Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Material

Spin crossover and reversible single-crystal to single-crystal transformation behaviour in two cyanide-bridged mixed-valence $\{Fe^{III}_2Fe^{II}_2\}$ clusters

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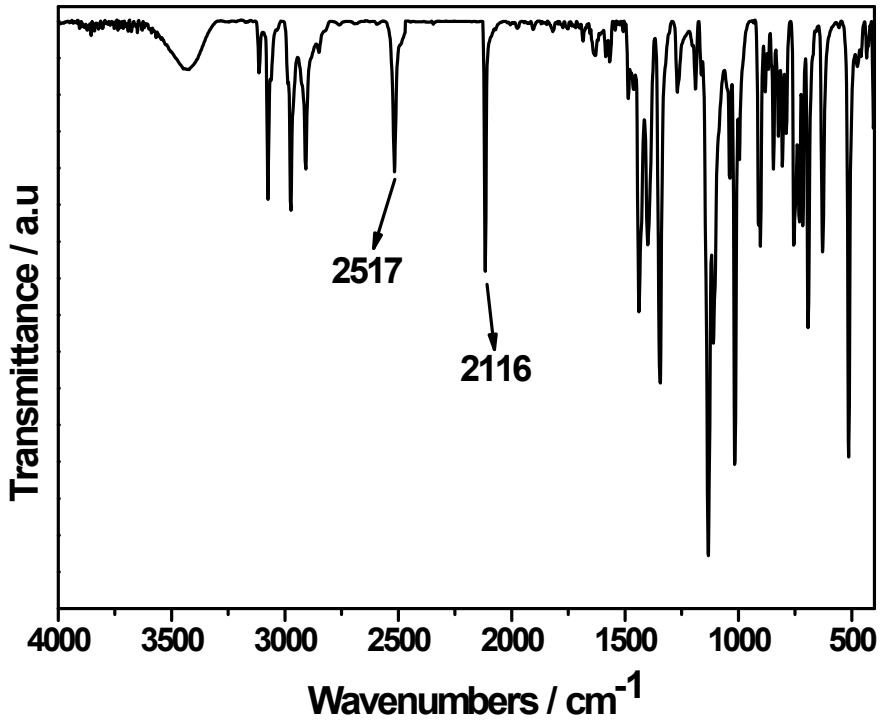
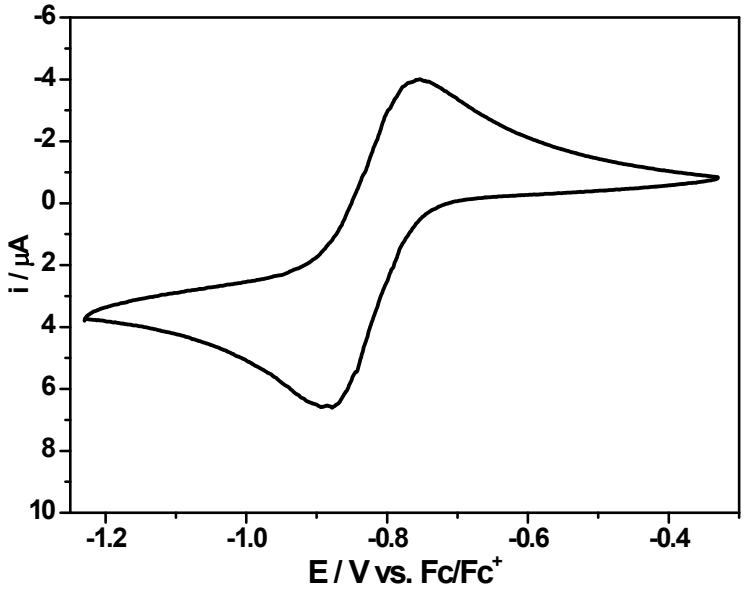


Figure S1 FT-IR for **1** at room temperature.



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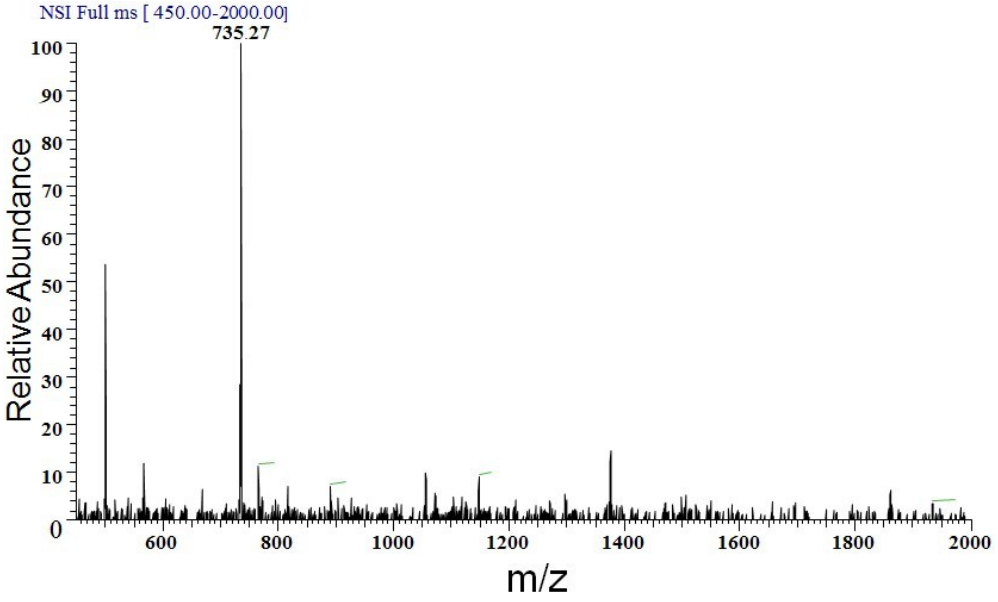


Figure S3 ESI-MS spectrum for **2·H_2O** in MeCN.

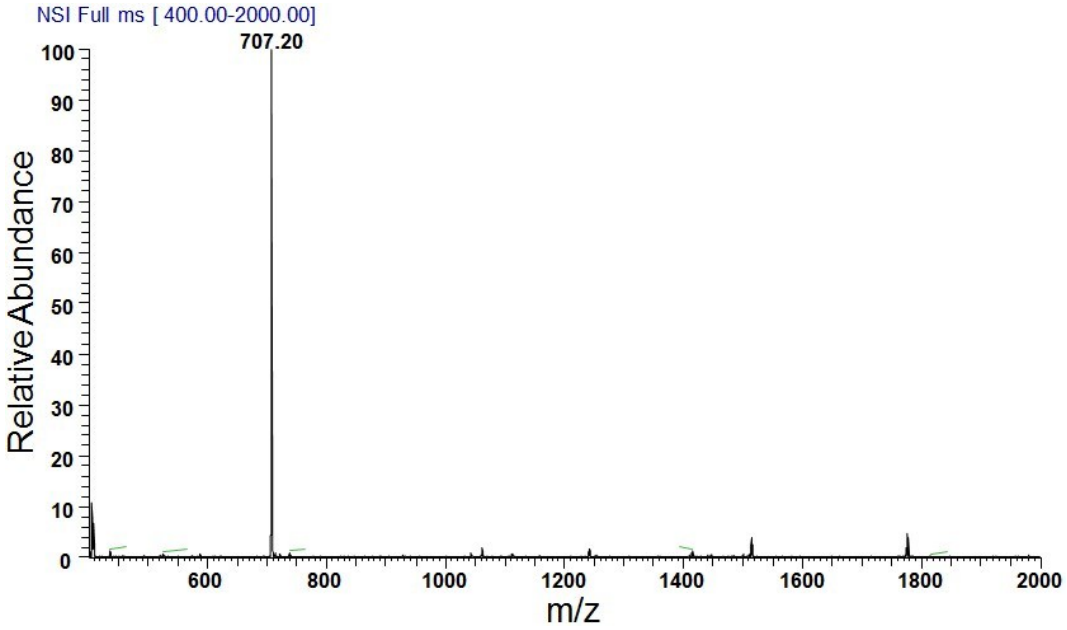


Figure S4 ESI-MS spectrum for **3·MeOH** in MeCN.

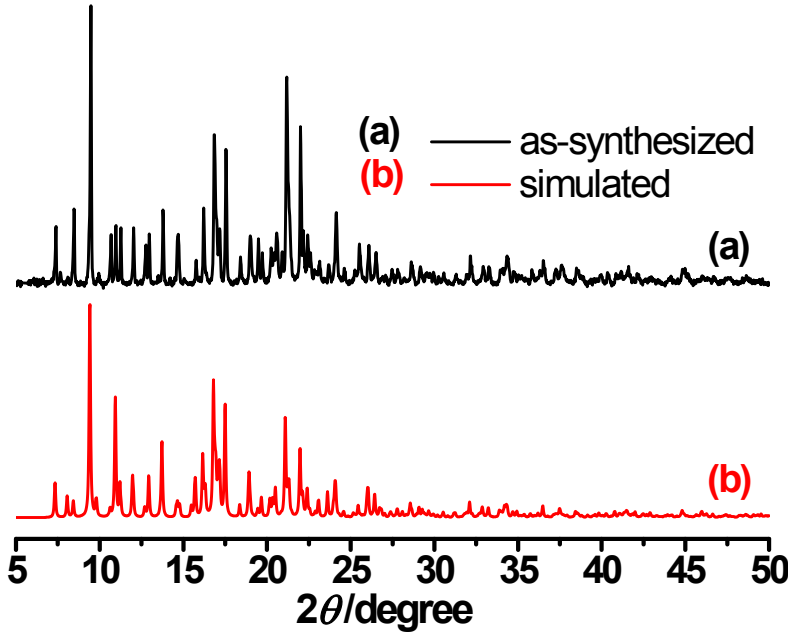


Figure S5 X-ray powder diffraction diagrams of **2·H_2O** and the simulated spectra from single crystal data.

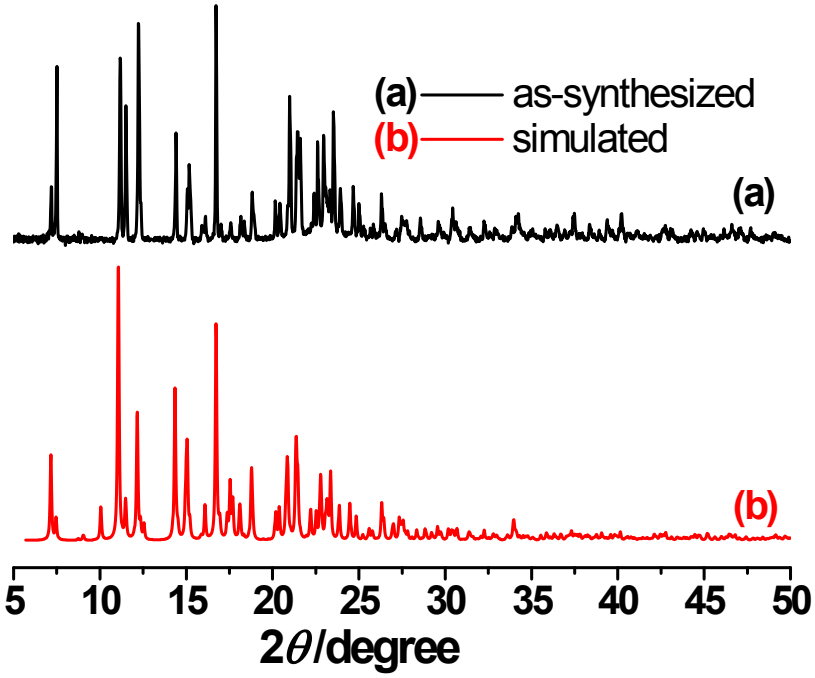


Figure S6 X-ray powder diffraction diagrams of **3·MeOH** and the simulated spectra from single crystal data.

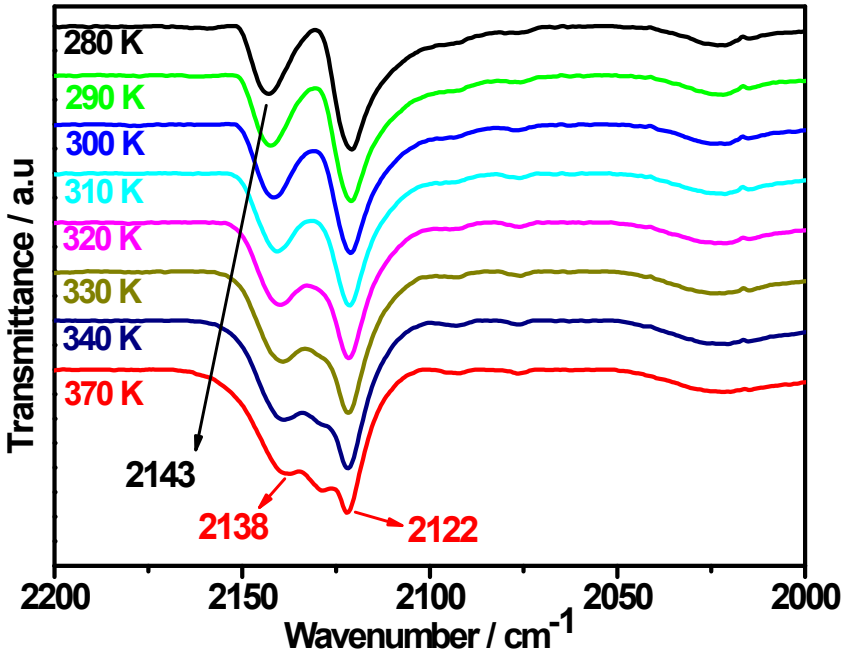
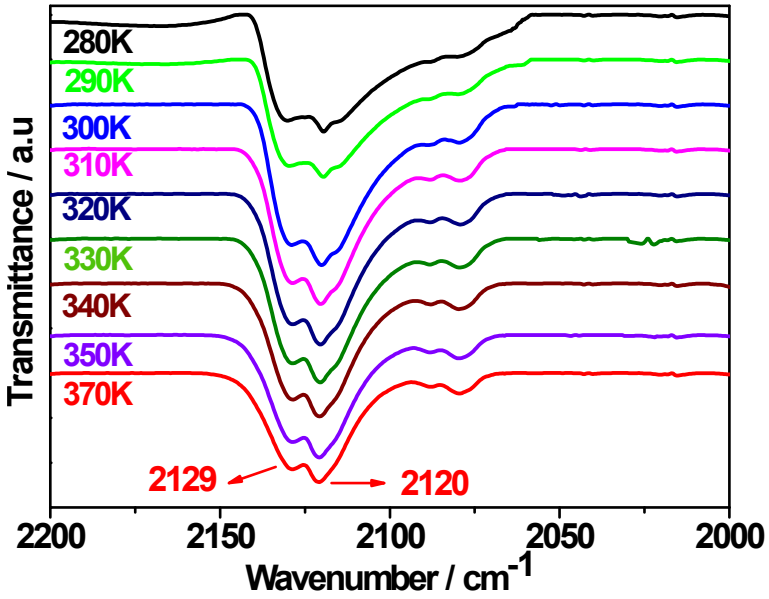


Figure S7 Variable-temperature FT-IR for **2·H_2O** (Nujol mull, KBr plates), heating from 280 to 370 K.



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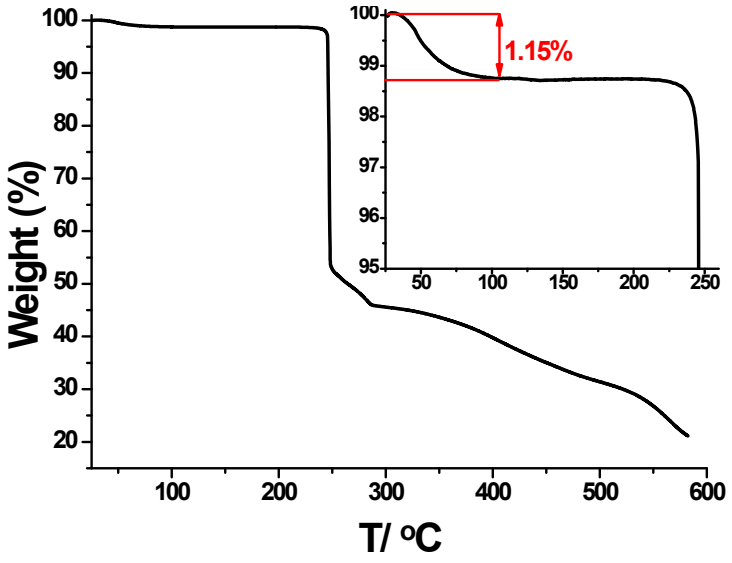

Figure S9 Thermogravimetric analysis of **2·H_2O**. The first weigh loss until 110 °C was due to the coordinated and uncoordinated H_2O molecule (obsd 1.15%, cacld 1.07%). The decomposition of the organic links in the anhydrous compound occurs at 220 °C.

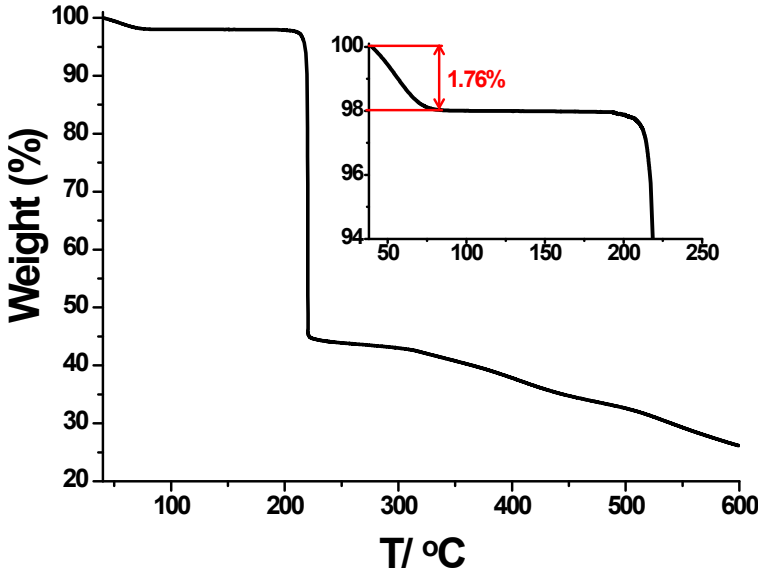

Figure S10 Thermogravimetric analysis of **3·MeOH**. The first weigh loss until 70 °C was due to the coordinated and uncoordinated MeOH molecule (obsd 1.76%, cacld 1.94%). The decomposition of the organic links in the anhydrous compound occurs at 208 °C.

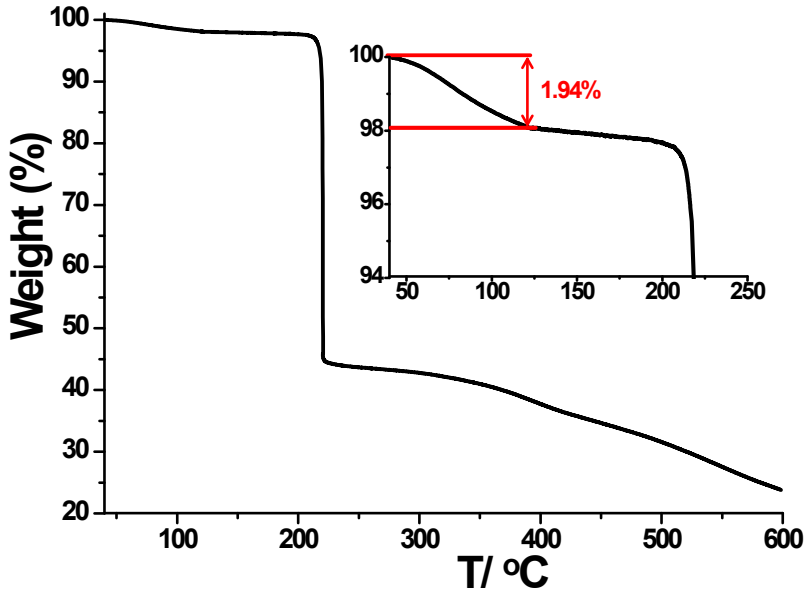

Figure S11 Thermogravimetric analysis of **3·2H$_2$O**. The first weigh loss until 124 °C was due to the loss of H_2O molecules (obsd 1.94%, cacld 2.21%). The decomposition of the organic links in the anhydrous compound occurs at 210 °C.

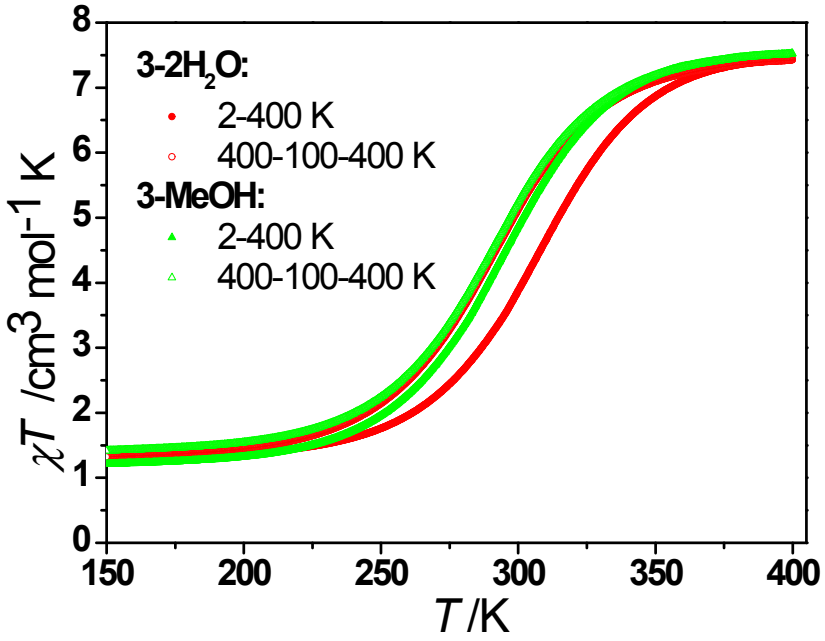

Figure S12 Temperature dependence of $\chi_M T$ plots for **3·MeOH** and **3·2H$_2$O**.

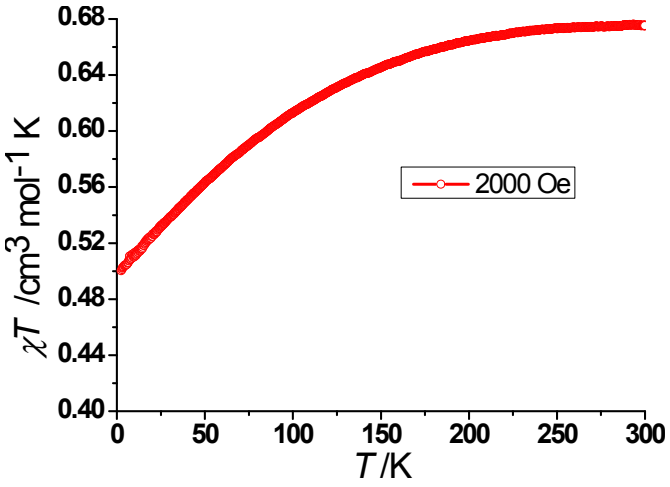

Figure S13 Temperature dependence of $\chi_M T$ plot for **1**.

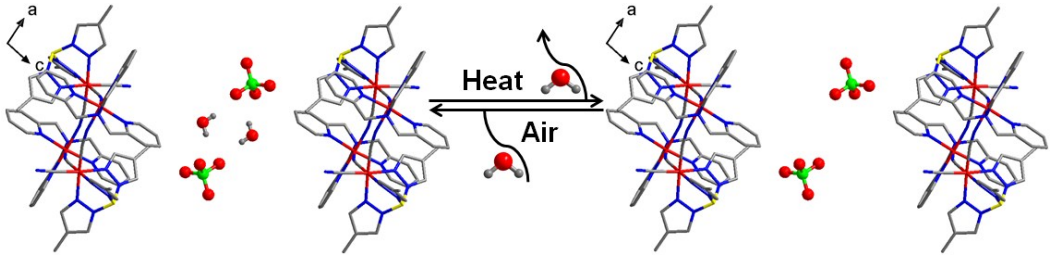

Figure S14 Schematic representation of reversible water desorption and re-sorption between **2·H$_2$O** and **2**.

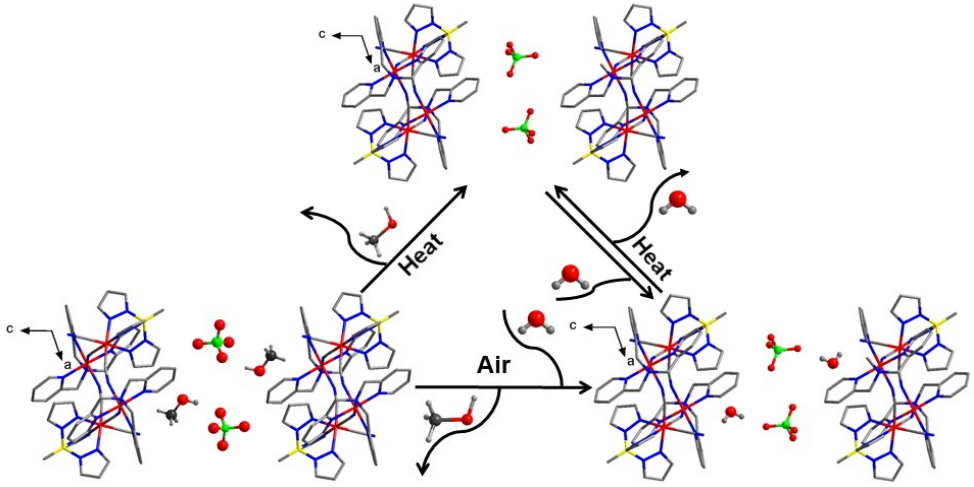

Figure S15 Schematic representation of reversible solvent molecule exchange between **3·MeOH** and **3·2H$_2$O**.

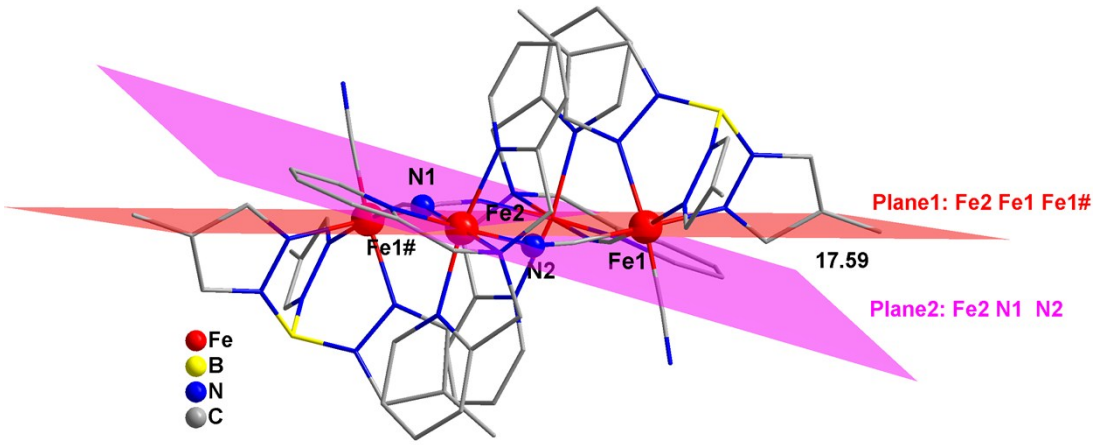

Figure S16 The dihedral angle between the plane1 (Fe2, Fe1, Fe1#) and the plane2 (Fe2, N1, N2) in **2**. # = 1-x, 2-y, -z

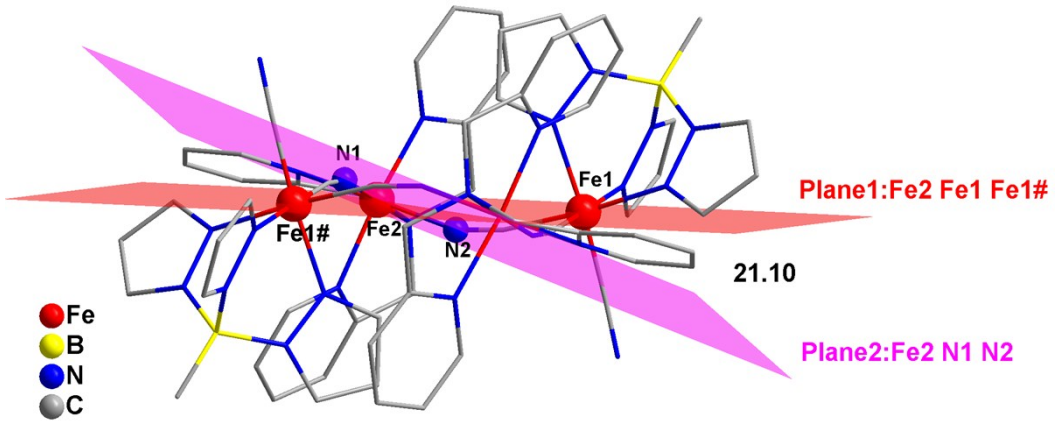

Figure S17 The dihedral angle between the plane1 (Fe2, Fe1, Fe1#) and the plane2 (Fe2, N1, N2) in **3**. # =1-x, 2-y, 1-z

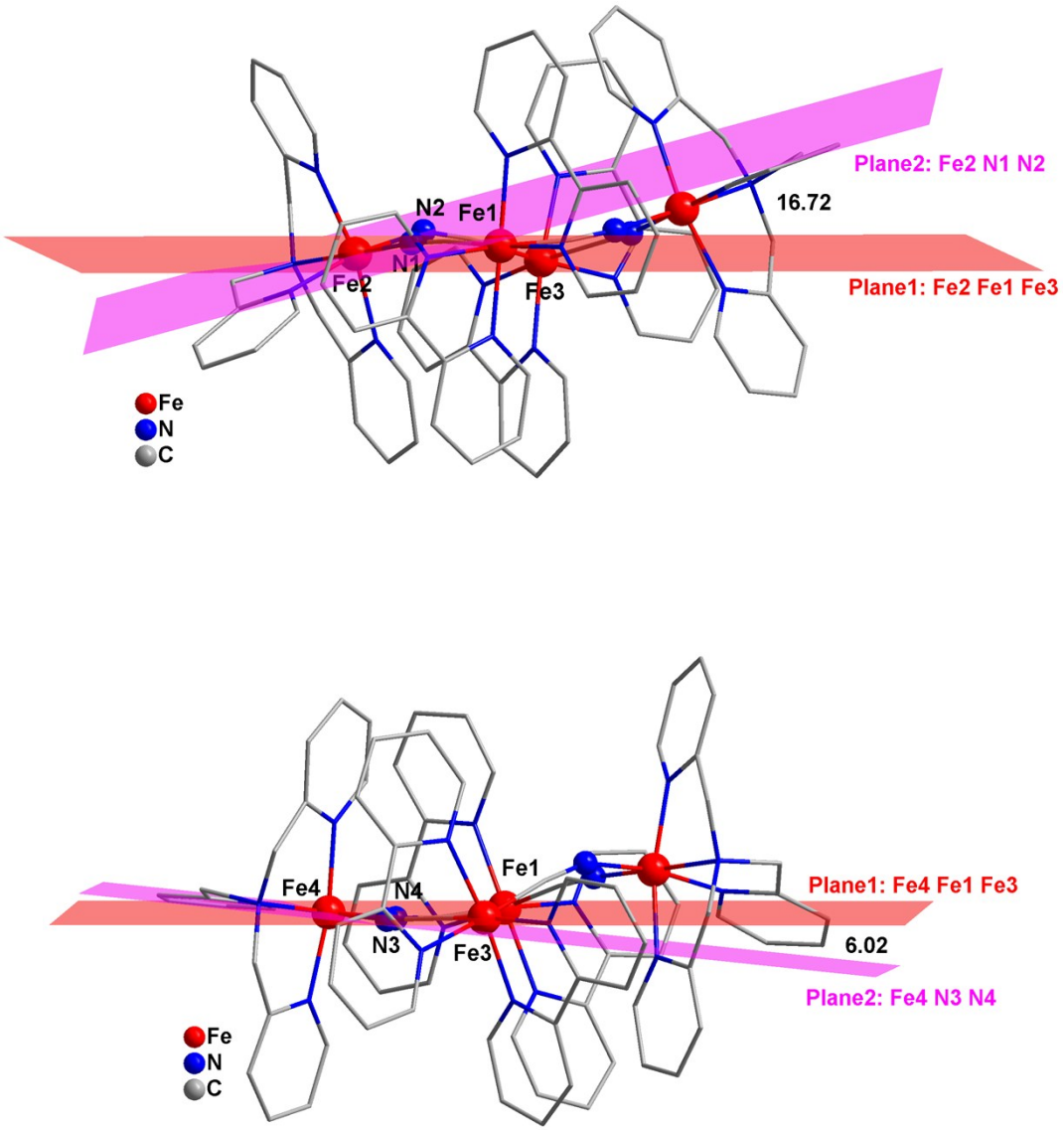

Figure S18 The dihedral angles between (top) the plane1 (Fe2, Fe1, Fe3) and the plane2 (Fe2, N1, N2), (bottom) the plane1 (Fe4, Fe1, Fe3) and the plane2 (Fe4, N3, N4) in $[Fe^{II}_4(CN)_4(bpy)_4(tpa)_4](PF_6)_4$. Crystallographic data of $[Fe^{II}_4(CN)_4(bpy)_4(tpa)_4](PF_6)_4$ is obtained from CCDC.

Table S1. Crystal data and structure refinement for **1**.

	1
Formula	$C_{35}H_{35.5}BFeN_{9.5}P$
Formula weight	686.86
Crystal system	Monoclinic
Space group	*C*2/c
Temperature/K	100
a /Å	40.799(9)
b /Å	8.793(2)
c /Å	23.324(5)
α /º	90
β /º	124.866 (2)
γ /º	90
V / Å^3	6865(3)
Z	8
ρ calcd/g cm^{-3}	1.329
μ / mm^{-1}	0.526
Collected reflections	26708
Unique reflections	6399
Goodness-of-fit on F^2	1.018
R_1 [I >2σ (I)]	0.0264
wR_2 [I >2σ (I)]	0.0697

Table S2. Selected bond lengths [Å] and angles [°] for **1**

1					
Fe1–C1	1.9322(14)	C1–Fe1–C2	88.36(6)	N1–C1–Fe1	177.77(13)
Fe1–C2	1.9224(14)	C1–Fe1–C3	89.49(6)	N2–C2–Fe1	176.57(12)
Fe1–C3	1.9266(14)	C2–Fe1–C3	86.16(6)	N3–C3–Fe1	178.42(13)
Fe1–N4	1.9911(12)	N4–Fe1–N6	87.52(5)		
Fe1–N6	1.9641(12)	N4–Fe1–N8	88.97(5)		
Fe1–N8	1.9772(12)	N6–Fe1–N8	87.63(5)		