 to 109.64	5.596 to 109.644
Reflections collected	41959	31325	28796
Independent reflections	13808 [R <sub>int</sub> = 0.0321]	9481 [R <sub>int</sub> = 0.0270]	9569 [R <sub>int</sub> = 0.0298]
Index range	-16 ≤ h ≤ 15, -20 ≤ k ≤ 20, -17 ≤ l ≤ 21	-14 ≤ h ≤ 14, -16 ≤ k ≤ 17, -18 ≤ l ≤ 16	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -18 ≤ l ≤ 17
Data/restraints/parameters	13808/124/687	9481/8/615	9569/16/615
Final R indexes [I>=2σ(I)]	R <sub>1</sub> = 0.0422, wR <sub>2</sub> = 0.1092	R <sub>1</sub> = 0.0540, wR <sub>2</sub> = 0.1508	R <sub>1</sub> = 0.0450, wR <sub>2</sub> = 0.1332
Final R indexes [all data]	R <sub>1</sub> = 0.0597, wR <sub>2</sub> = 0.1179	R <sub>1</sub> = 0.0604, wR <sub>2</sub> = 0.1549	R <sub>1</sub> = 0.0515, wR <sub>2</sub> = 0.1384
Goodness-of-fit	0.997	1.043	1.001

$$R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|; wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}$$

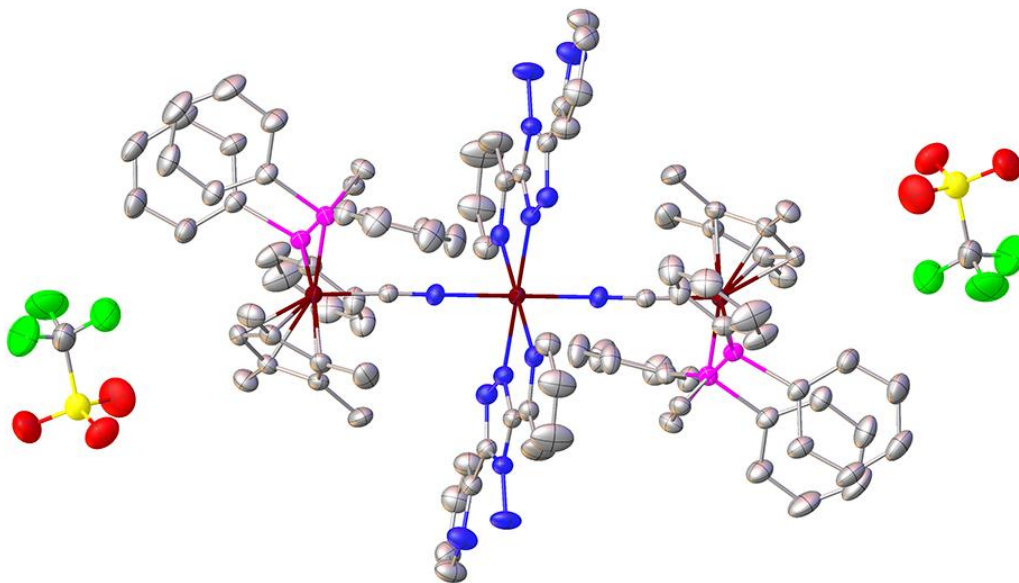
## Thermal ellipsoid figure of complexes



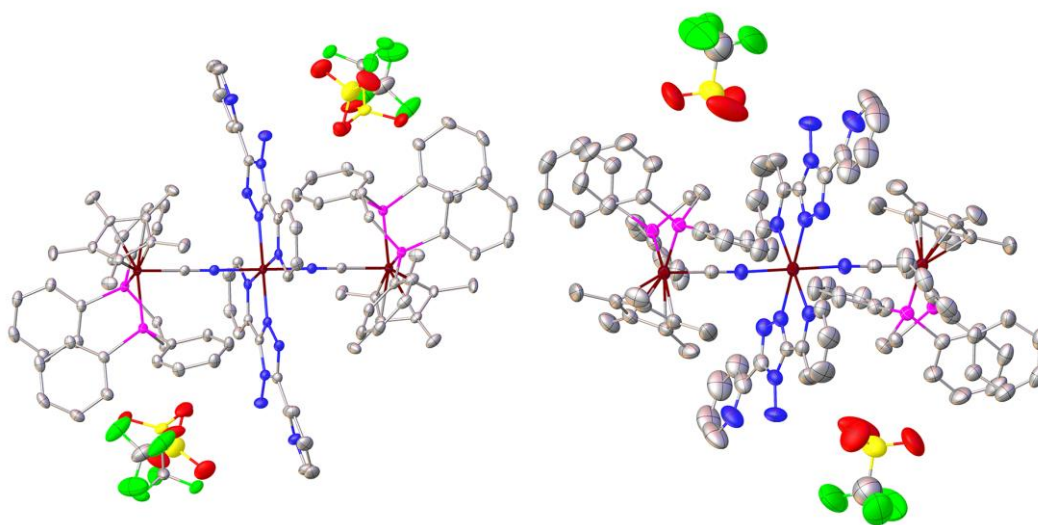
**Fig. S2** Thermal ellipsoid figure of **0** at 293 K. Hydrogen atoms have been omitted for clarity. Reddish brown, Fe; pink, P; green, F; faint yellow; S; red, O; gray, C; dark blue, N.



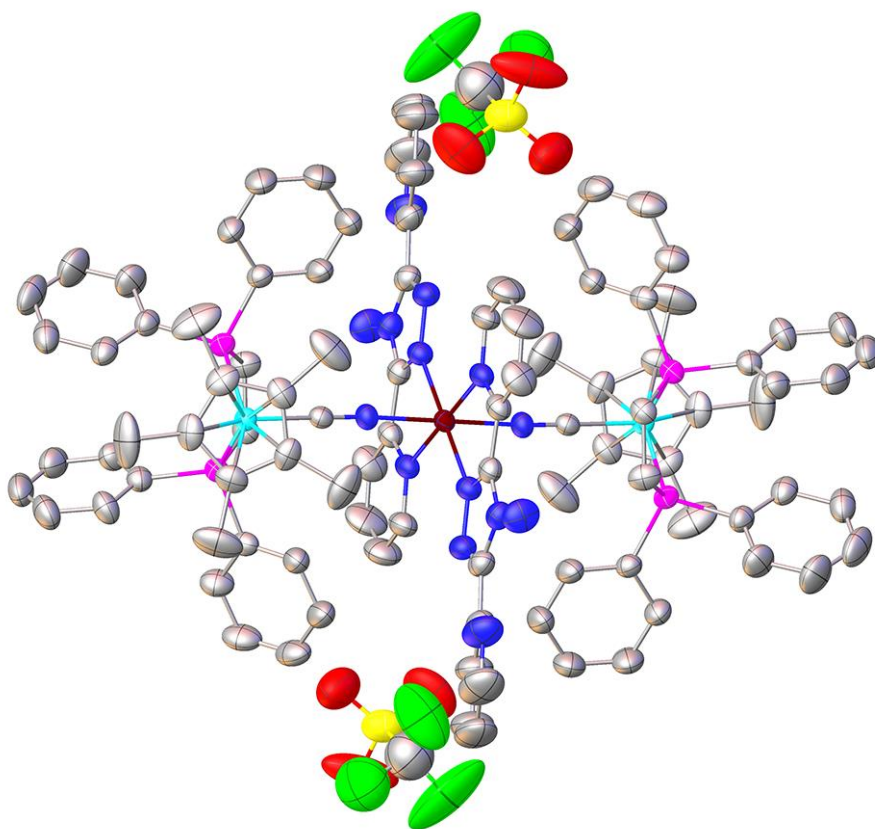
**Fig. S3** Thermal ellipsoid figure of **1** at 293 K. Hydrogen atoms have been omitted for clarity. Reddish brown, Fe; Tiffany blue, Ru; pink, P; green, F; faint yellow; S; red, O; gray, C; dark blue, N.



**Fig. S4** Thermal ellipsoid figure of **2** at 293 K. Hydrogen atoms have been omitted for clarity. Reddish brown, Fe; pink, P; green, F; faint yellow, S; red, O; gray, C; dark blue, N.



**Fig. S5** Thermal ellipsoid figure of **3** at 100 K and 293 K. Hydrogen atoms have been omitted for clarity. Reddish brown, Fe; pink, P; green, F; faint yellow, S; red, O; gray, C; dark blue, N.



**Fig. S6** Thermal ellipsoid figure of **4** at 100 K and 293 K. Hydrogen atoms have been omitted for clarity. Reddish brown, Fe; pink, P; green, F; faint yellow; S; red, O; gray, C; dark blue, N.



## Crystal packing figure of the complexes

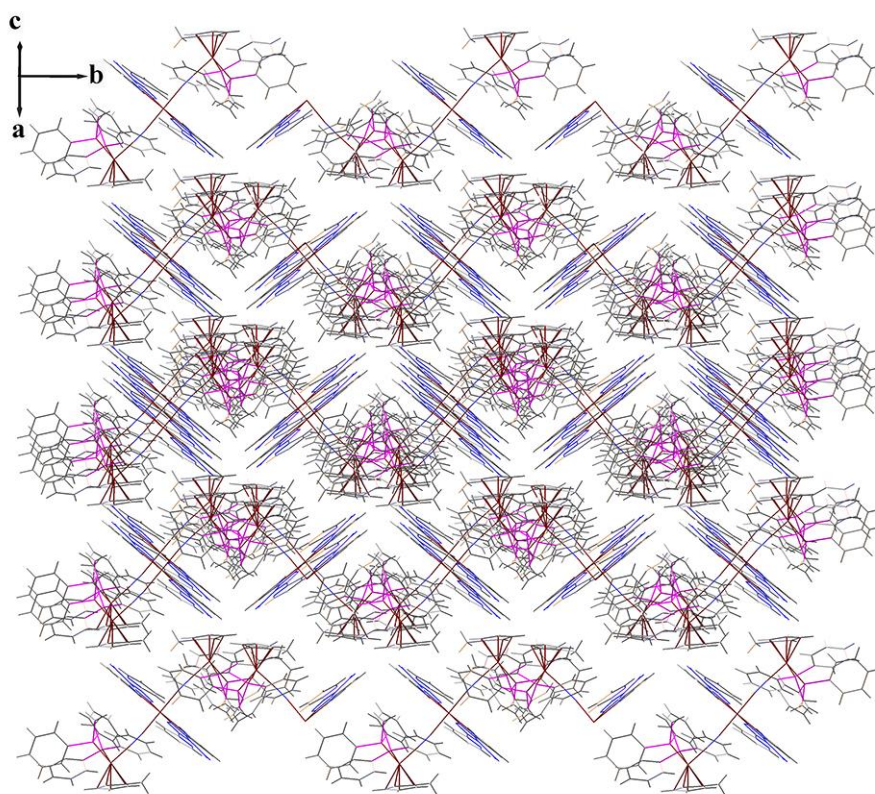


Fig. S7 Molecular packing figure of **1** at 293 K, and  $\text{CF}_3\text{SO}_3^-$  anions have been removed for clarity.

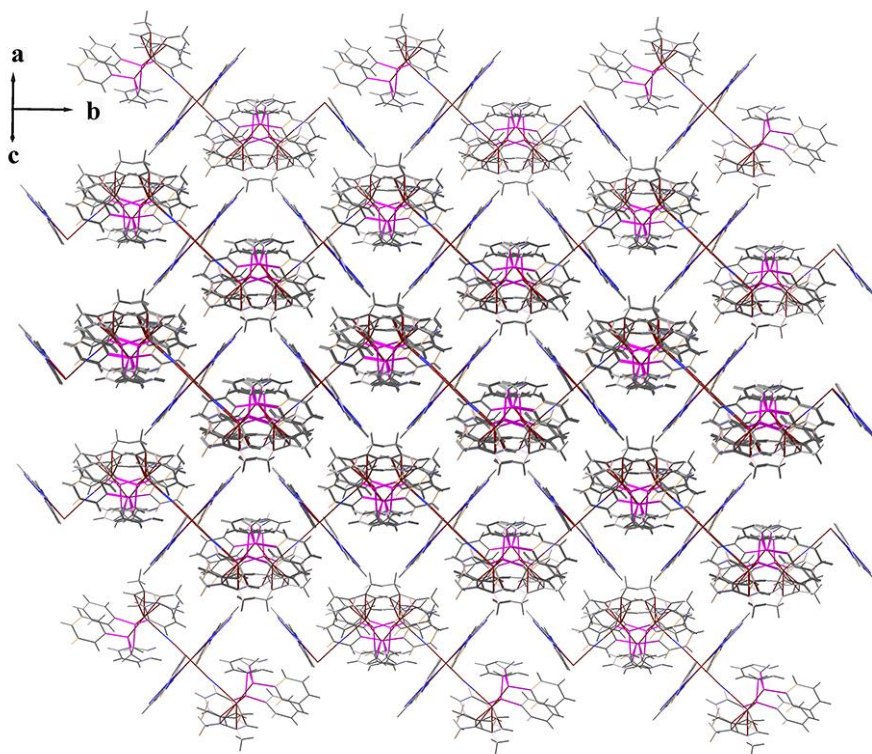
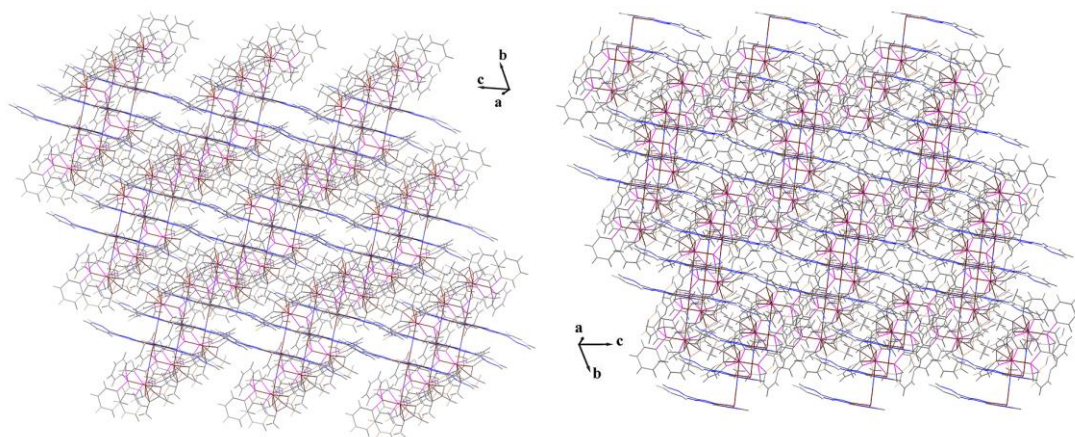
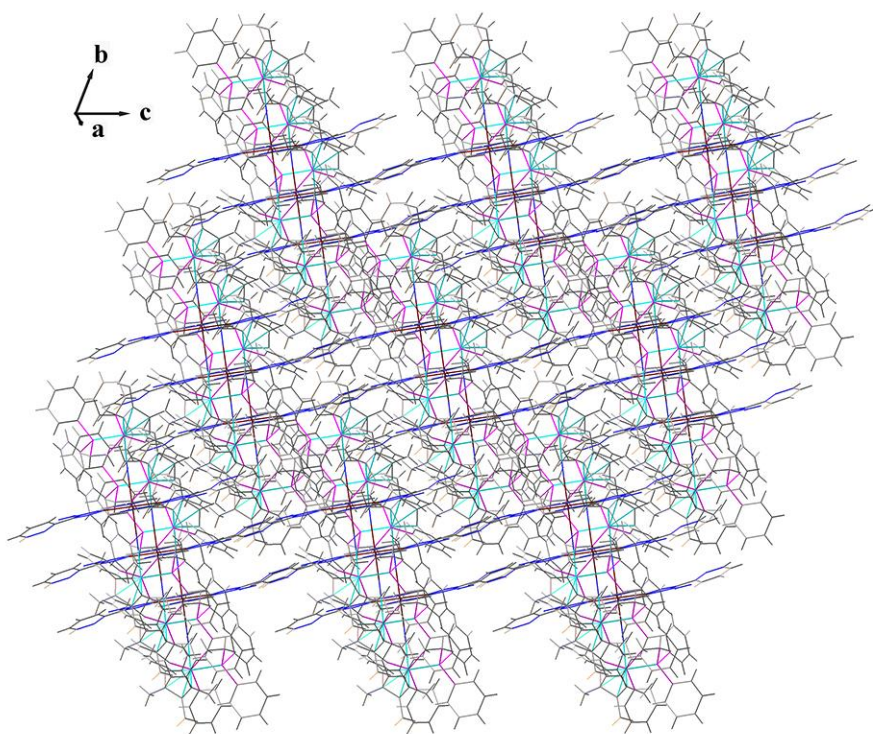


Fig. S8 Molecular packing figure of **2** at 293 K, and  $\text{CF}_3\text{SO}_3^-$  anions have been removed for clarity.



**Fig. S9** Molecular packing figure of **3** at 100 K (left) and 293 K (right), and  $\text{CF}_3\text{SO}_3^-$  anions have been removed for clarity.



**Fig. S10** Molecular packing figure of **4** at 293 K, and  $\text{CF}_3\text{SO}_3^-$  anions have been removed for clarity.

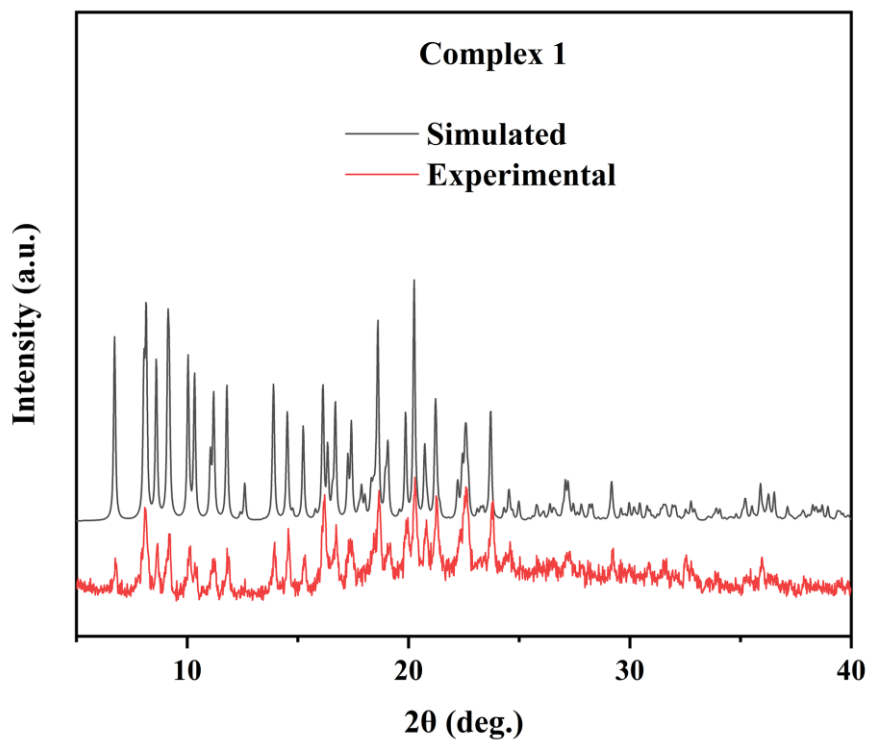


Fig. S11. Powder X-ray diffraction of 1.

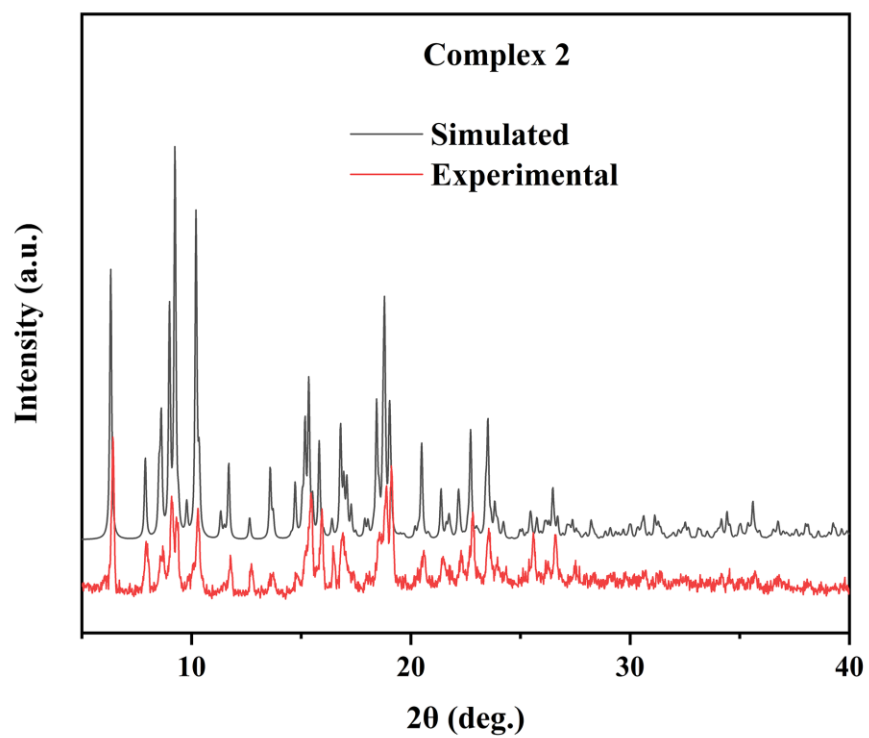


Fig. S12. Powder X-ray diffraction of 2.



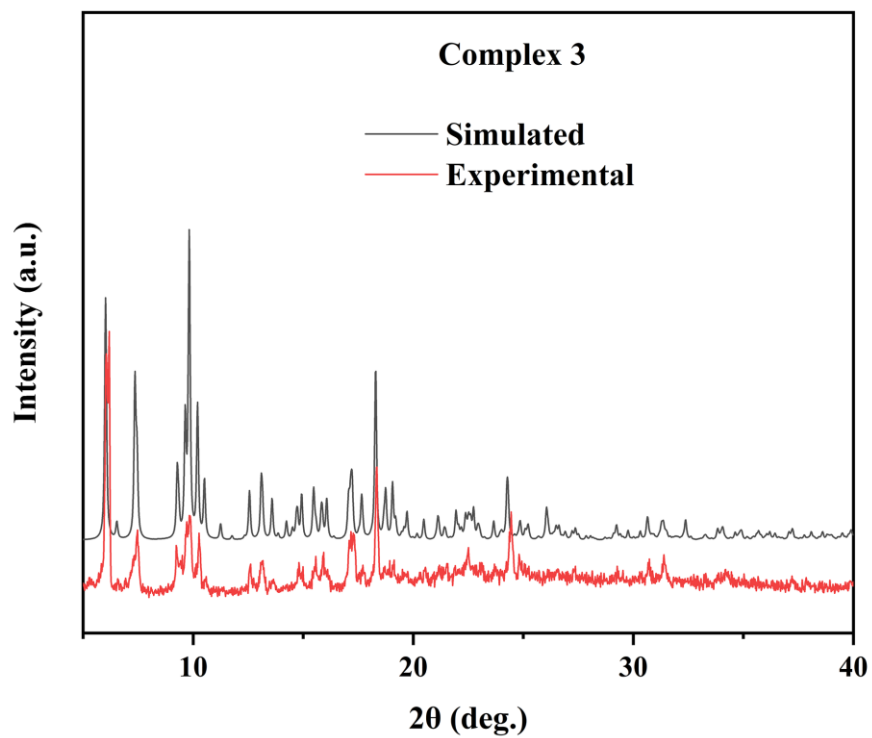


Fig. S13. Powder X-ray diffraction of 3.

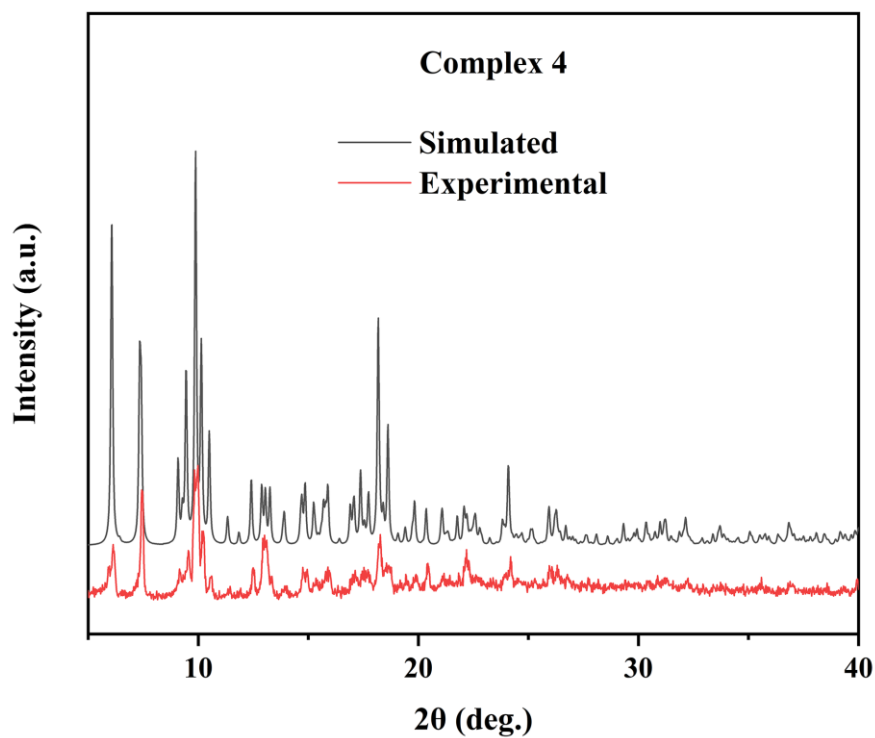


Fig. S14. Powder X-ray diffraction of 4.