

# **Water-Induced Reversible Structural Phase Transformation with Chromotropism in Metal Supramolecular Frameworks Containing Aminopyrazine and Sulfate Anions**

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**Table S1.** Selected bond lengths (Å) and angles (deg) for compounds **1–4**.

Compound 1 <sup>a</sup>			
Co1–O9	2.0436(12)	Co2–O3	2.0691(14)
Co1–O9 <sup>i</sup>	2.0436(12)	Co2–O3 <sup>ii</sup>	2.0691(14)
Co1–O1 <sup>i</sup>	2.0968(13)	Co2–O2 <sup>ii</sup>	2.1030(14)
Co1–O1	2.0968(13)	Co2–O2	2.1030(14)
Co1–N1 <sup>i</sup>	2.2071(16)	Co2–O4 <sup>ii</sup>	2.1113(15)
Co1–N1	2.2071(15)	Co2–O4	2.1113(15)
O9–Co1–O9 <sup>i</sup>	180	O3–Co2–O3 <sup>ii</sup>	180
O9–Co1–O1 <sup>i</sup>	92.49(5)	O3–Co2–O2 <sup>ii</sup>	91.09(6)
O9 <sup>i</sup> –Co1–O1 <sup>i</sup>	87.51(5)	O3 <sup>ii</sup> –Co2–O2 <sup>ii</sup>	88.91(6)
O9–Co1–O1	87.51(5)	O3–Co2–O2	88.91(6)
O9 <sup>i</sup> –Co1–O1	92.49(5)	O3 <sup>ii</sup> –Co2–O2	91.09(6)
O1 <sup>i</sup> –Co1–O1	180	O2 <sup>ii</sup> –Co2–O2	180
O9–Co1–N1 <sup>i</sup>	88.62(5)	O3–Co2–O4 <sup>ii</sup>	87.33(7)
O9 <sup>i</sup> –Co1–N1 <sup>i</sup>	91.38(5)	O3 <sup>ii</sup> –Co2–O4 <sup>ii</sup>	92.67(7)
O1 <sup>i</sup> –Co1–N1 <sup>i</sup>	89.83(6)	O2 <sup>ii</sup> –Co2–O4 <sup>ii</sup>	90.06(6)
O1–Co1–N1 <sup>i</sup>	90.17(6)	O2–Co2–O4 <sup>ii</sup>	89.94(6)
O9–Co1–N1	91.38(5)	O3–Co2–O4	92.67(7)
O9 <sup>i</sup> –Co1–N1	88.62(5)	O3 <sup>ii</sup> –Co2–O4	87.33(7)
O1 <sup>i</sup> –Co1–N1	90.17(6)	O2 <sup>ii</sup> –Co2–O4	89.94(6)
O1–Co1–N1	89.83(6)	O2–Co2–O4	90.06(6)
N1 <sup>i</sup> –Co1–N1	180	O4 <sup>ii</sup> –Co2–O4	180
Compound 2 <sup>a</sup>			
Fe1–O9 <sup>i</sup>	2.0867(13)	Fe2–O3	2.1070(15)
Fe1–O9	2.0867(13)	Fe2–O3 <sup>ii</sup>	2.1070(15)

Fe1–O1 <sup>i</sup>	2.0977(12)	Fe2–O2 <sup>ii</sup>	2.1139(14)
Fe1–O1	2.0977(12)	Fe2–O2	2.1139(14)
Fe1–N1 <sup>i</sup>	2.2492(15)	Fe2–O4 <sup>ii</sup>	2.1522(14)
Fe1–N1	2.2492(15)	Fe2–O4	2.1522(14)
O9 <sup>i</sup> –Fe1–O9	180	O3–Fe2–O3 <sup>ii</sup>	180
O9 <sup>i</sup> –Fe1–O1 <sup>i</sup>	87.44(6)	O3–Fe2–O2 <sup>ii</sup>	90.47(6)
O9–Fe1–O1 <sup>i</sup>	92.56(6)	O3 <sup>ii</sup> –Fe2–O2 <sup>ii</sup>	89.53(6)
O9 <sup>i</sup> –Fe1–O1	92.56(6)	O3–Fe2–O2	89.53(6)
O9–Fe1–O1	87.44(6)	O3 <sup>ii</sup> –Fe2–O2	90.47(6)
O1 <sup>i</sup> –Fe1–O1	180	O2 <sup>ii</sup> –Fe2–O2	180
O9 <sup>i</sup> –Fe1–N1 <sup>i</sup>	92.22(5)	O3–Fe2–O4 <sup>ii</sup>	86.15(6)
O9–Fe1–N1 <sup>i</sup>	87.78(5)	O3 <sup>ii</sup> –Fe2–O4 <sup>ii</sup>	93.85(6)
O1 <sup>i</sup> –Fe1–N1 <sup>i</sup>	88.56(6)	O2 <sup>ii</sup> –Fe2–O4 <sup>ii</sup>	89.65(6)
O1–Fe1–N1 <sup>i</sup>	91.44(6)	O2–Fe2–O4 <sup>ii</sup>	90.35(6)
O9 <sup>i</sup> –Fe1–N1	87.78(5)	O3–Fe2–O4	93.85(6)
O9–Fe1–N1	92.22(5)	O3 <sup>ii</sup> –Fe2–O4	86.15(6)
O1 <sup>i</sup> –Fe1–N1	91.44(6)	O2 <sup>ii</sup> –Fe2–O4	90.35(6)
O1–Fe1–N1	88.56(6)	O2–Fe2–O4	89.65(6)
N1 <sup>i</sup> –Fe1–N1	180	O4 <sup>ii</sup> –Fe2–O4	180
Compound 3 <sup>a</sup>			
Co1–O9 <sup>i</sup>	2.0596(13)	Fe1–O3 <sup>ii</sup>	2.0904(15)
Co1–O9	2.0596(13)	Fe1–O3	2.0904(15)
Co1–O1 <sup>i</sup>	2.0974(13)	Fe1–O2	2.1116(15)
Co1–O1	2.0974(13)	Fe1–O2 <sup>ii</sup>	2.1116(14)
Co1–N1	2.2237(14)	Fe1–O4 <sup>ii</sup>	2.1375(15)
Co1–N1 <sup>i</sup>	2.2237(14)	Fe1–O4	2.1375(15)
O9 <sup>i</sup> –Co1–O9	180	O3 <sup>ii</sup> –Fe1–O3	180

O9 <sup>i</sup> -Co1-O1 <sup>i</sup>	87.47(6)	O3 <sup>ii</sup> -Fe1-O2	90.71(6)
O9-Co1-O1 <sup>i</sup>	92.53(6)	O3-Fe1-O2	89.29(6)
O9 <sup>i</sup> -Co1-O1	92.53(6)	O3 <sup>ii</sup> -Fe1-O2 <sup>ii</sup>	89.29(6)
O9-Co1-O1	87.47(6)	O3-Fe1-O2 <sup>ii</sup>	90.71(6)
O1 <sup>i</sup> -Co1-O1	180	O2-Fe1-O2 <sup>ii</sup>	180
O9 <sup>i</sup> -Co1-N1	88.30(5)	O3 <sup>ii</sup> -Fe1-O4 <sup>ii</sup>	93.39(7)
O9-Co1-N1	91.70(5)	O3-Fe1-O4 <sup>ii</sup>	86.61(7)
O1 <sup>i</sup> -Co1-N1	90.60(6)	O2-Fe1-O4 <sup>ii</sup>	90.19(6)
O1-Co1-N1	89.40(6)	O2 <sup>ii</sup> -Fe1-O4 <sup>ii</sup>	89.81(6)
O9 <sup>i</sup> -Co1-N1 <sup>i</sup>	91.70(5)	O3 <sup>ii</sup> -Fe1-O4	86.61(7)
O9-Co1-N1 <sup>i</sup>	88.30(5)	O3-Fe1-O4	93.39(7)
O1 <sup>i</sup> -Co1-N1 <sup>i</sup>	89.40(6)	O2-Fe1-O4	89.81(6)
O1-Co1-N1 <sup>i</sup>	90.60(6)	O2 <sup>ii</sup> -Fe1-O4	90.19(6)
N1-Co1-N1 <sup>i</sup>	180	O4 <sup>ii</sup> -Fe1-O4	180
Compound 4 <sup>b</sup>			
Cd1-O2 <sup>i</sup>	2.297(5)	Cd1-N1 <sup>ii</sup>	2.315(4)
Cd1-O4	2.303(6)	Cd1-O2	2.587(5)
Cd1-N1	2.315(4)	O2-Cd1 <sup>i</sup>	2.297(5)
O2 <sup>i</sup> -Cd1-O4	165.5(2)	O2 <sup>i</sup> -Cd1-O2	68.7(2)
O2 <sup>i</sup> -Cd1-N1	91.0(1)	O4-Cd1-O2	125.8(2)
O4-Cd1-N1	90.55(10)	N1-Cd1-O2	84.68(10)
O2 <sup>i</sup> -Cd1-N1 <sup>ii</sup>	91.0(1)	N1 <sup>ii</sup> -Cd1-O2	84.68(10)
O4-Cd1-N1 <sup>ii</sup>	90.55(10)	Cd1 <sup>i</sup> -O2-Cd1	111.3(2)
N1-Cd1-N1 <sup>ii</sup>	167.6(2)		

<sup>a</sup> Symmetry codes for **1-3**: (i)  $-x, 1-y, 1-z$ ; (ii)  $-x, 2-y, -z$ . <sup>b</sup>For **4**: (i)  $1-x, -y, 1-z$ ; (ii)  $x, -y, z$ .

**Table S2.** Intermolecular hydrogen bonds for compounds **1–4**.

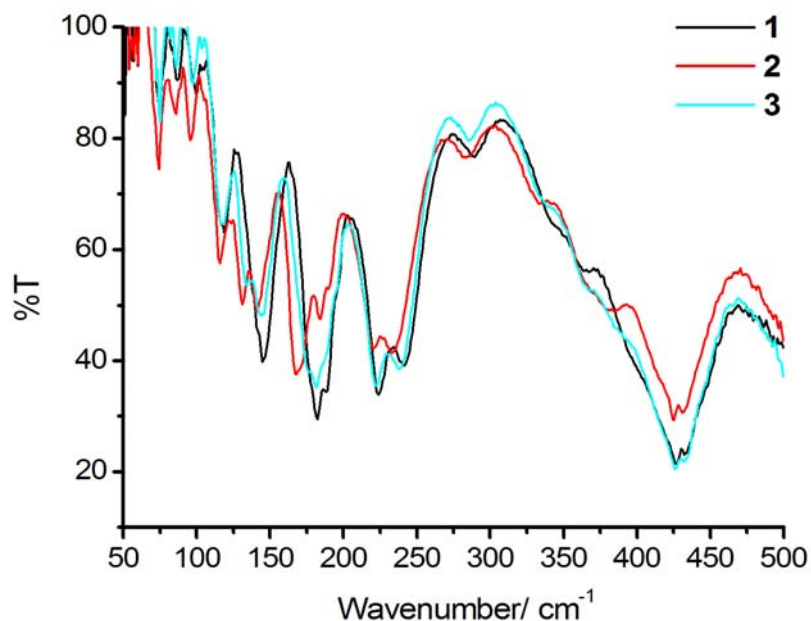
D–H...A	H...A/Å	D...A /Å	D–H...A /°
Compound <b>1</b> <sup>a</sup>			
O1–H1A...O6 <sup>i</sup>	1.84	2.764(2)	169
O1–H1B...O7 <sup>ii</sup>	1.88	2.771(2)	162
O2–H2A...O8 <sup>iii</sup>	1.79	2.733(2)	172
O2–H2B...O7	1.87	2.815(2)	171
N3–H3A...O6 <sup>iv</sup>	2.19	3.034(2)	169
N3–H3B...O3 <sup>v</sup>	2.61	3.347(3)	145
N3–H3B...O4 <sup>ii</sup>	2.52	3.277(2)	147
O3–H3C...O10 <sup>vi</sup>	1.81	2.732(2)	167
O3–H3D...O5 <sup>vii</sup>	1.81	2.739(2)	171
O4–H4A...O5	1.80	2.741(2)	172
O4–H4B...O10 <sup>viii</sup>	1.85	2.780(2)	167
O9–H9...N2 <sup>viii</sup>	1.86	2.792(2)	173
O9–H9A...O6	1.83	2.755(2)	169
O10–H10...O7	1.84	2.779(2)	169
O10–H10A...O8 <sup>vi</sup>	1.78	2.704(2)	165
Compound <b>2</b> <sup>a</sup>			
O1–H1A...O6 <sup>i</sup>	1.87	2.748(2)	170
O1–H1B...O7 <sup>ii</sup>	1.88	2.760(2)	174
O2–H2A...O8 <sup>iii</sup>	1.81	2.725(2)	170
O2–H2B...O7	1.90	2.811(2)	167
N3–H3A...O6 <sup>iv</sup>	2.18	3.030(2)	169
N3–H3B...O3 <sup>v</sup>	2.57	3.312(3)	145
N3–H3B...O4 <sup>ii</sup>	2.54	3.283(2)	147
O3–H3C...O10 <sup>vi</sup>	1.83	2.728(2)	168
O3–H3D...O5 <sup>vii</sup>	1.84	2.735(2)	168
O4–H4A...O5	1.85	2.739(2)	167

O4–H4B...O10 <sup>viii</sup>	1.88	2.780(2)	164
O9–H9...N2 <sup>viii</sup>	1.88	2.790(2)	171
O9–H9A...O6	1.91	2.775(2)	167
O10–H10...O7	1.86	2.787(2)	171
O10–H10A...O8 <sup>vi</sup>	1.78	2.700(2)	167
Compound <b>3</b> <sup>a</sup>			
O1–H1A...O6 <sup>i</sup>	1.87	2.758(2)	170
O1–H1B...O7 <sup>ii</sup>	1.9	2.769(2)	171
O2–H2A...O8 <sup>iii</sup>	1.84	2.732(2)	169
O2–H2B...O7	1.91	2.810(2)	168
N3–H3A...O6 <sup>iv</sup>	2.18	3.031(2)	169
N3–H3B...O3 <sup>v</sup>	2.60	3.342(3)	145
N3–H3B...O4 <sup>ii</sup>	2.53	3.283(2)	146
O3–H3C...O10 <sup>vi</sup>	1.87	2.732(2)	166
O3–H3D...O5 <sup>vii</sup>	1.86	2.737(2)	167
O4–H4A...O5	1.83	2.742(2)	170
O4–H4B...O10 <sup>viii</sup>	1.89	2.780(2)	164
O9–H9...N2 <sup>viii</sup>	1.89	2.794(2)	174
O9–H9A...O6	1.88	2.762(2)	169
O10–H10...O7	1.85	2.781(2)	175
O10–H10A...O8 <sup>vi</sup>	1.78	2.708(2)	167
Compound <b>4</b> <sup>b</sup>			
N2–H2B...O1 <sup>i</sup>	2.24	3.057(11)	158
N2–H2A...O5	2.70	3.391(10)	138
O5...O4	-	2.677(11)	-
O3...O5 <sup>ii</sup>	-	2.888(7)	-

A= acceptor; D= donor.

<sup>a</sup> Symmetry codes for **1–3**: (i)  $I-x, I-y, I-z$ ; (ii)  $-x, I-y, I-z$ ; (iii)  $-I+x, y, z$ ; (iv)  $I-x, -y, I-z$ ; (v)  $x, -I+y, I+z$ ; (vi)  $I-x, I-y, -z$ ; (vii)  $I-x, 2-y, -z$ ; (viii)  $x, I+y, z$ . <sup>b</sup>For **4**: (i)  $I/2-x, -1/2+y, I-z$ ; (ii)  $I/2-x, 1/2+y, I-z$ .

### Far-infrared spectra of 1–3



The far-IR spectrum of **3** almost shows close resemblance to the spectrum of **1**, especially in the range of 160–250 cm<sup>-1</sup>, where the deformations of N–M–N and the asymmetric stretching vibrations of M–N are expected.<sup>a</sup> These low-frequency modes are sensitive to metal-ion mass and provide a clue to metal-site preference. This result strongly suggests that the Co(II) ion in **3** is accommodated in [M(H<sub>2</sub>O)<sub>4</sub>(ampyz)<sub>2</sub>]<sup>2+</sup> unit rather than [M(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> unit, and supports the X-ray structure of [Co(H<sub>2</sub>O)<sub>4</sub>(ampyz)<sub>2</sub>][Fe(H<sub>2</sub>O)<sub>6</sub>](SO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> for **3**.

<sup>a</sup> **Table.** IR-active vibrational modes of  $[\text{Fe}(\text{ampyz})_2(\text{H}_2\text{O})_4]^{2+}$  complex calculated by Gaussian03.<sup>b</sup>

Vibrational mode	Wavenumber (cm <sup>-1</sup> )	IR intensity (a.u.)
O–Fe–O def	97	5.44
	112	12.30
N–Fe–N def	166	1.50
	173	8.59
	179	5.69
Fe–N stretch	223	1.35
	227	1.40
Fe–O stretch	316	4.05
H <sub>2</sub> O twist + ampyz def	390	16.85
H <sub>2</sub> O twist + NH <sub>2</sub> rock	400	48.50
H <sub>2</sub> O wagg + ampyz def	436	50.98
H <sub>2</sub> O wagg + NH <sub>2</sub> twist	469	140.96
	483	271.70
H <sub>2</sub> O rock	538	374.91

All assignments are in the usual ranges of vibrational frequencies of aqua and pyridine complexes.<sup>†</sup>

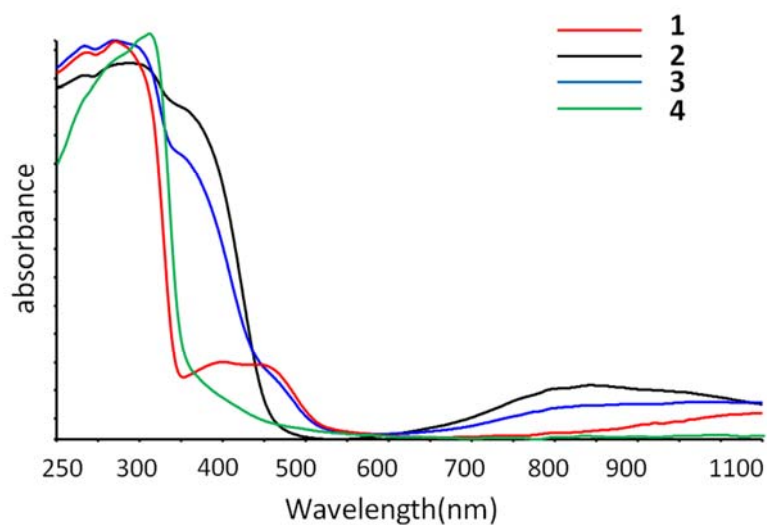
<sup>b</sup>The vibrational assignments were performed on high-spin  $[\text{Fe}(\text{ampyz})_2(\text{H}_2\text{O})_4]^{2+}$  ( $S=2$ ) with the Gaussian 03 program suite<sup>‡</sup> where the effective core potential (ECP) basis set CEP-121G was used with the hybrid density functional B3PW91.

## References

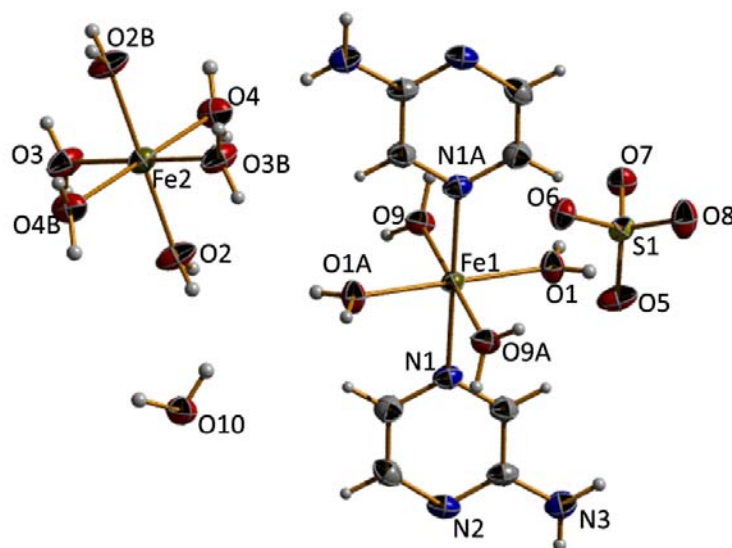
<sup>†</sup> (a) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, New York, 1997. (b) A. A. Jarz cki, A. D. Anbar and T. G. Spiro. *J. Phys. Chem. A.*, 2004, **108**, 2726.

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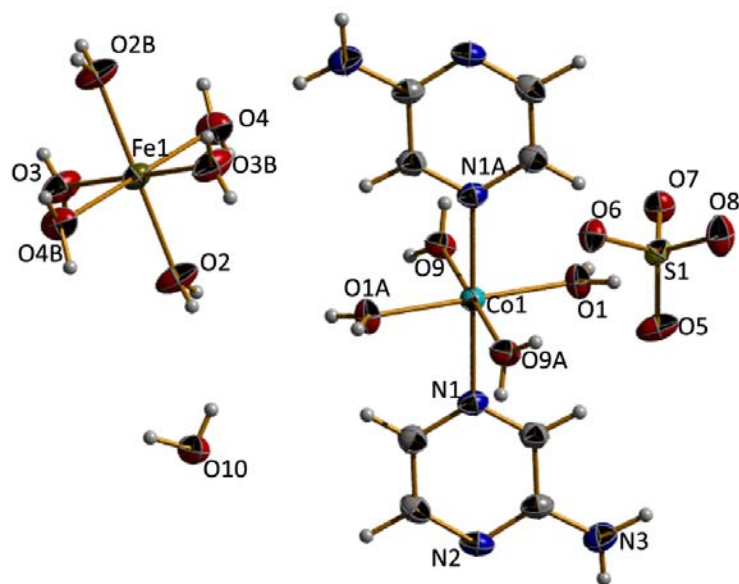




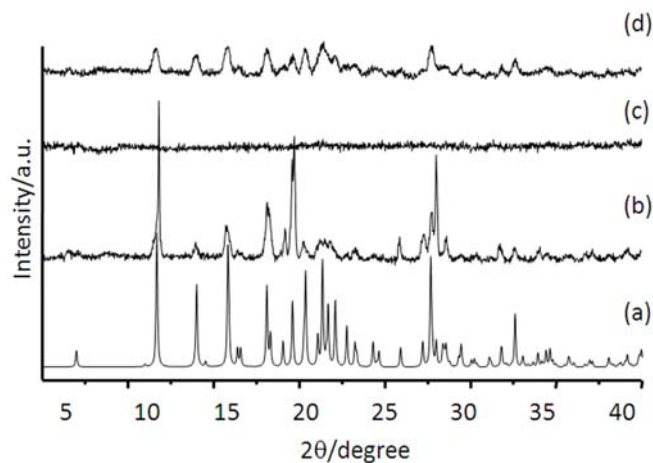
**Fig. S1** UV-vis diffuse reflectance spectra of as-synthesized compounds **1–4**.



**Fig. S2** Crystal structure and atom labeling scheme of **2**. The ellipsoids are shown at 50% probability level. Atoms labeled with the notation “A” and “B” are symmetry-generated equivalents, (A)  $-x, 1-y, 1-z$ ; (B)  $-x, 2-y, -z$ .

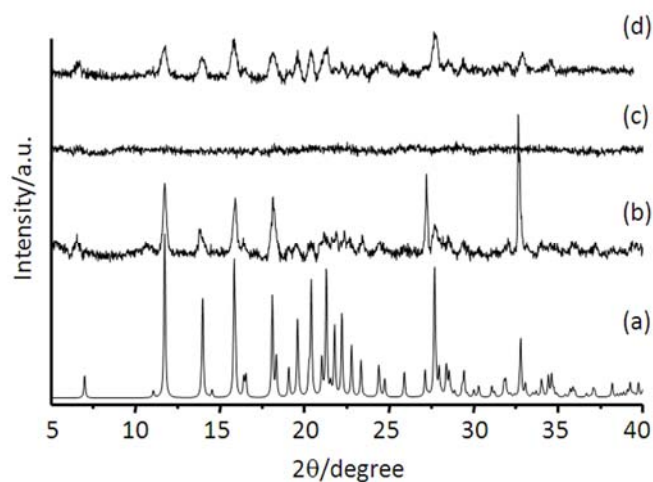


**Fig. S3** Crystal structure and atom labeling scheme of **3**. The ellipsoids are shown at 50% probability level. Atoms labeled with the notation “A” and “B” are symmetry-generated equivalents, (A)  $-x, 1-y, 1-z$ ; (B)  $-x, 2-y, -z$ .



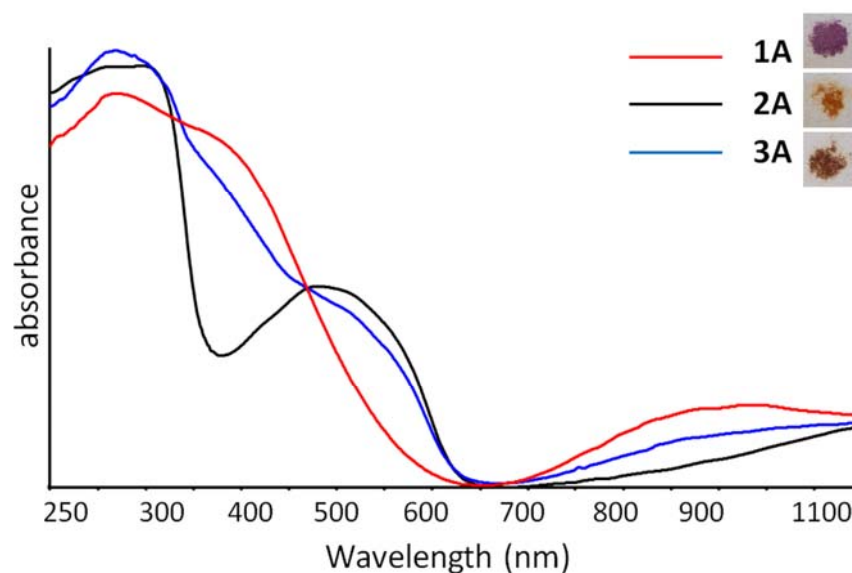
**Fig. S4** XRPD patterns: (a) simulated from single-crystal X-ray data; (b) as-synthesize **2**; (c) the dehydrated form **2A**; (d) the rehydrated form **2'**.

(The elemental analysis for **2'**: Anal. Calcd: C, 13.53; H, 4.38; N, 11.83 %. Found: C,13.72; H, 4.26; N, 12.00%.)

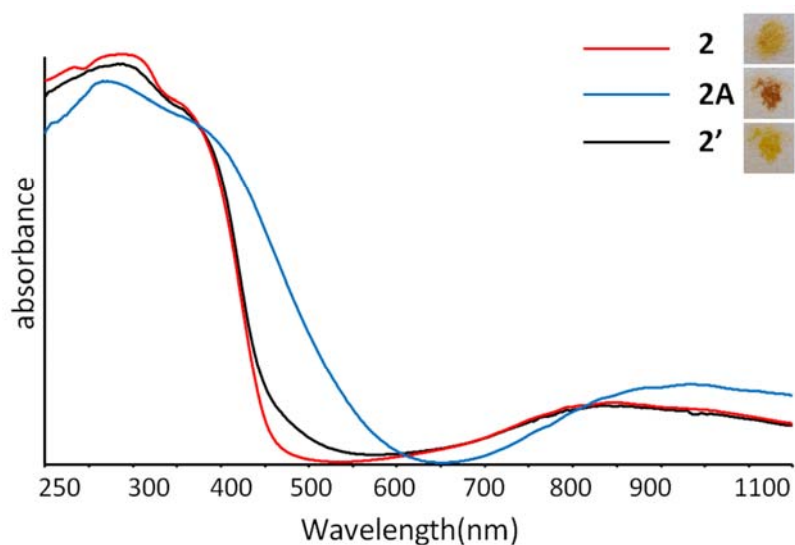


**Fig. S5** XRPD patterns: (a) simulated from single-crystal X-ray data; (b) as-synthesize **3**; (c) the dehydrated form **3A**; (d) the rehydrated form **3'**.

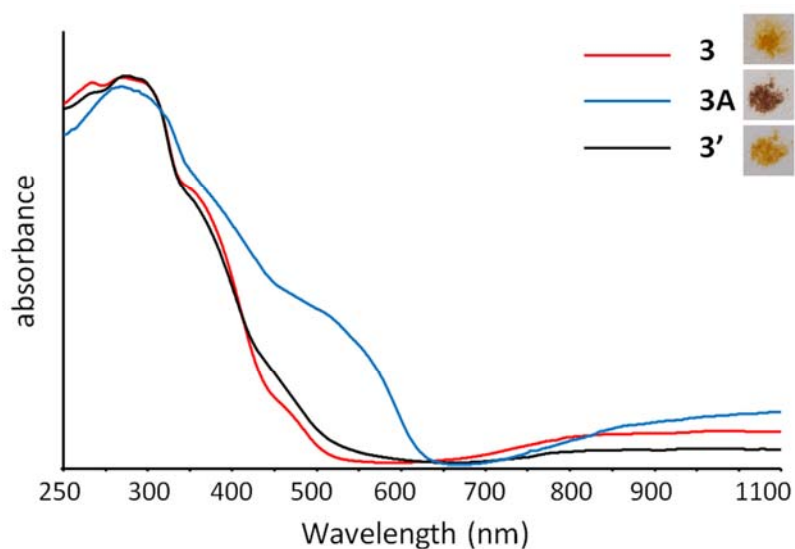
(The elemental analysis for **3'**: Anal. Calcd: C, 13.47; H, 4.80; N, 11.78 %. Found: C,13.12; H, 3.87; N, 12.03%.)



**Fig. S6** UV-vis diffuse reflectance spectra of the dehydrated compounds **1A–3A**, represented together with the colors of their dehydrated samples. The spectrum of **3A** shows the overlap bands between **1A** and **2A** indicating that **3A** is also a hetero-metallic compound.



**Fig. S7** The UV-vis diffuse reflectance spectra of as-synthesize **2** (red line), the dehydrated form **2A** (blue line), and the rehydrated form **2'** (black line), represented together with the chromatic changes in bulk samples.



**Fig. S8** The UV-vis diffuse reflectance spectra of as-synthesize **3** (red line), the dehydrated form **3A** (blue line), and the rehydrated form **3'** (black line), represented together with the chromatic changes in bulk samples.