Electronic Supplementary Material (ESI) for Dalton Transactions

Support Information

The supramolecular interaction mediated chiral 1D cyanide-bridged metamagnet: synthesis, crystal structures and magnetic properties

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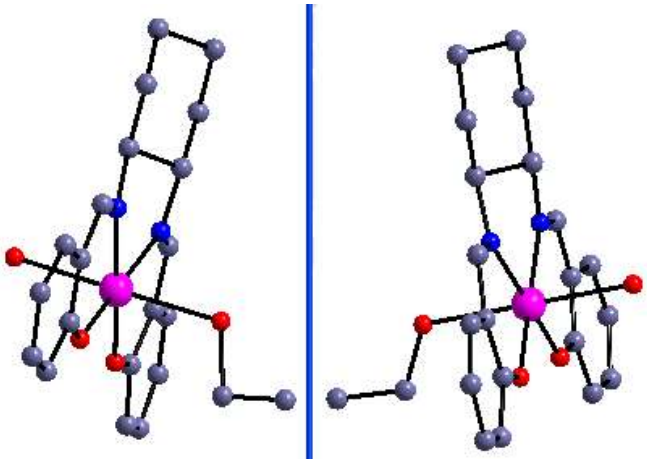

Fig. S1. Perspective view of the cationic structure of $[Mn(Salcy)(H_2O)(C_2H_5OH)]^+$ (R,R isomer, left and S,S isomer, right), respectively. The solvent molecule and all the H atoms have been omitted for clarity.

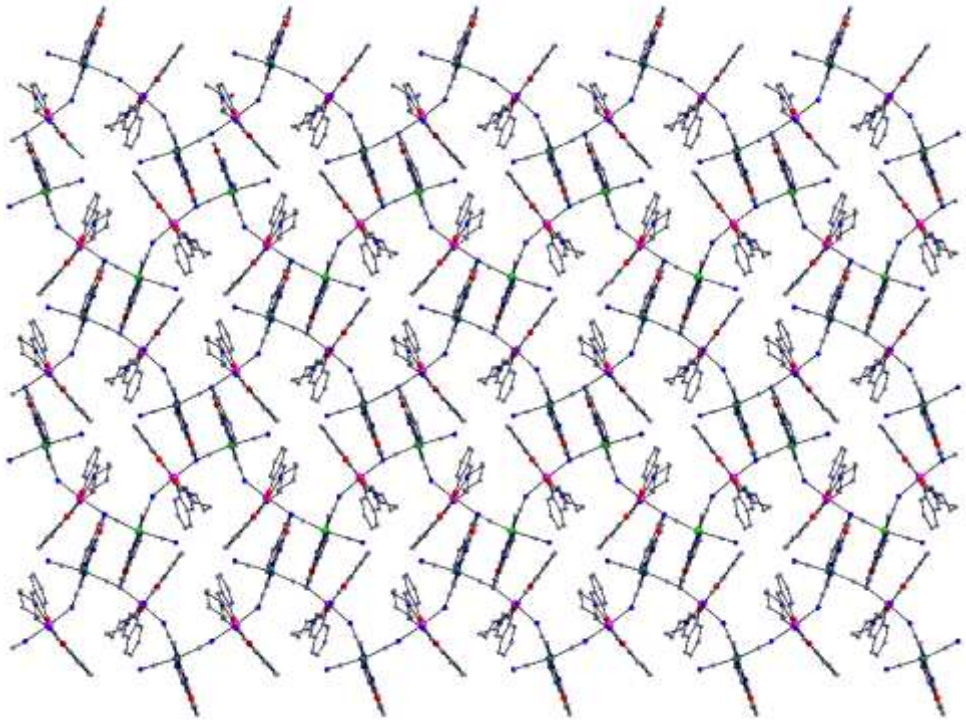

Fig. S2. The cell packing diagram of complexes **1** and **2** along *c* axis. All the H atoms and the solvent DMF have been omitted for clarity.

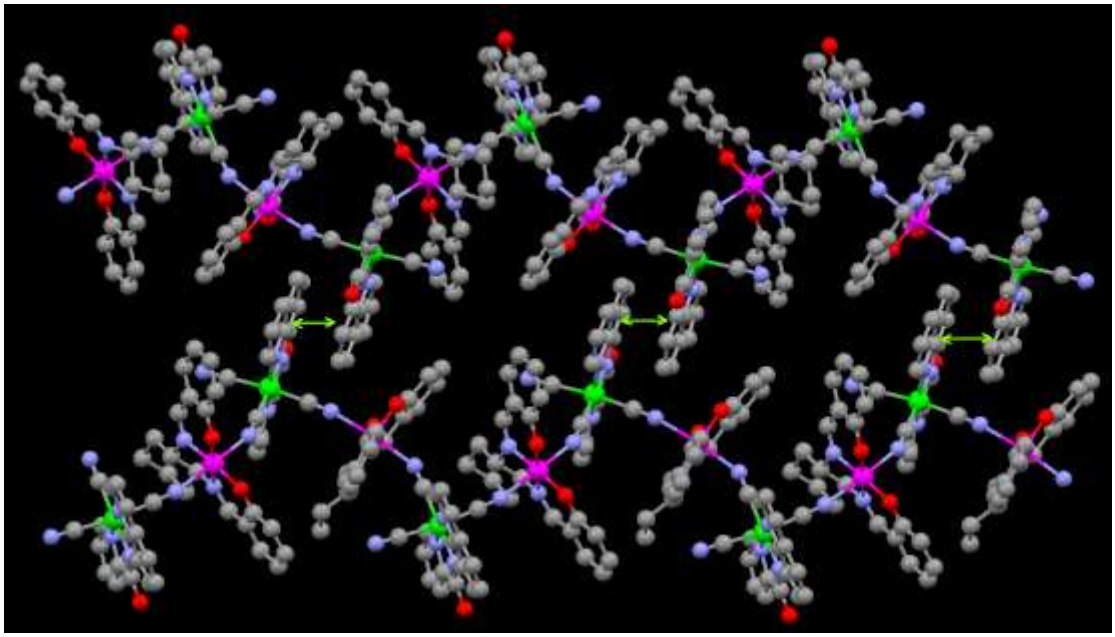

Fig. S3. The π-π interactions between the quinoline groups of pcq ligands.

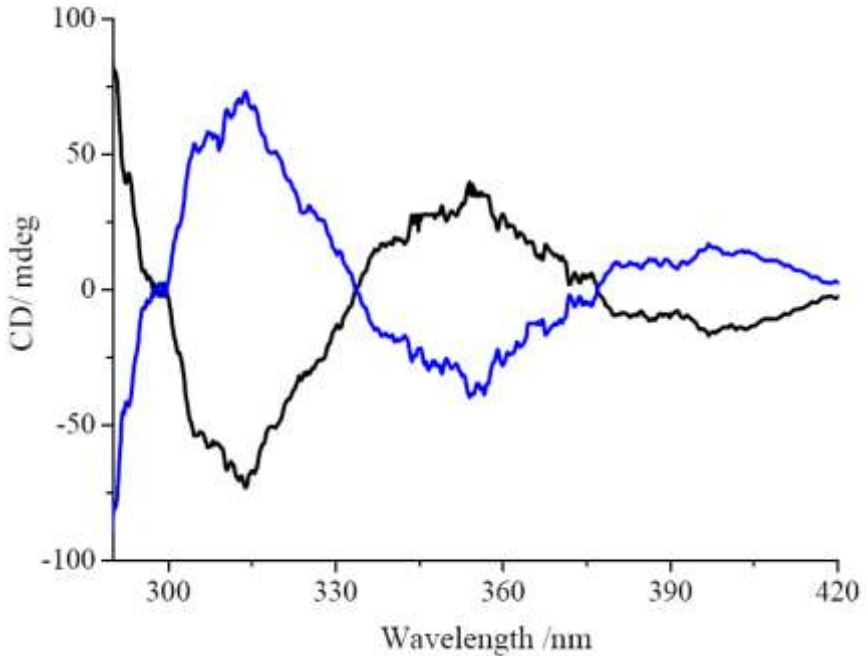

Fig. S4. CD spectra of **1** (*R* isomer, black) and **2** (*S* isomer, blue) in KBr pellets.

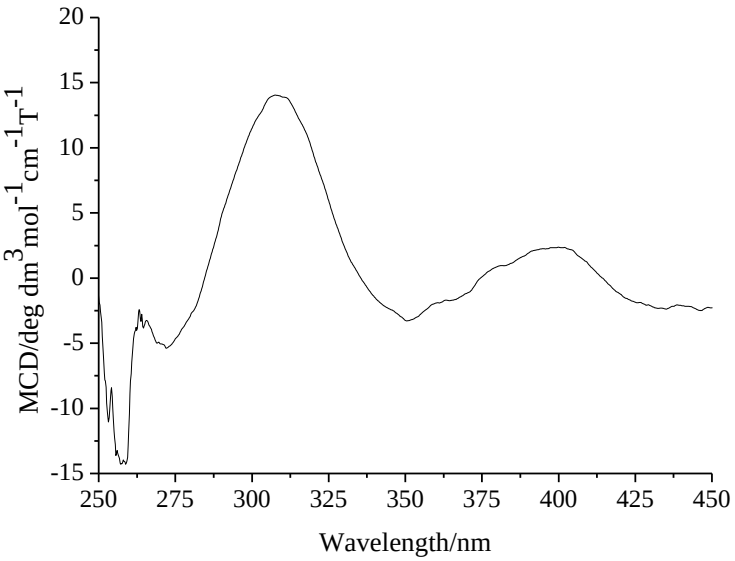

Fig. S5. The MCD spectra of complex **1**.

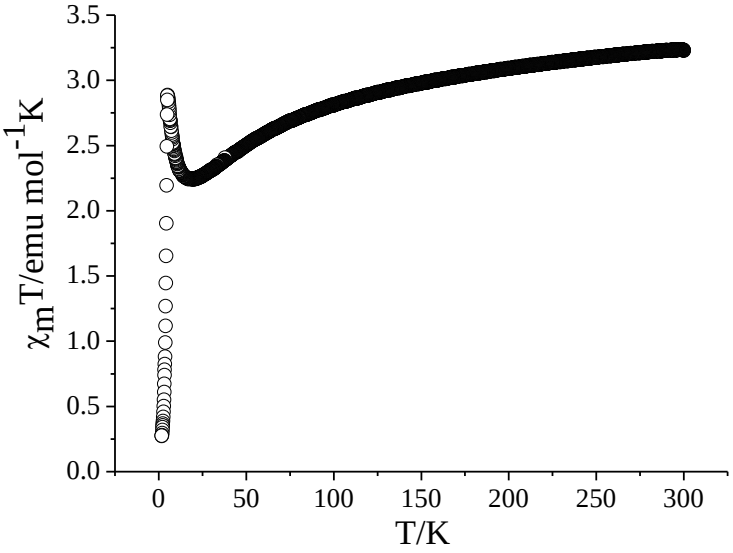

Fig. S6. Temperature dependence of $\chi_m T$ of complex **2**.

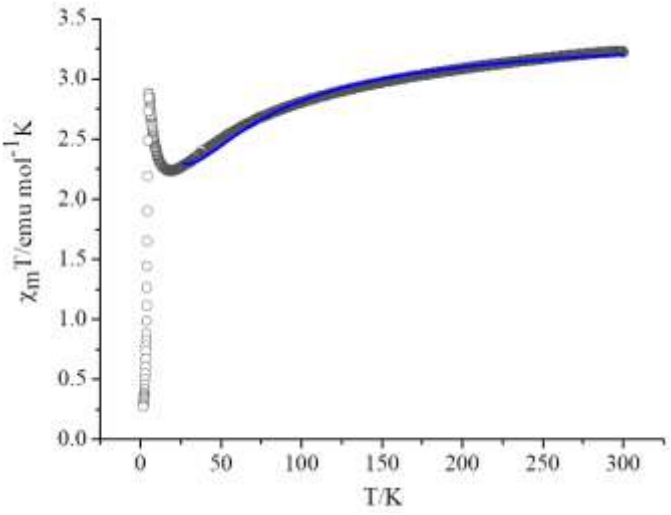

Fig. S7. Temperature dependence of $\chi_m T$ of complex **1** (the blue solid line represents the best fit based on the parameters discussed in the text by using Magpack).

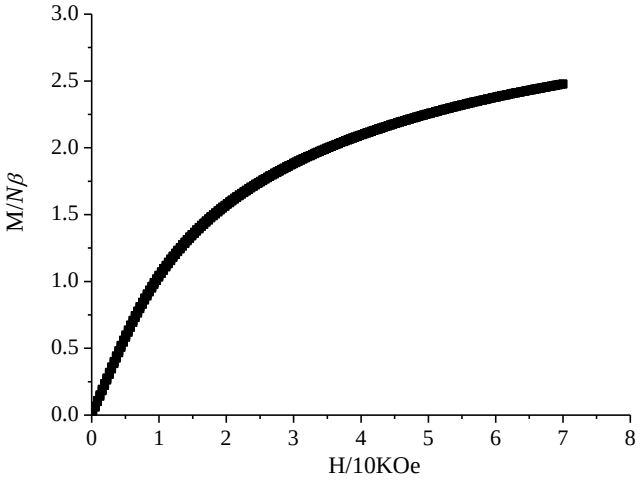

Fig. S8. The field dependence of magnetization at 5 K for complex **1**.

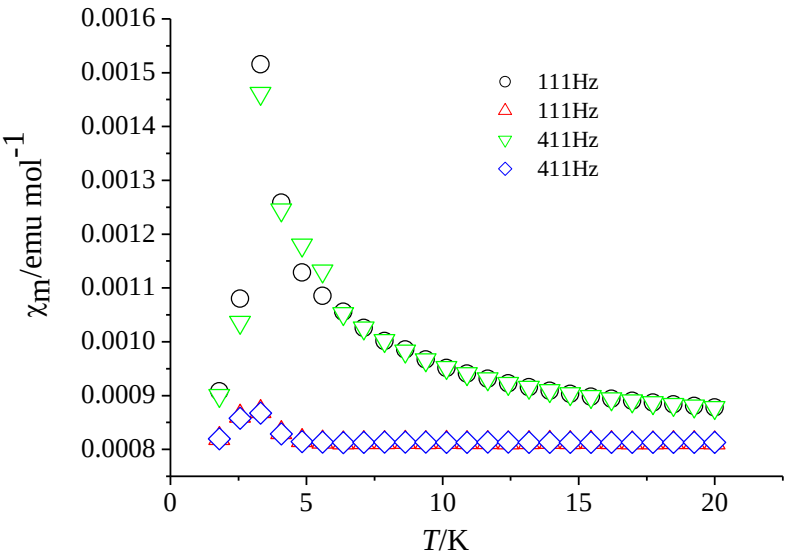

Fig. S9. Temperature dependence of ac magnetization of complex **1** in dc field of 5 kOe and ac field of 2 Oe at frequencies of 111 and 411Hz.

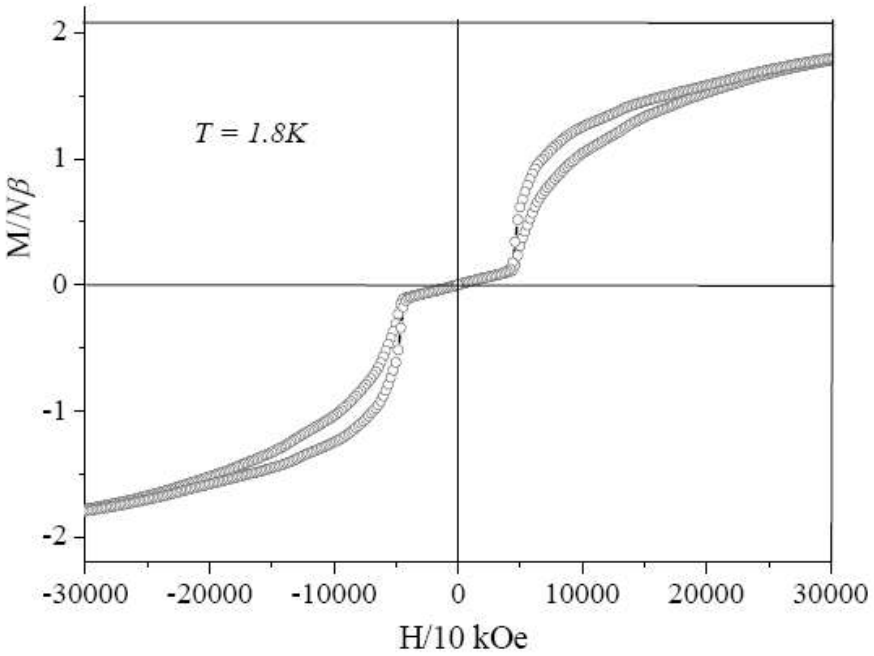

Fig. S10. Magnetic hysteresis loop for complex **1** at 1.8 K.

The preparation of complexes **1** and **2**:

A red-brown CH_3CN and CH_3OH solution (10 mL, v/v = 2:1) of [Mn((*R*,*R*)-Salcy)(H_2O)(C_2H_5OH)]ClO_4 or [Mn((*S*,*S*)-Salcy)(H_2O)(C_2H_5OH)]ClO_4 (0.1 mmol, 53.9 mg) was carefully layered onto a dark red DMF solution (10 mL) of *mer*-[PPh_4][Fe(pcq)$(CN)_3$] (0.1 mmol, 72.1mg). After the mixture stood for a few days in the dark box with the aim to avoid decomposing the cyanide-containing building block, dark brown crystals (Fig. S11) suitable for X-ray diffraction were obtained. They were collected by filtration, washed with cooled methanol, and dried at room temperature.

Complex **1**: Yield: 48.1 mg, 59.2%. Anal. Calcd for $C_{80.5}H_{70.5}Fe_2Mn_2N_{17.5}O_{7.5}$ (**1**): C, 59.51; H, 4.37; N, 15.09, Mn, 6.76, Fe, 6.88. Found: C, 59.45; H, 4.39; N, 15.16, Mn, 6.57, Fe, 6.66. Main IR bands (cm^{-1}): 2149 (s, νC≡N), 2115 (s, νC≡N), 1611 (vs, νC=N).

Complex **2**: Yield: 50.8 mg, 61.2%. Anal. Calcd for $C_{80.5}H_{70.5}Fe_2Mn_2N_{17.5}O_{7.5}$ (**2**): C, 59.51; H, 4.37; N, 15.09, Mn, 6.76, Fe, 6.88. Found: C, 59.21; H, 4.43; N, 15.26, Mn, 6.55, Fe, 6.67. Main IR bands (cm^{-1}): 2148 (s, νC≡N), 2116 (s, νC≡N), 1613 (vs, νC=N).

Fig. S11. The dark brown crystal mounted on a fiber.

Single Crystal X-ray Diffraction Determination. Data were collected on a Oxford Diffraction Gemini E diffractometer with Cu *Kα* radiation (λ = 0.71073 Å) at 293 K. Final unit cell parameters were derived by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated by using the preliminary cell-orientation matrix. CrysAlisPro Agilent Technologies software was used for collecting frames of data, indexing reflections, and determination of lattice constants; CrysAlisPro Agilent Technologies for integration of intensity of reflections and scaling, SCALE3 ABSPACK for absorption correction, The structures were solved by the direct method (*SHELXS-97*) and refined by full-matrix least-squares (*SHELXL-97*) on F^2.[1] Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Selected bond distances and bond angles for complexes **1** and **2** with their estimated standard deviation are listed in Table S1 (Supporting Information). CCDC 951679 and 951680 for complexes **1** and **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

(1) Sheldrick, G. M. SHELX-97, Universität Göttingen, Germany, **1997**.

Table S1.Crystallographic data for the schiff-base manganese compounds and complexes **1** and **2**.

	[Mn((*R*,*R*)-Salcy)-	**[Mn((*S*,*S*)-Salcy)-**	**1**	**2**
chemical formula	$C_{44}H_{56}Cl_2Mn_2N_4O_{16}$	$C_{44}H_{56}Cl_2Mn_2N_4O_{16}$	$C_{80.5}H_{70.5}Fe_2Mn_2N_{17.5}O_{7.5}$	$C_{80.5}H_{70.5}Fe_2Mn_2N_{17.5}O_{7.5}$
Fw	1077.71	1077.71	1624.62	1624.62
crystal system	monoclinic	monoclinic	Monoclinic	Monoclinic
Space group	P21	P21	P21	P21
a/Å	11.7676(4)	11.7752(4)	12.4204(6)	12.4080(6)
b/Å	15.5594(7)	15.5328(7)	20.4162(7)	20.4024(9)
c/Å	13.3423(5)	13.3312(6)	14.9983(6)	15.0189(9)
α/deg	90	90	90	90
β/deg	92.746(3)	92.818(4)	93.042(4)	92.969(5)
γ/deg	90	90	90	90
V/Å^3	2440.14(16)	2435.35(18)	3797.9(3)	3797.0(3)
Z	2	2	2	2
completeness	99.7%	99.6%	99.7%	99.3%
F(000)	1120	1120	1676	1676
θ/deg	1.51 to 26.00	1.52 to 25.01	1.48 to 25.01	1.48 to 25.01
GOF	1.021	0.979	1.046	1.033
$R_1[I>2\sigma(I)]$	0.0520	0.0744	0.0523	0.0934
wR_2 (all data)	0.1280	0.1447	0.1355	0.2692

Table S2. Selected bond lengths (Å) and angles (°) for complexes **1** and **2**.

	1	**2**
Fe(1)-C(1)	1.972(9)	1.981(15)
Fe(1)-C(2)	1.947(8)	1.957(15)
Fe(1)-C(3)	1.956(10)	1.984(17)
Fe(1)-N(4)	1.947(7)	1.980(11)
Fe(1)-N(6)	1.961(7)	1.967(10)
Fe(1)-N(7)	1.884(7)	1.879(12)
Mn(1)-N(8)	2.003(6)	1.988(11)
Mn(1)-N(9)	1.983(7)	1.984(11)
Mn(1)-N(1)	2.275(7)	2.305(13)
Mn(1)-N(10)	2.279(7)	2.280(13)
Mn(1)-O(2)	1.889(5)	1.891(9)
Mn(1)-O(3)	1.869(5)	1.862(9)
N(1)-C(1)-Fe(1)	177.9(8)	177.1(13)
N(2)-C(2)-Fe(1)	178.5(9)	178.3(14)
N(3)-C(3)-Fe(1)	178.1(8)	178.9(16)
C(1)-N(1)-Mn(1)	166.4(7)	165.5(13)
C(39)-N(10)-Mn(1)	153.0(7)	152.7(12)