Supplementary Material (ESI) for Chemical Communications

Support Information

Heterobimetallic Porphyrin-basd Single-Chain Magnet Constructed from Manganese(III)-Porphyrin and *trans*-Dicyanobis(acetylacetonato)ruthenate(III) Containing Co-crystallized Bulk Anions and Cations

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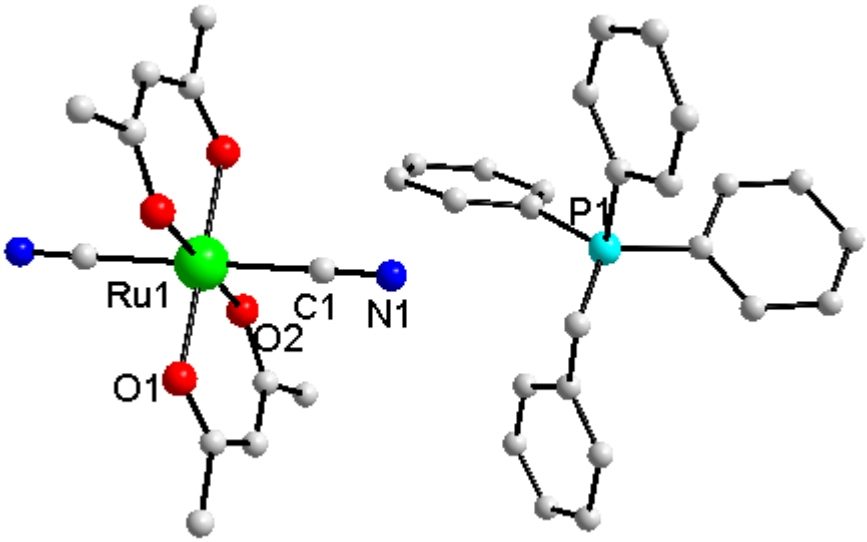

Fig. S1. The crystal structure of compound **1**. The solvent H_2O and all the H atoms have been omitted for clarity.

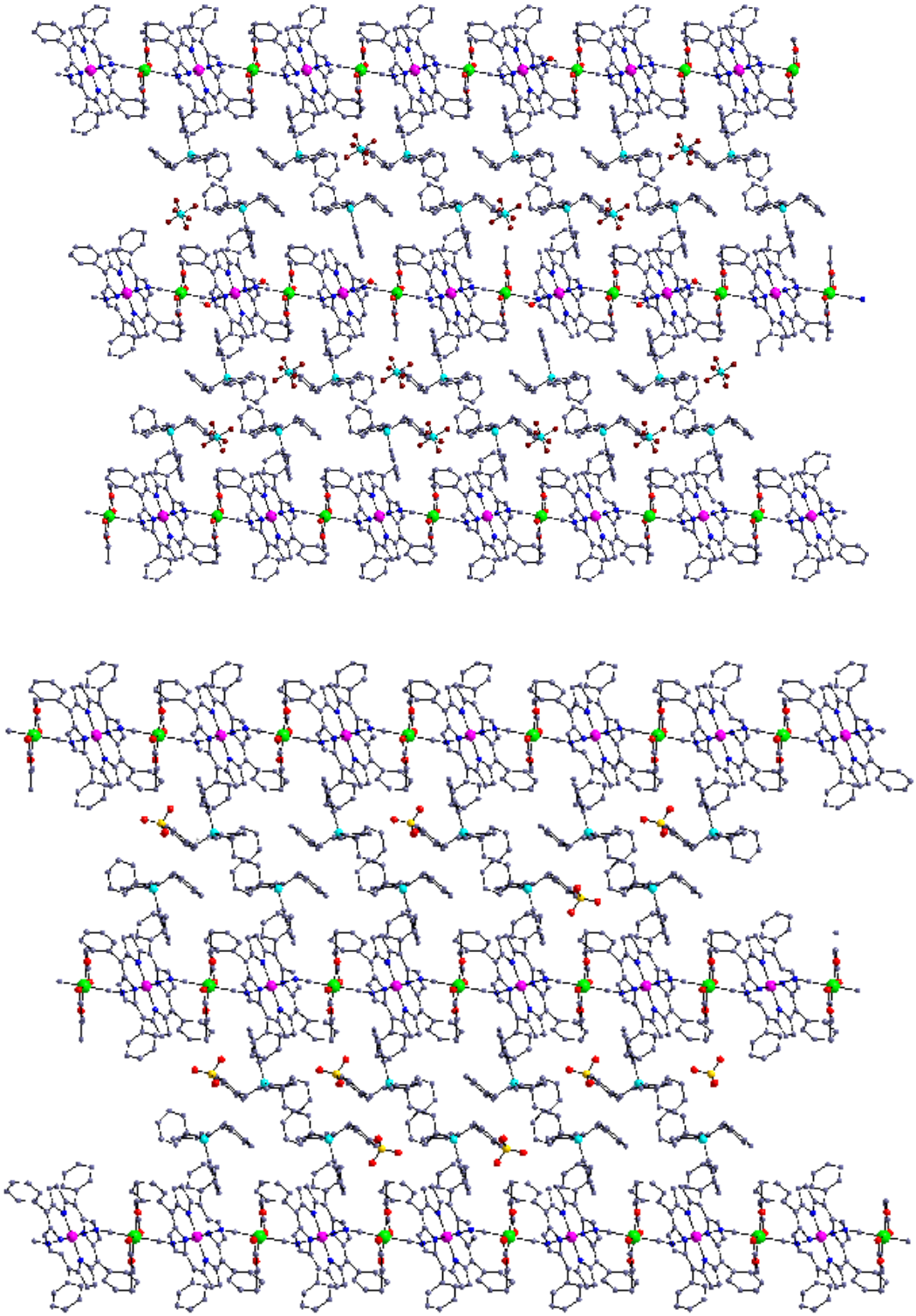

Fig. S2. The cell packing diagrams of complexes **2** (Top) and **3** (Bottom) along *c* axis. All the H atoms and the solvent methanol have been omitted for clarity.

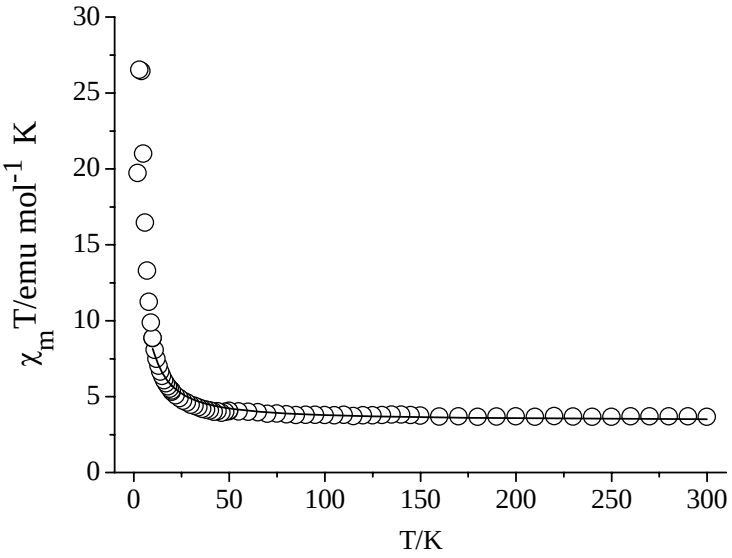

Fig. S3. Temperature dependence of $\chi_m T$ (the solid line represents the best fit based on the parameters discussed in the text) for complex **3**.

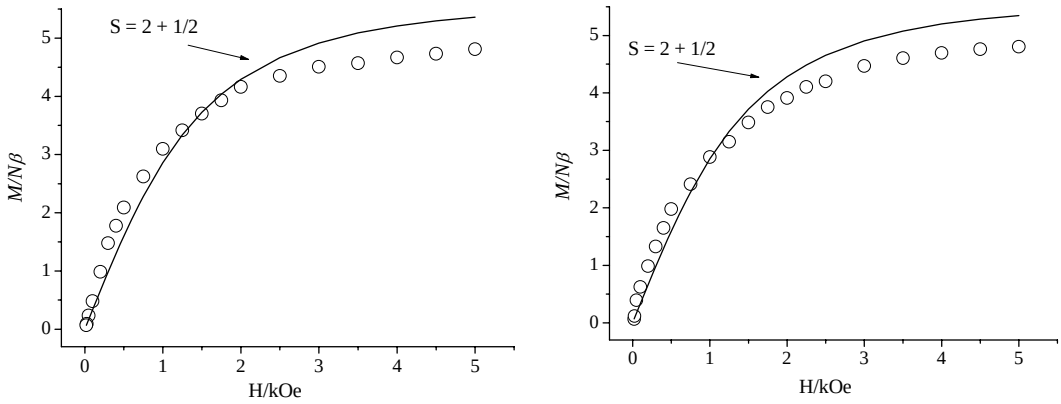

Fig. S4. The field-dependent magnetization of complex **2** (Left) and **3** (Right). The solid line represents the Brillouin function that corresponds to noninteracting $S = S_{Mn} + S_{Ru}$ with $g = 2.0$.

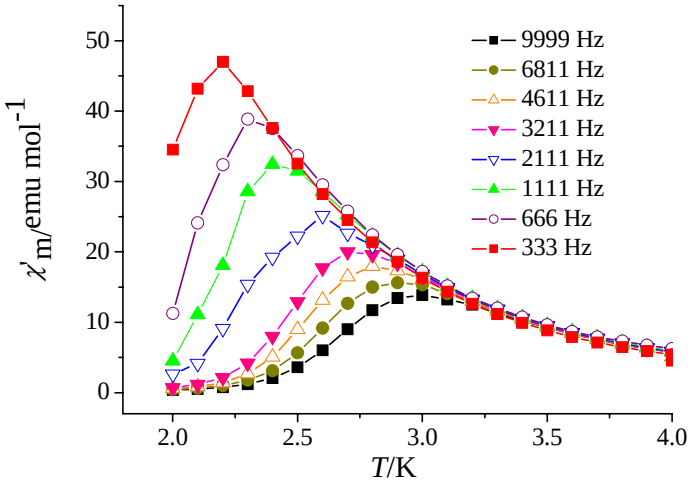

Fig. S5. The in-phase (χ') ac susceptibility of complex **2**.

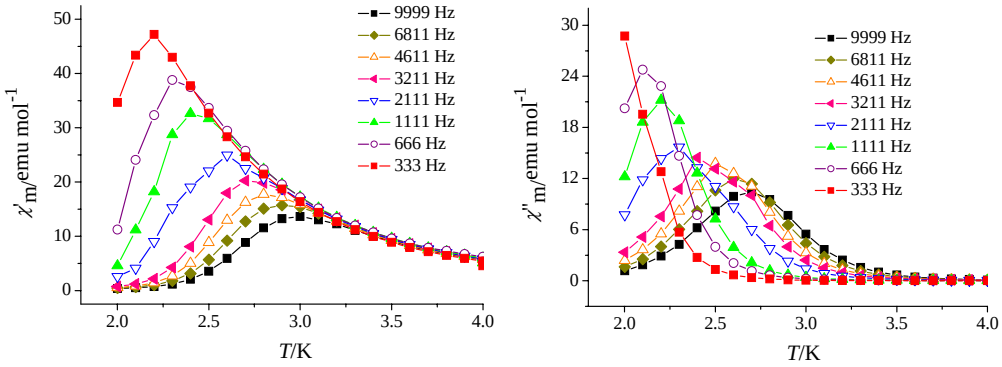

Fig. S6. The in-phase (χ') (left) and out-of-phase(χ") (right) ac susceptibility of complex **3**.

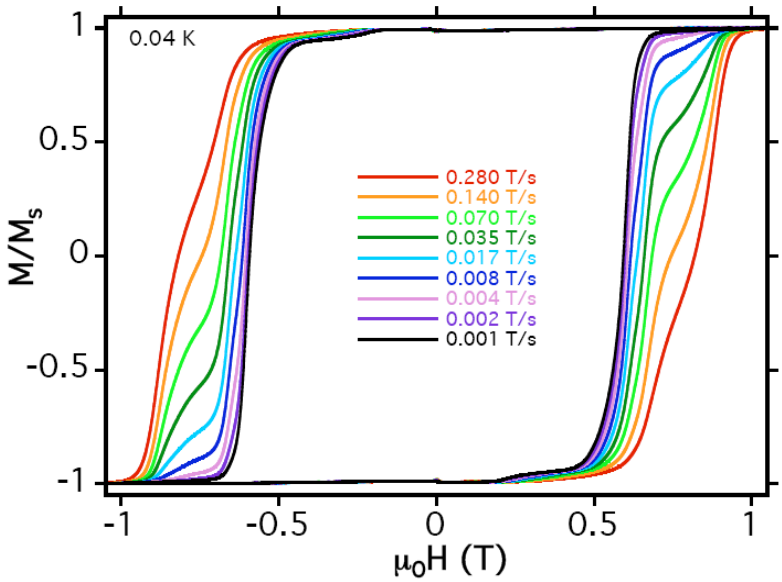

Figure S7. Hysteresis loop for complex **2** at different scan magnetic field speed at 0.04 K.

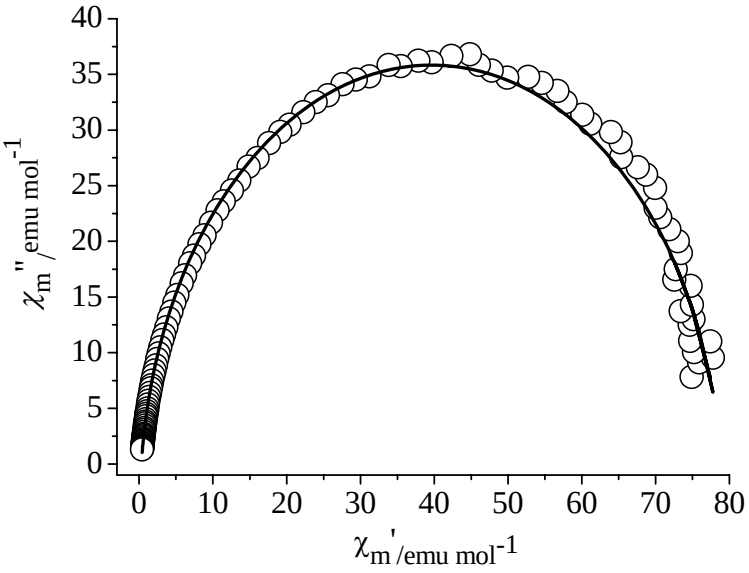

Figure S8. Cole–Cole plot of χ'' versus χ' at 2 K in zero applied dc field for complex **2**. The solid curves represent the least-squares fit to a generalized Debye model with α = 0.059(5).

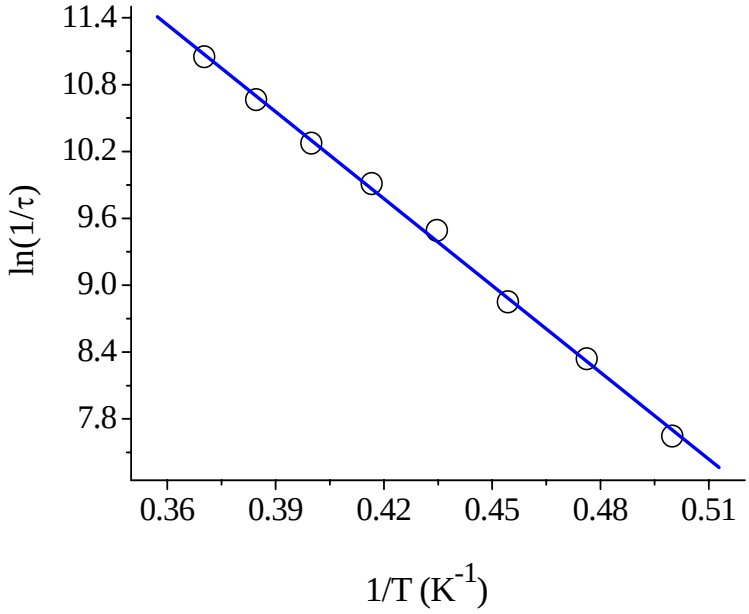

Fig. S9. Plot of ln(1/τ) versus 1/T for complex **2**. The solid line represents the best fit of the data.

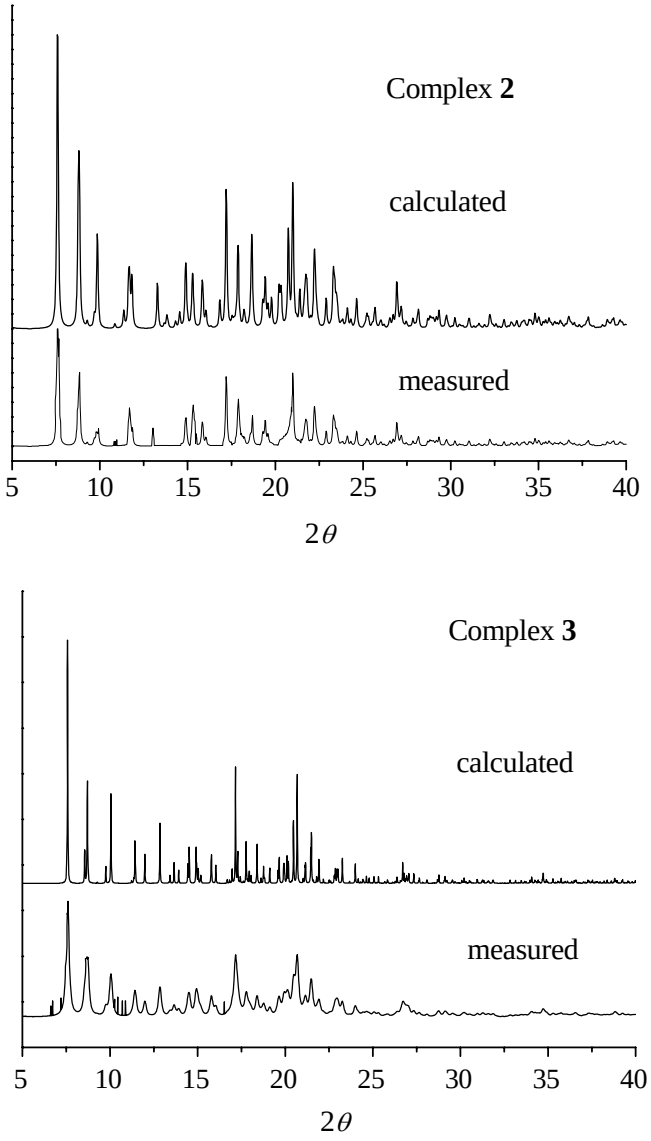

Fig. S10. The XPRD pattern of complex **2** (Top) and **3** (Bottom).

The preparation procedure of complexes 2 and 3:

To a solution of $[Mn(TPP)(H_2O)_2]PF_6$ or $[Mn(TPP)(H_2O)_2]ClO_4$ (0.10 mmol) in methanol (10 mL), $[Ph_3(PhCH_2)P][Ru(acac)_2(CN)_2]\cdot H_2O$ (0.10 mmol) dissolved in methanol (5 mL) was carefully added. The resulting mixture was filtered at once and the filtrate kept undisturbed in the dark at room temperature. After about one week, dark brown block crystals were collected by filtration and washed the cooled methanol, giving the yield about 40%.

X-ray data collection and structure refinement. Single crystals of all the complexes for X-ray diffraction analysis with suitable dimensions were mounted on the glass rod and the crystal data were collected on a Bruker SMART CCD diffractometer with a MoKα sealed tube (λ = 0.71073 Å) at 293 K, using a ω scan mode. The structures were solved by direct method and expanded using Fourier difference techniques with the SHELXTL-97 program package. The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced as fixed contributors. All the nonhydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients U(H) =1.2U(C) or 1.5U(C) and their coordinates were allowed to ride on their respective carbons using SHELXL97 except the H atoms of the solvent molecules. For these H atoms, they were refined isotropically with fixed U values and the DFIX command was used to rationalize the bond parameter.

Equations used to fit the magnetic data of complexes 2 and 3:

$$\chi_{chain} = \frac{2N\beta^2}{3kT}\left[M^2\frac{1+p}{1-P} + (\delta M)^2\frac{1+p}{1-P}\right]$$

$$P = \coth(J_{eff}/kT) - kT/J_{eff}$$

$$M = [g_{Mn}[S_{Mn}(S_{Mn}+1)]^{1/2} + g_{Ru}[S_{Ru}(S_{Ru}+1)]^{1/2}]/2$$

$$\delta M = [g_{Mn}[S_{Mn}(S_{Mn}+1)]^{1/2} - g_{Ru}[S_{Ru}(S_{Ru}+1)]^{1/2}]/2$$

$$J_{eff} = J[S_{Mn}(S_{Mn}+1)S_{Ru}(S_{Ru}+1)]^{1/2}$$

$$\chi_m = \frac{\chi_{chain}}{1-\chi_{chain}(2zJ'/Ng^2\beta^2)}$$

Table S1. Selected bond lengths (Å) and angles (°) for complexes **2** and **3**.

	2	**3**
Ru(1)-O(1)	2.000(4)	2.000(2)
Ru(1)-O(2)	1.975(4)	2.009(2)
Ru(1)-C(1)	2.042(5)	2.052(3)
Mn(1)-N(1)	2.251(4)	2.250(3)
Mn(1)-N(2)	2.000(5)	2.017(3)
Mn(1)-N(3)	2.017(4)	2.016(3)
N(1)-C(1)	1.151(6)	1.143(4)
C(1)-N(1)-Mn(1)	152.3(4)	153.0(2)
N(1)-C(1)-Ru(1)	177.5(5)	177.9(3)