

**Supporting Information for:**

**Effects of Ru (II/III) redox on the Co (II)  
coordination number and magnetic property  
of 1D cyanide-bridged Co-Ru compound**

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and Tianlu Sheng\*

**Preparation of compounds and Physical Measurements** All manipulations are performed under a nitrogen atmosphere with the use of standard Schlenk techniques unless otherwise stated. The complexes trans-Ru(dmap)<sub>4</sub>(CN)<sub>2</sub>, trans-Ru(dmap)<sub>4</sub>(CN)<sub>2</sub>(PF<sub>6</sub>)<sup>1</sup> and Co(dipic)(DMSO)<sub>2</sub>(H<sub>2</sub>O)<sup>2</sup> (dmap = 4-dimethylaminopyridine, dipic<sup>2-</sup> = pyridine-2,6-dicarboxylate) were prepared according to literature procedures. All other reagents were available commercially and used without further purification. Elemental analyses (C, H, N) was carried out on Vario MICRO elemental analyzer. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer with KBr pellet. Magnetic susceptibilities on crystalline samples were measured with a Quantum Design MPMS-XL SQUID suscepto-meter under an applied magnetic field of 1 kOe in the 2-300 K range. Diamagnetic corrections were made using Pascal's constants.<sup>4</sup> The single crystal data for complexes **1a** and **1b** were collected on a Saturn724 + CCD diffractometer equipped with graphite monochromatic Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation by using an  $\omega$ -scan model technique at 123 K. All the structures were solved using SHELXL-97 and refined by the full-matrix least-squares techniques on F<sup>2</sup> with SHELXL-97.<sup>5</sup>

**Synthesis of {[trans-Ru(dmap)<sub>4</sub>(CN)<sub>2</sub>Co(dipic)(MeOH)](PF<sub>6</sub>)}<sub>n</sub> (**1a**).**

Trans-Ru(dmap)<sub>4</sub>(CN)<sub>2</sub>(PF<sub>6</sub>) (157.2mg, 0.2mmol) was dissolved in 60mL methanol, and Co(dipic)(DMSO)<sub>2</sub>(H<sub>2</sub>O) (87.6mg, 0.22mmol) was added. The solution was refluxed for over-night and then filtrated. The filtrate was layered with diethyl ether and dark blue crystals 1·2MeOH·H<sub>2</sub>O were obtained after one week. The pure crystals were collected after washed with methanol and diethyl ether (yield: 38.6mg, 18.52%). Anal. Calc for RuCoC<sub>38</sub>H<sub>47</sub>N<sub>11</sub>O<sub>5</sub>PF<sub>6</sub>·6H<sub>2</sub>O: C 39.66, H 5.17, N 13.39%. Found: C 39.50, H 4.65, N 13.70%.

**Synthesis of [trans-Ru(dmap)<sub>4</sub>(CN)<sub>2</sub>Co(dipic)]<sub>n</sub> (**1b**).**

This way of synthesizing compound **1b** was similar to compound **1a**: trans-Ru(dmap)<sub>4</sub>(CN)<sub>2</sub> (320.5mg, 0.5mmol) was dissolved in 60mL methanol, and Co(dipic)(DMSO)<sub>2</sub>(H<sub>2</sub>O) (218.9mg, 0.55mmol) was added. The solution was refluxed for over-night. The resulting solution was layered with diethyl ether and green crystals were obtained after one week. The pure product was collected after washed with methanol, isopropanol and diethyl ether, and dried in vacuum (yield: 257.3mg, 59.49%). Anal. Calc for RuCoC<sub>37</sub>H<sub>43</sub>N<sub>11</sub>O<sub>4</sub>·H<sub>2</sub>O: C 49.28, H 5.25, N 17.08%. Found: C 49.42, H 5.14, N 17.48%.

**Table S1.** Crystallographic data for compounds **1a**, and **1b**

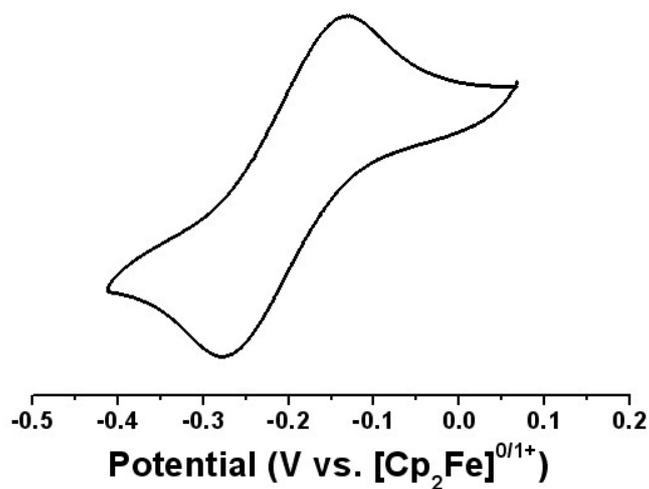
	<b>1a • 2MeOH • H<sub>2</sub>O</b>	<b>1b • 0.5MeOH • 3.5H<sub>2</sub>O • 0.25DMSO</b>
Empirical formula	C <sub>40</sub> H <sub>45</sub> CoF <sub>6</sub> N <sub>11</sub> O <sub>8</sub> PRu	C <sub>38</sub> H <sub>46</sub> CoN <sub>11</sub> O <sub>8.25</sub> RuS <sub>0.25</sub>
Color and Habit	blue Prism	green Prism
Crystal Size (mm)	0.762×0.205 ×0.180	0.386×0.114×0.097
Crystal system	Orthorhombic	Monoclinic
Space group	Cmc2(1)	C2/c
a (Å)	17.335(4)	45.67(3)
b (Å)	14.154(4)	9.691(7)
c (Å)	20.474(4)	22.736(16)
alpha (deg.)	90	90
beta (deg.)	90	93.931(16)
gamma (deg.)	90	90
Volume(Å <sup>3</sup> )	5023.6(19)	10039(12)
Z	4	8
Formula weight	1112.84	956.87
Density(cal.)(Mg/m <sup>3</sup> )	1.471	1.266
Absorption coefficient(mm <sup>-1</sup> )	0.743	0.696
F(000)	2264	3936
Reflections measured	19106	30500
Independent reflections	5909 (Rint = 0.0718)	8728 (Rint = 0.0895)
Observed Reflection	4686 (>2sigma(I))	5264 (>2sigma(I))
Parameter/Restraints/Data(obs.)	330 / 17 / 4686	556 / 67 / 5264
Final R indices (obs.)	R1 = 0.0676, wR2 = 0.1916	R1 = 0.1172, wR2 = 0.2165
R indices (all)	R1 = 0.0777, wR2 = 0.2046	R1 = 0.1648, wR2 = 0.2408
Goodness-of-fit	1.000	0.994

**Table S2.** Bond lengths (Å) and angles (deg.) for compound **1a**

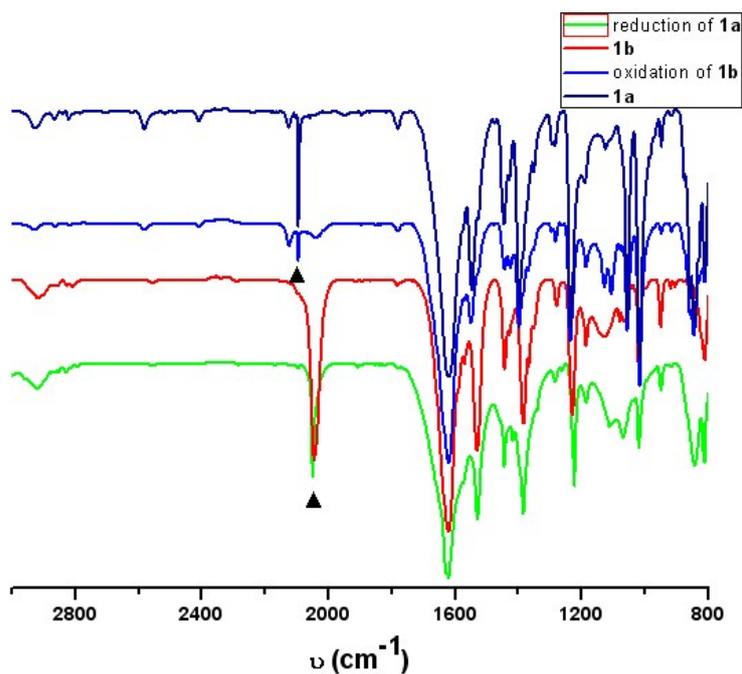
Ru(1)-C(19)	2.034(9)	C(19)-Ru(1)-C(20)	180.0(4)
Ru(1)-C(20)	2.062(8)	C(19)-Ru(1)-N(3)	90.1(2)
Ru(1)-N(3)	2.077(5)	C(20)-Ru(1)-N(3)	90.0(2)
Ru(1)-N(1)	2.112(6)	C(19)-Ru(1)-N(1)	89.8(2)
Co(1)-N(5)	2.095(6)	C(20)-Ru(1)-N(1)	90.2(2)
Co(1)-N(7)	2.113(8)	N(3)-Ru(1)-N(1)	90.20(17)
Co(1)-N(6)	2.124(8)	O(3)-Co(1)-N(5)	177.9(3)
Co(1)-O(2)	2.170(5)	O(3)-Co(1)-N(7)	87.4(3)
Co(1)-O(3)	2.012(6)	N(5)-Co(1)-N(7)	90.5(4)
		O(3)-Co(1)-N(6)	92.4(3)
		N(5)-Co(1)-N(6)	89.7(4)
		N(7)-Co(1)-N(6)	179.9(3)
		O(3)-Co(1)-O(2)	104.61(12)
		N(5)-Co(1)-O(2)	75.40(13)
		N(7)-Co(1)-O(2)	90.8(2)
		N(6)-Co(1)-O(2)	89.3(2)
		O(2)-Co(1)-O(2)'	150.8(2)

**Table S3.** Bond lengths (Å) and angles (deg.) for compound **1b**

Ru(1)-C(37)	2.027(9)	C(37)-Ru(1)-C(1)	176.0(4)
Ru(1)-C(1)	2.028(9)	C(37)-Ru(1)-N(4)	91.3(4)
Ru(1)-N(4)	2.088(8)	C(1)-Ru(1)-N(4)	92.1(4)
Ru(1)-N(6)	2.098(8)	C(37)-Ru(1)-N(6)	88.6(3)
Ru(1)-N(2)	2.111(8)	C(1)-Ru(1)-N(6)	89.5(3)
Ru(1)-N(8)	2.135(8)	N(4)-Ru(1)-N(6)	87.1(3)
Co(1)-N(1)	1.973(9)	C(37)-Ru(1)-N(2)	89.0(4)
Co(1)-N(11)	1.977(8)	C(1)-Ru(1)-N(2)	87.6(4)
Co(1)-N(10)	2.006(11)	N(4)-Ru(1)-N(2)	179.4(3)
Co(1)-O(3)	2.125(10)	N(6)-Ru(1)-N(2)	93.4(3)
Co(1)-O(1)	2.273(10)	C(37)-Ru(1)-N(8)	91.3(3)
		C(1)-Ru(1)-N(8)	90.7(3)
		N(4)-Ru(1)-N(8)	91.0(3)
		N(6)-Ru(1)-N(8)	178.1(3)
		N(2)-Ru(1)-N(8)	88.5(3)
		N(1)-Co(1)-N(11)	115.0(4)
		N(1)-Co(1)-N(10)	129.3(4)
		N(11)-Co(1)-N(10)	114.0(4)
		N(1)-Co(1)-O(3)	103.9(4)
		N(11)-Co(1)-O(3)	102.0(4)
		N(10)-Co(1)-O(3)	77.5(4)
		N(1)-Co(1)-O(1)	90.2(4)
		N(11)-Co(1)-O(1)	91.2(4)
		N(10)-Co(1)-O(1)	76.7(4)
		O(3)-Co(1)-O(1)	154.1(3)

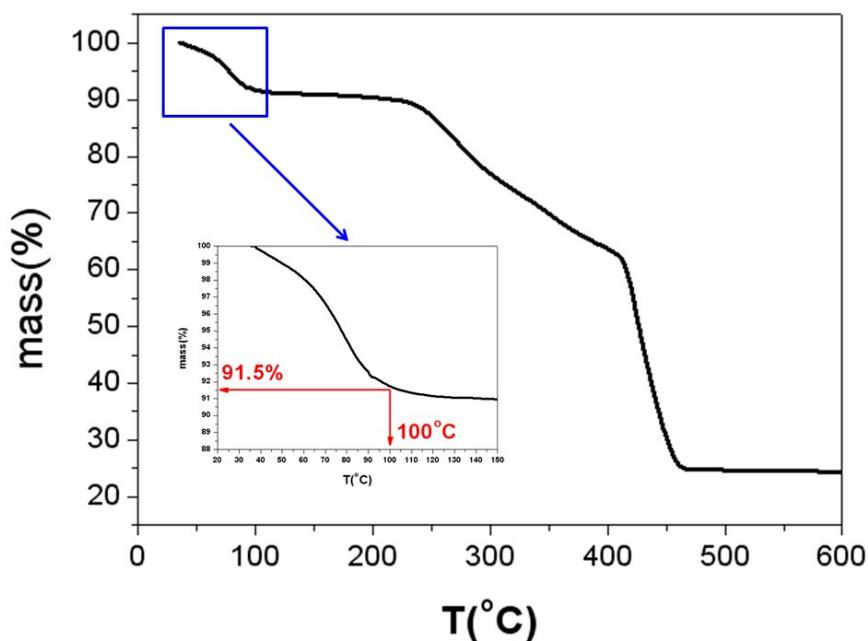


**Figure S1.** Cyclic voltammogram of **1a** in the MeOH solution of 0.1 M (Bu<sub>4</sub>N)PF<sub>6</sub> using a glassy carbon working electrode, 100 mV/s scan rate.

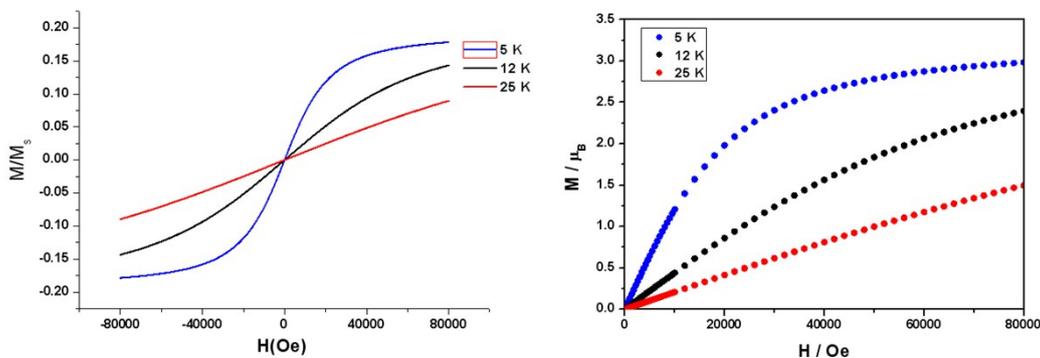


**Figure S2.** IR spectroscopic data of **1a** (blue) and **1b** (red). The weak absorption peak at 2095cm<sup>-1</sup> of **1a** is attributed to the stretching vibration of C≡N bonding with Ru<sup>III</sup>, and the strong absorption peak at 2049cm<sup>-1</sup> of **1b** is attributed to the stretching vibration of C≡N bonding with Ru<sup>II</sup>.<sup>1</sup> (The reduction of **1a** and oxidation of **1b** are

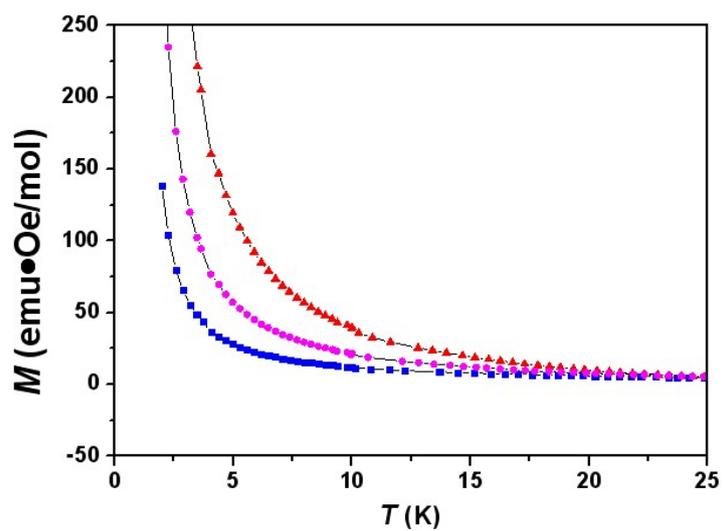
the products of **1a** and **1b** reacted with  $\text{Cp}_2\text{Co}$  and  $\text{Cp}_2\text{Fe}(\text{PF}_6)$ , respectively. )



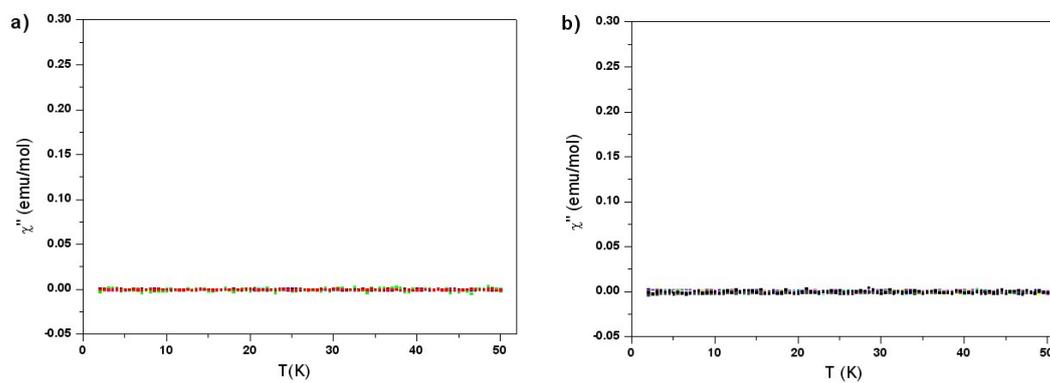
**Figure S3.** Thermogravimetric analysis (TGA) of crystal **1a**·2MeOH·H<sub>2</sub>O, scan rate 10 K/min. The calculated value for loss of three MeOH (one coordinated MeOH, two crystallographic MeOH) is about 8.53%, which corresponds well with the experimental mass loss of about 8.5% until 100 °C. It reveals that crystal **1a**·2MeOH·H<sub>2</sub>O loses three MeOH molecules smoothly from room temperature to 100 °C.



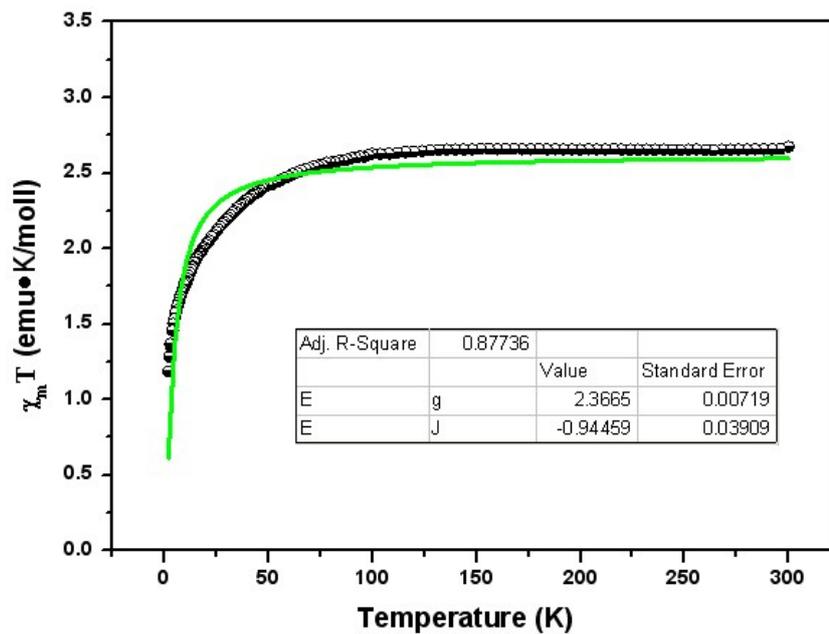
**Figure S4.** Magnetization versus dc magnetic field of **1a** measured at 5K (blue), 12K (black) and 25K (red).



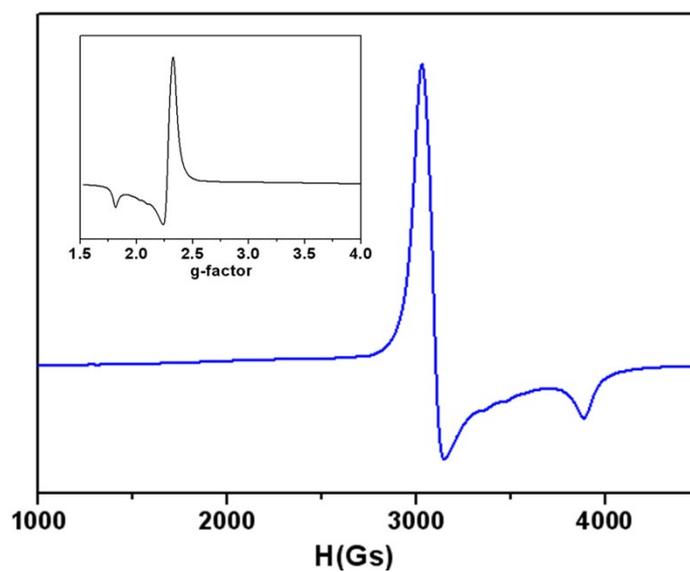
**Figure S5.** Magnetization curves of **1a** at 50 Oe ( $\square$ , blue), 100 Oe ( $\circ$ , pink) and 200 Oe ( $\Delta$ , red)



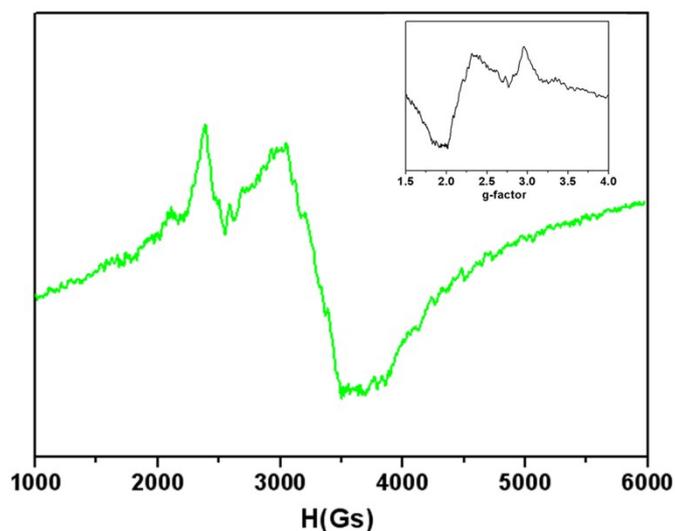
**Figure S6.** Out-of-phase AC magnetic susceptibility vs. temperature for **1a** (a) and **1b** (b) under zero DC field from 0.1 to 10kHz.



**Figure S7.** Variable-temperature dc magnetic susceptibility data for **1b** (circle) and its best-fit result (solid line) using the Fisher model.<sup>3</sup>

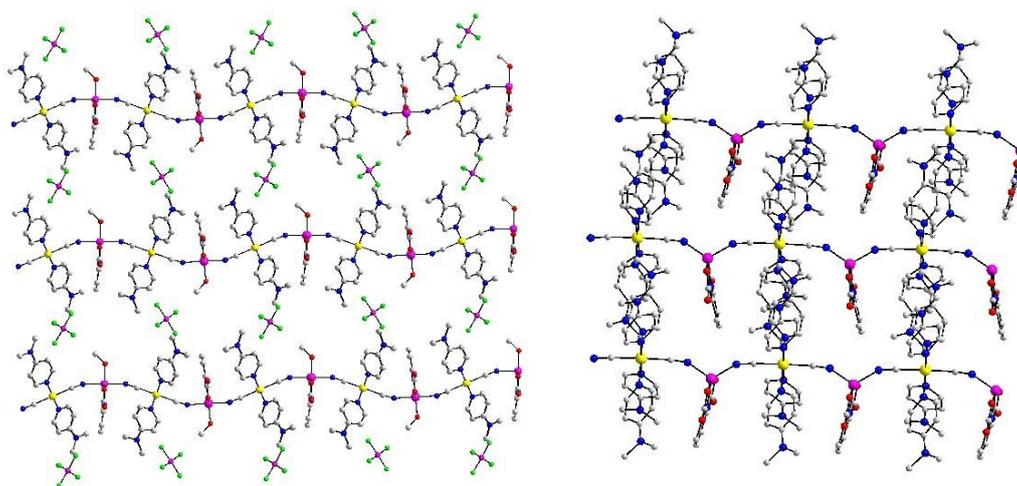


**Figure S8.** EPR spectra of **1a** recorded at room temperature (inset: the g factor).



**Figure S9.** EPR spectra of **1b** recorded at room temperature (inset: the g factor).

(Note: the curve looks noisy due to the weak EPR signal of **1b**.)



**Figure S10.** The crystal packing of **1a** (left) and **1b** (right) in the ab-plane. (Hydrogen atoms and crystallization solvent were omitted for clarity.)

## REFERENCES

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