Electronic Supplementary Material (ESI) for Dalton Transactions.

Solvation/Desolvation Induced Reversible Distortion Change and Switching between Spin Crossover and Single Molecular Magnet Behaviour in a Cobalt(II) Complex

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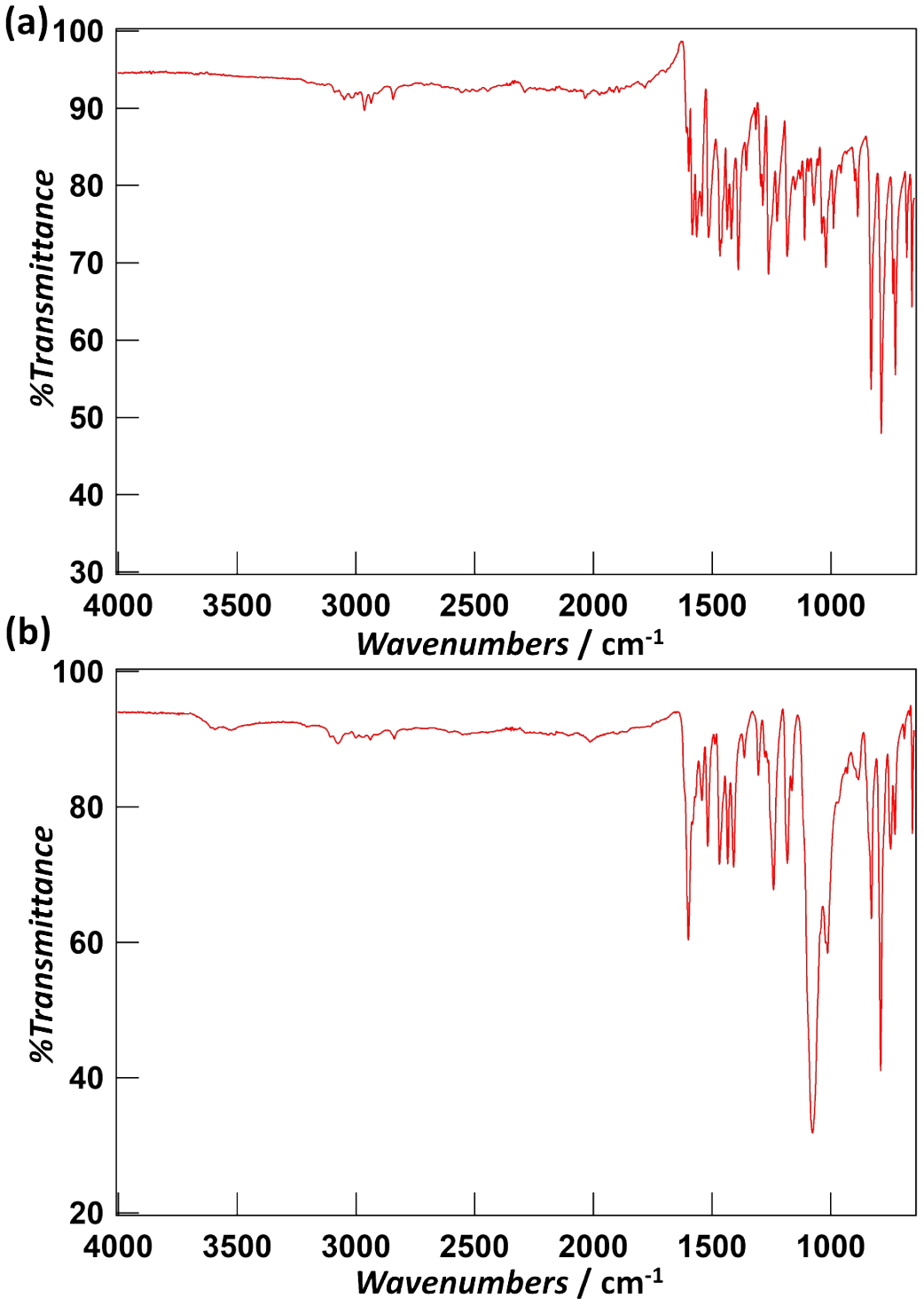
(a)
100
90
80
70
60
50
40
30
%Transmittance
4000
3500
3000
2500
2000
1500
1000
Wavenumbers / cm-1
(b)
100
80
60
40
20
%Transmittance
4000
3500
3000
2500
2000
1500
1000
Wavenumbers / cm-1

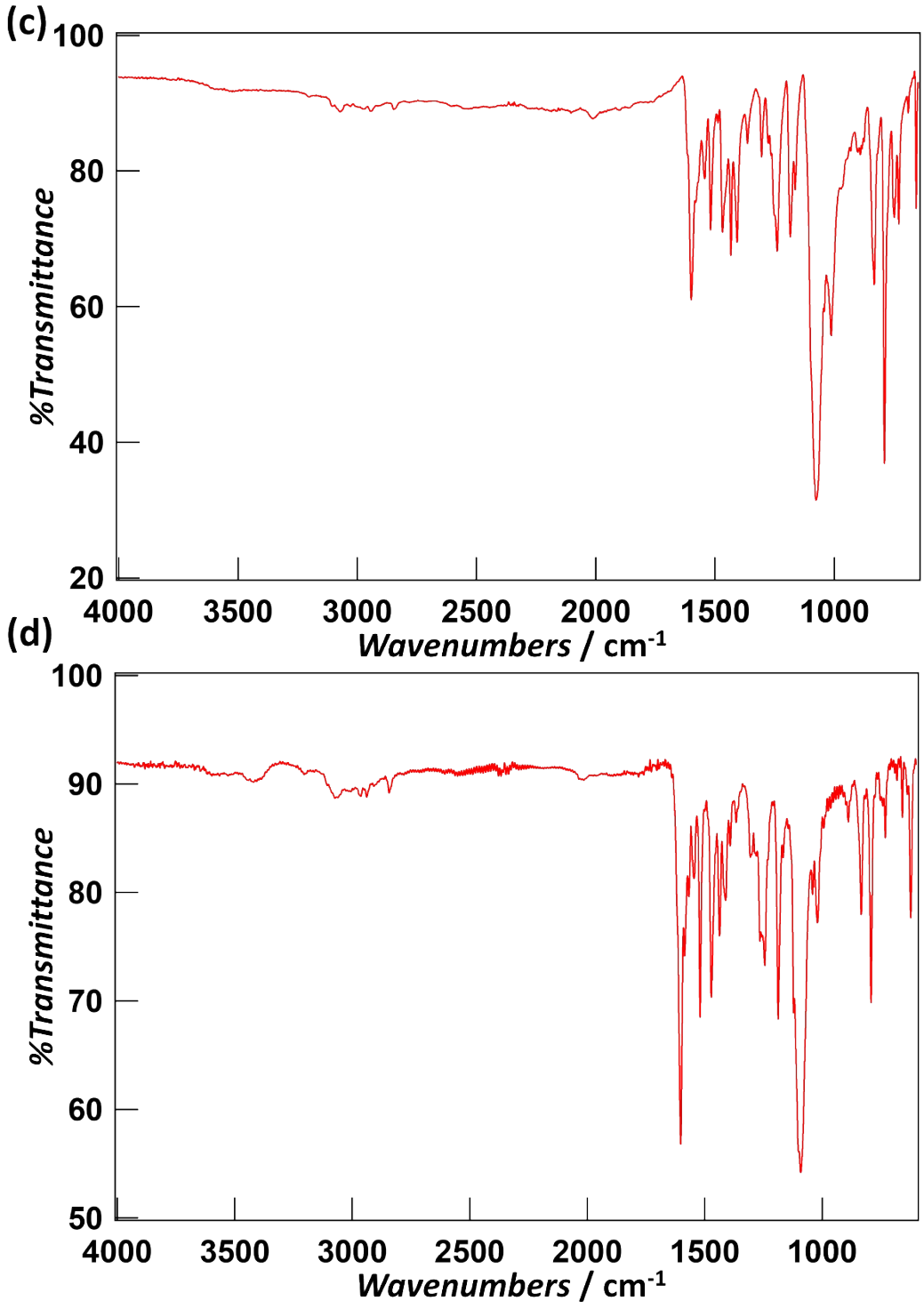

Fig. S1 FT-IR spectra for (a) MeOphterpy, (b) **1**·1.5MeOH, (c) **1** and (d) **1**·1.5MeOH′

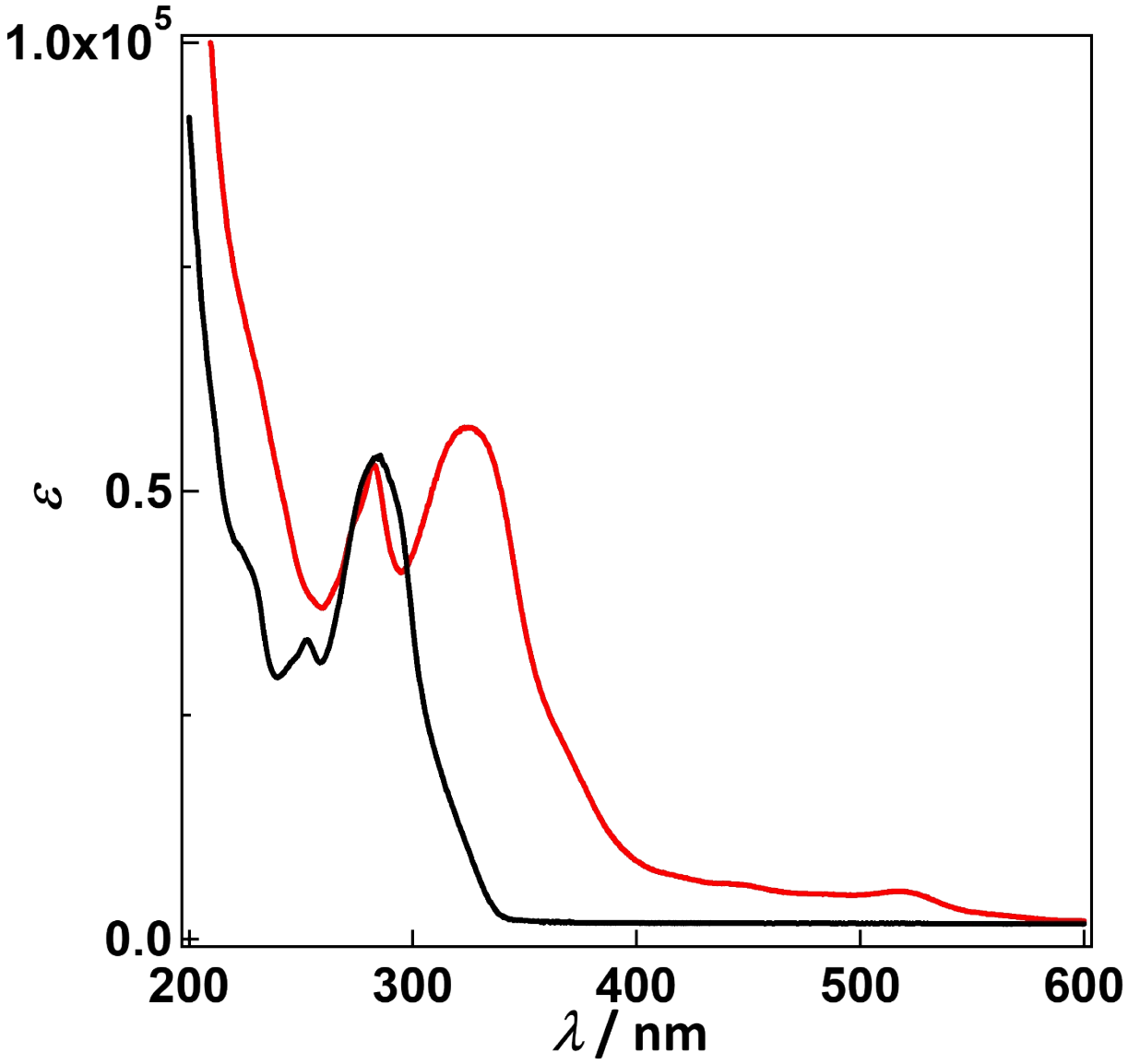

Fig. S2 UV-VIS spectra for acetonitrile solutions of MeOphterpy (back solid line) and **1**(red solid line)

Table. S1. Crystallographic parameters

Compound	**1**·1.5MeOH		**1**	
Formula	$C_{45.5}H_{40}Cl_2CoN_6O_{11.5}$		$C_{44}H_{34}Cl_2CoN_6O_{10}$	
Temperature (K)	110	273	110	300
Crystal system	Monoclinic			
Space group	$P2_1/c$			
a (Å)	18.5673(4)	18.8486(9)	17.9066(10)	17.9555(15)
b (Å)	14.9013(3)	15.2034(7)	15.2903(5)	15.5934(11)
c (Å)	16.1628(3)	16.2749(8)	16.1139(7)	16.1013(13)
α (°)	90.0000	90.0000	90.0000	90.0000
β (°)	104.196(2)	104.515(5)	112.673(6)	110.289(9)
γ (°)	90.0000	90.0000	90.0000	90.0000
V (Å^3)	4335.31(16)	4514.9(4)	4071.0(4)	4228.5(6)
Z	4	4	4	4
R1	0.0433	0.0611	0.0577	0.0849
wR2	0.1163	0.1469	0.1284	0.2106
R1(all)	0.0568	0.1218	0.0961	0.1723
wR2(all)	0.1225	0.1678	0.1435	0.2540
CCDC	2289952	2289953	2289954	2289955

Table S2. Representative bond distances (Å) around cobalt(II) centers

Compound	**1**·1.5MeOH		**1**	
Temperature (K)	110	273	110	300
Co-N1	2.067(2)	2.109(3)	2.152(3)	2.145(5)
Co-N2	1.891(2)	1.954(3)	2.065(3)	2.053(5)
Co-N3	2.054(2)	2.095(3)	2.163(3)	2.157(4)
Co-N4	2.097(2)	2.115(3)	2.136(3)	2.148(5)
Co-N5	1.910(2)	1.966(3)	2.065(3)	2.068(5)
Co-N6	2.100(2)	2.122(3)	2.144(3)	2.164(5)

Table S3. Bond angles (°) and distortion Σ values (°) around cobalt(II) centers

Compound	**1**·1.5MeOH		**1**	
Temperature (K)	110	273	110	300
N(1)-Co-N(2)	79.88(8)	78.37(11)	76.48(11)	76.30(18)
N(1)Co-N(4)	91.66(7)	92.27(11)	96.11(11)	96.08(17)
N(1)-Co-N(5)	98.69(8)	99.60(12)	94.83(11)	96.69(18)
N(1)-Co-N(6)	96.56(8)	97.48(12)	94.37(11)	94.64(19)
N(2)-Co-N(3)	80.08(8)	78.29(12)	75.10(12)	75.10(17)
N(2)-Co-N(4)	101.53(8)	103.33(11)	105.53(11)	105.50(17)
N(2)-Co-N(6)	99.74(8)	100.60(12)	104.42(11)	104.19(19)
N(3)-Co-N(4)	91.29(8)	90.84(11)	91.87(11)	91.51(16)
N(3)-Co-N(5)	101.36(8)	103.79(11)	113.59(12)	111.91(18)
N(3)-Co-N(6)	87.86(8)	89.06(12)	92.22(11)	92.31(18)
N(4)-Co-N(5)	79.23(8)	78.13(11)	75.61(11)	75.39(17)
N(5)-Co-N(6)	79.62(8)	78.14(12)	75.35(11)	75.63(18)
Σ (°)	94.16	105.92	130.40	130.41

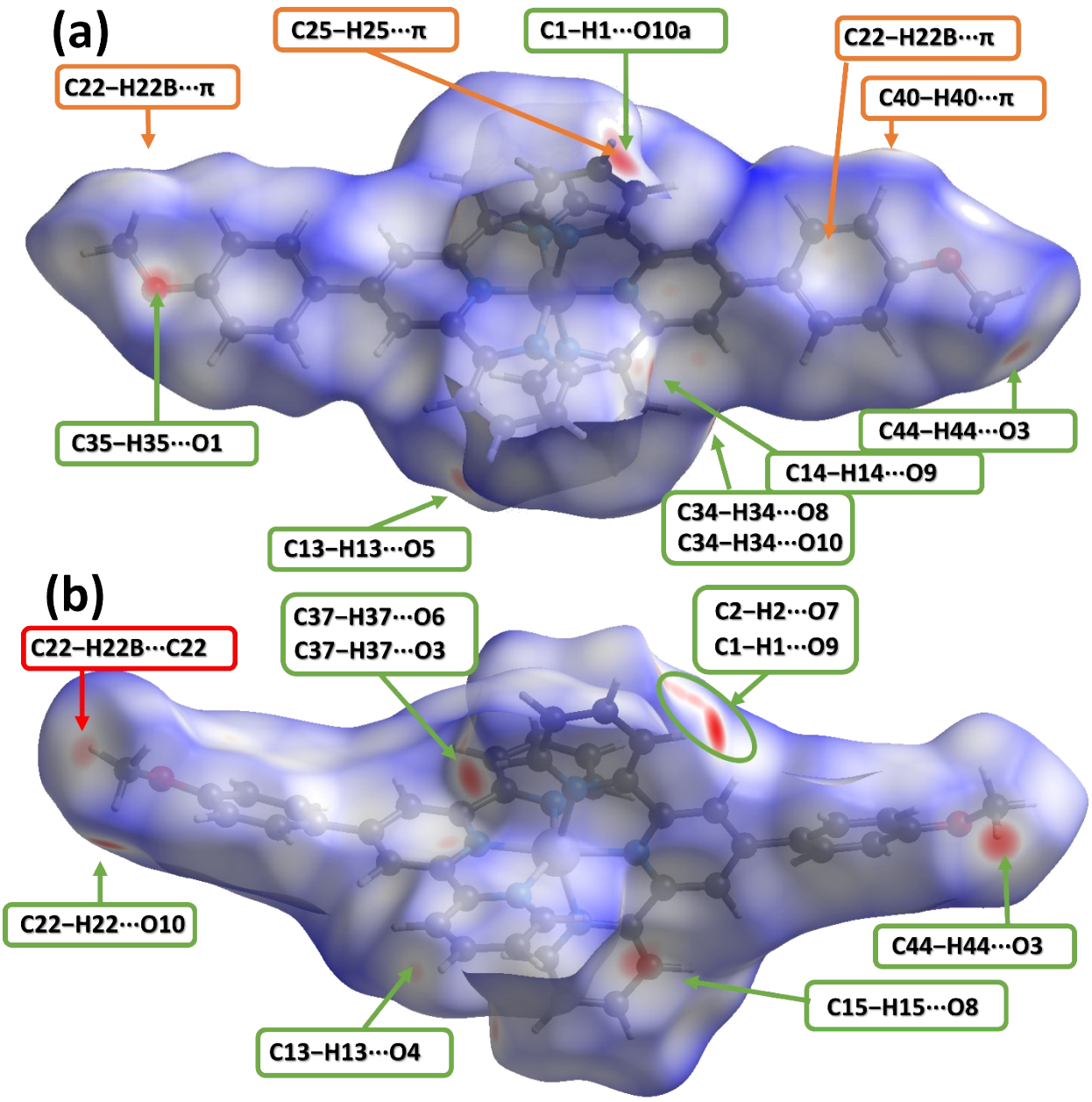

Fig. S3 Hirshfeld surface for (a) **1**·1.5MeOH and (b) **1** mapped with d_{norm} in the range from –0.1734 to 1.5686 a.u. The red dots indicate intermolecular contacts occurring due to shorter distances than the sum of the van der Waals radii. Green enclosure lines indicate hydrogen bonds between $[Co(MeOphterpy)_2]^{2+}$ cations and perchlorate anions. Orange enclosure lines indicate C–H···π interactions. Red enclosure lines indicate intermolecular interactions between adjacent $[Co(MeOphterpy)_2]^{2+}$ cations

Table S4. Selected intermolecular separations (Å) for **1**·1.5MeOH and **1** at 110K

1·1.5MeOH		**1**	
$[Co(MeOphterpy)_2]^{2+}\cdots ClO_4^-$		$[Co(MeOphterpy)_2]^{2+}\cdots ClO_4^-$	
C1−H1···O10a	2.914	C1−H1···O9	3.204
C3−H3···O6	3.374	C2−H2···O7	3.209
C13−H13···O5	3.435	C3−H3···O3	3.191
C14−H14···O9	3.316	C13−H13···O5	3.526
C34−H34···O8	3.395	C15−H15···O8	3.345
C34−H34···O8a	3.470	C22−H22···O10	3.369
C34−H34···O10	3.207	C34−H34···O8	3.248
C37−H37···O3	3.216	C35−H35···O10	3.103
C44−H44B···O3	3.041	C37−H37···O3	3.101
$[Co(MeOphterpy)_2]^{2+}\cdots$ $[Co(MeOphterpy)_2]^{2+}$		C37−H37···O6	3.352
C22−H22··· **π** (C(38-43))	3.675	C44−H44···O5	3.267
C25−H25··· **π** (C(38-43))	3.387	$[Co(MeOphterpy)_2]^{2+}\cdots$ $[Co(MeOphterpy)_2]^{2+}$	
C40−H40··· **π** (N6C(33-37))	4.080	C22−H22B···C22	3.3235
C35−H35···O1	3.491		
π–π interaction			
π (C(1−5)N1)··· **π** (C(11−15)N3)	4.001	**π** (C(1−5)N1)··· **π** (C(11−15)N(3))	3.756
π (C(1−5)N1)··· **π** (C(16−21)	3.819	**π** (C(1−5)N1)··· **π** (C(16−21)	3.820

CH···π is the distance between CH and the centroid of pyridine and benzene rings.

π···π is the distance between centroids of pyridine and benzene rings.

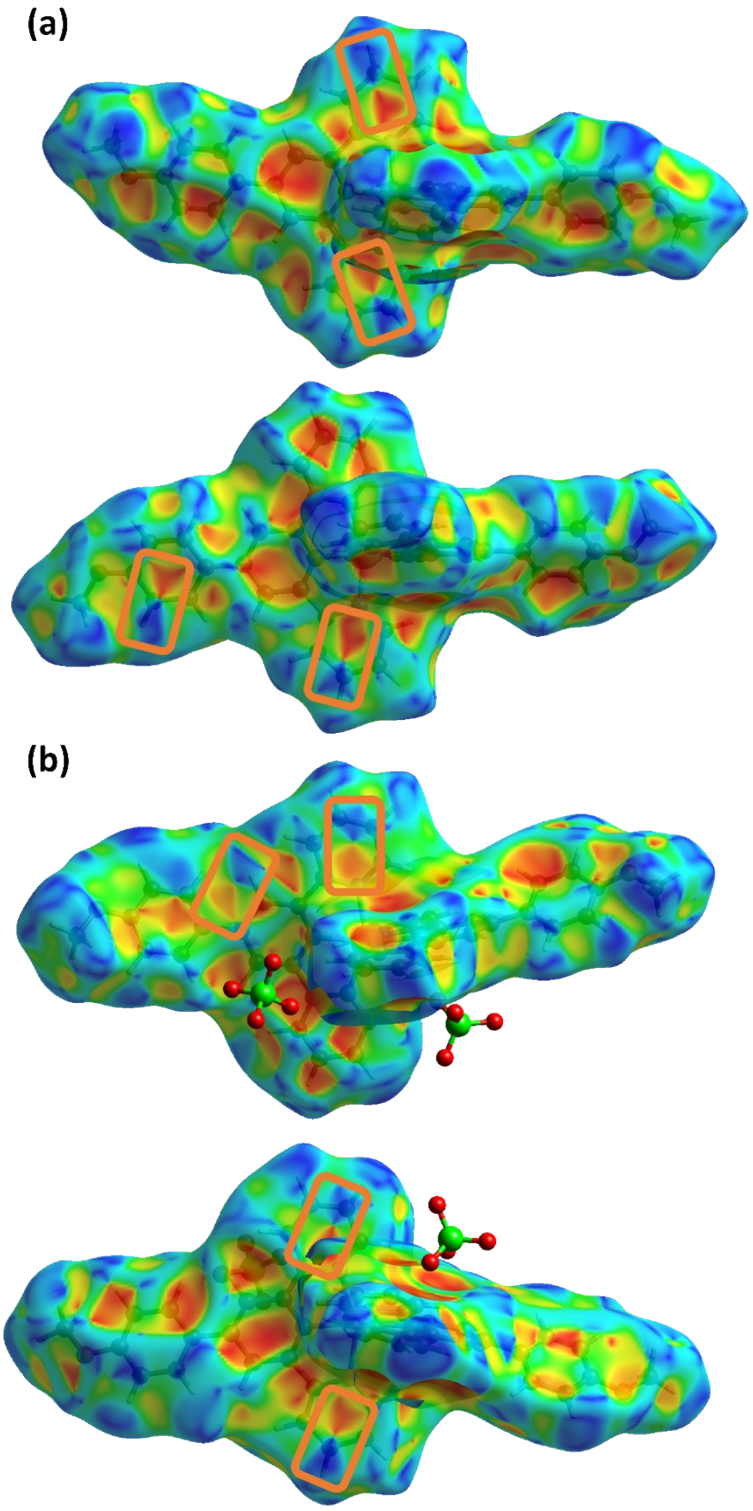

Figure S4. Hirshfeld surface for (a) **1**·1.5MeOH and (b) **1** mapped with shape index. The adjacent red and blue triangles and the orange enclosure lines indicate the π-π interactions

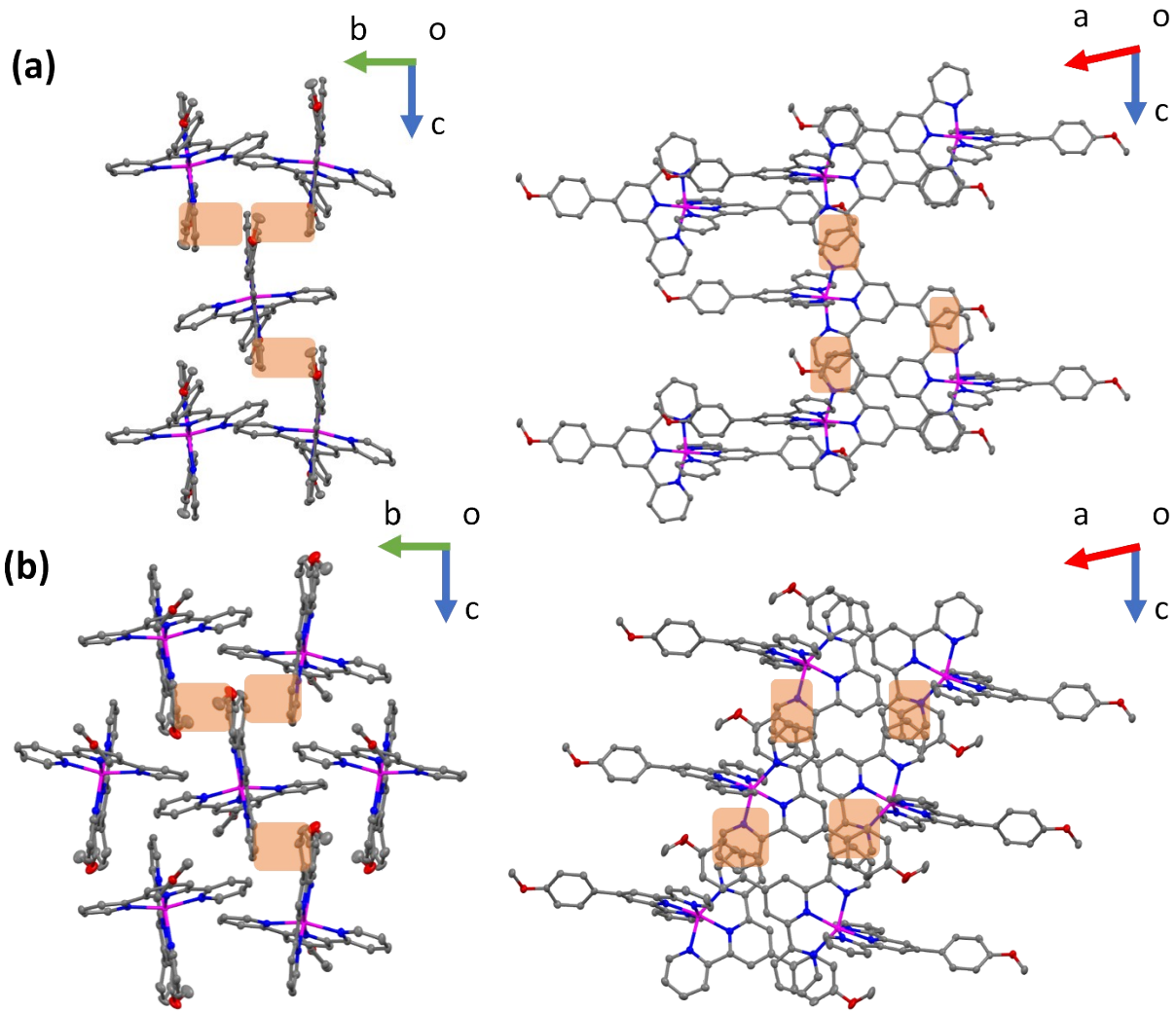

Figure S5. π–π interactions in packing structures for (a) **1**·1.5MeOH and (b) **1**

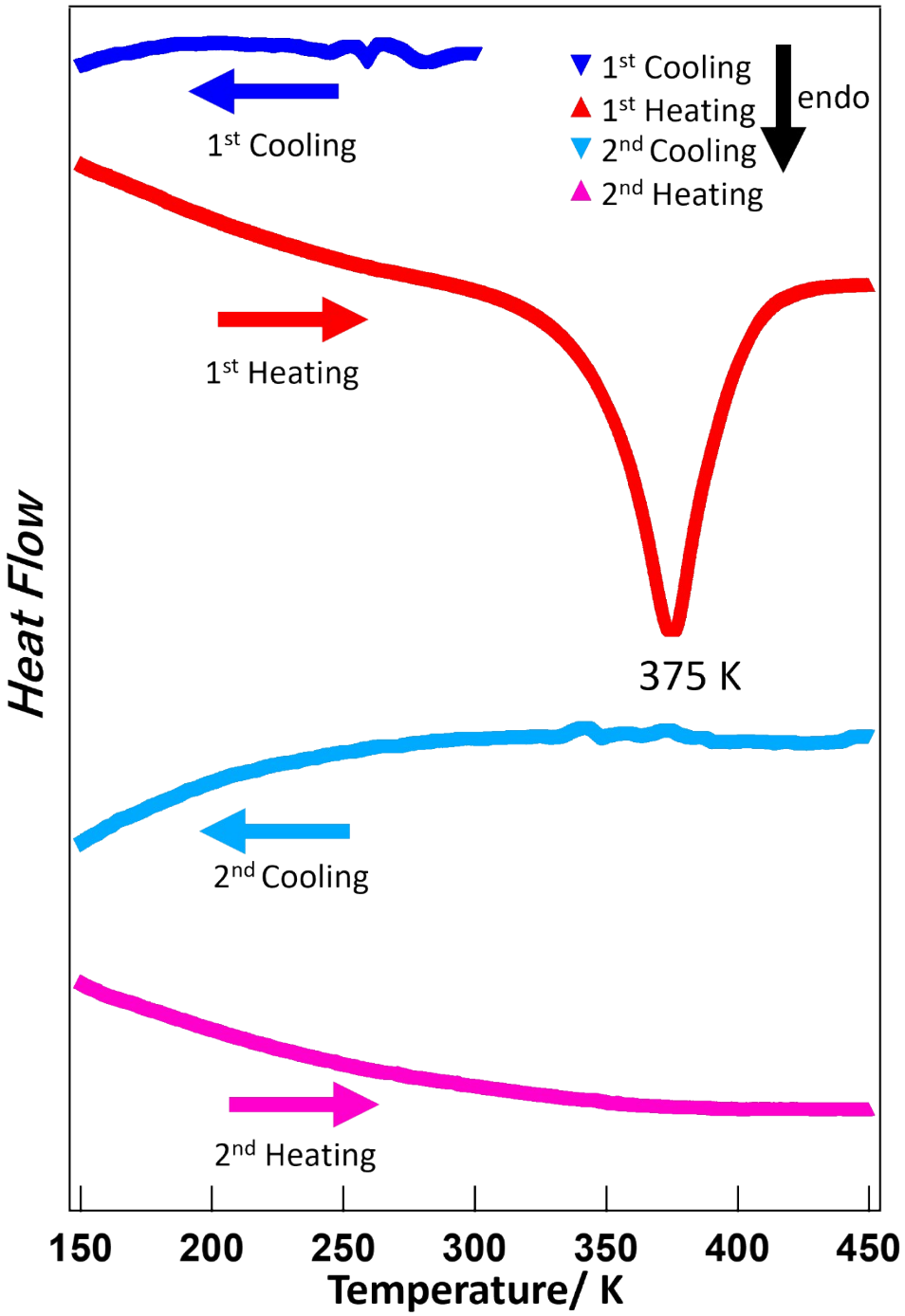

Figure S6. DSC curves for **1**·1.5MeOH in the range 150–450 K at 10 K min^{-1} (blue: 1st cooling process, red: 1st heating process, light blue: 2nd cooling process, and pink: 2nd Heating process)

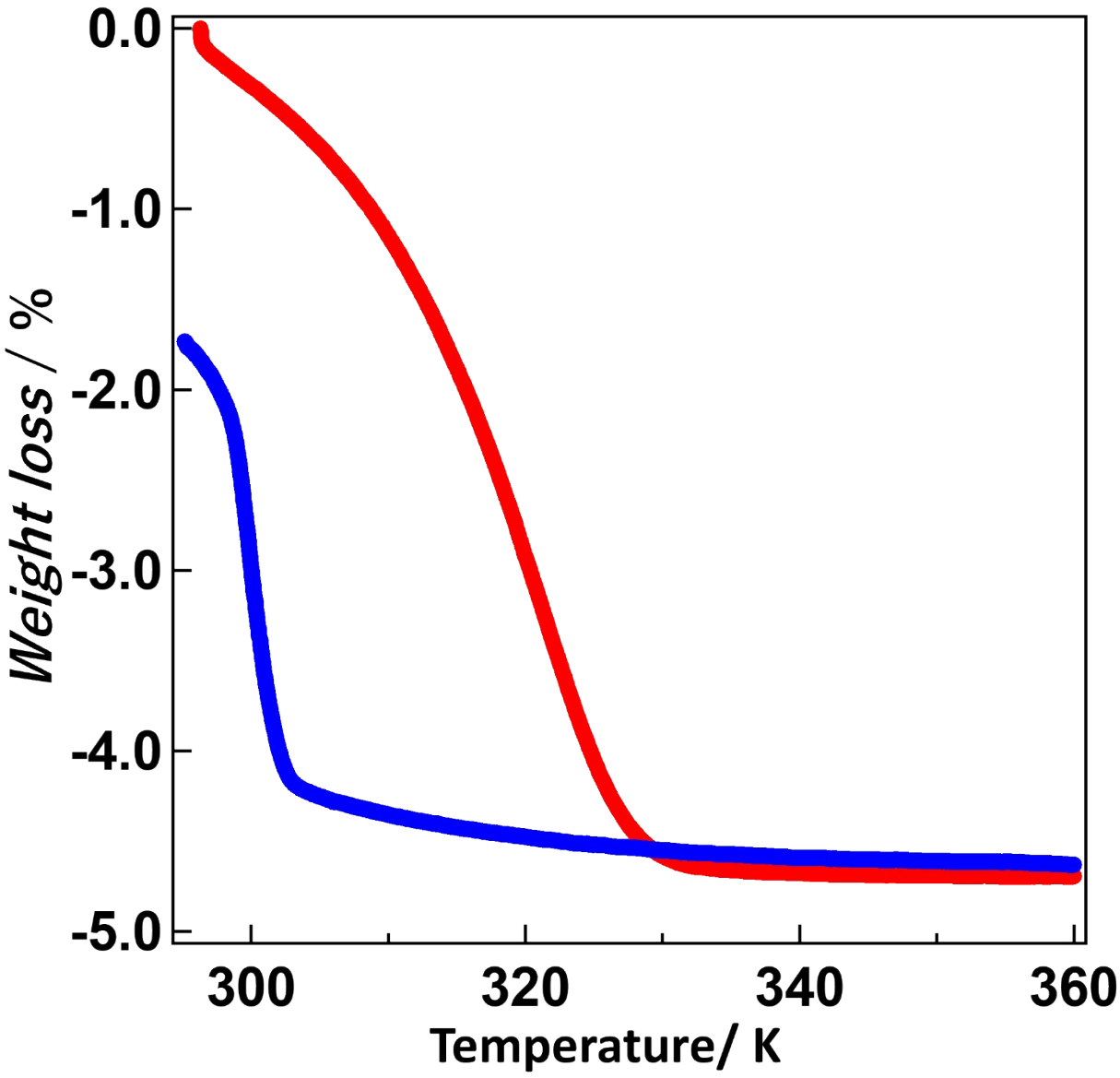

Fig. S7. Thermogravimetric analysis (TGA) for **1**·1.5MeOH. The red line is heating, and the blue line is cooling. In the heating range, **1**·1.5MeOH revealed *ca* 4.7% weight loss in the 300 K-360 K, corresponding to the removal of 1.5MeOH molecules (calc.4.8%). This compound re-absorbed H_2O in the atmosphere under the 300 K-360 K cooling range

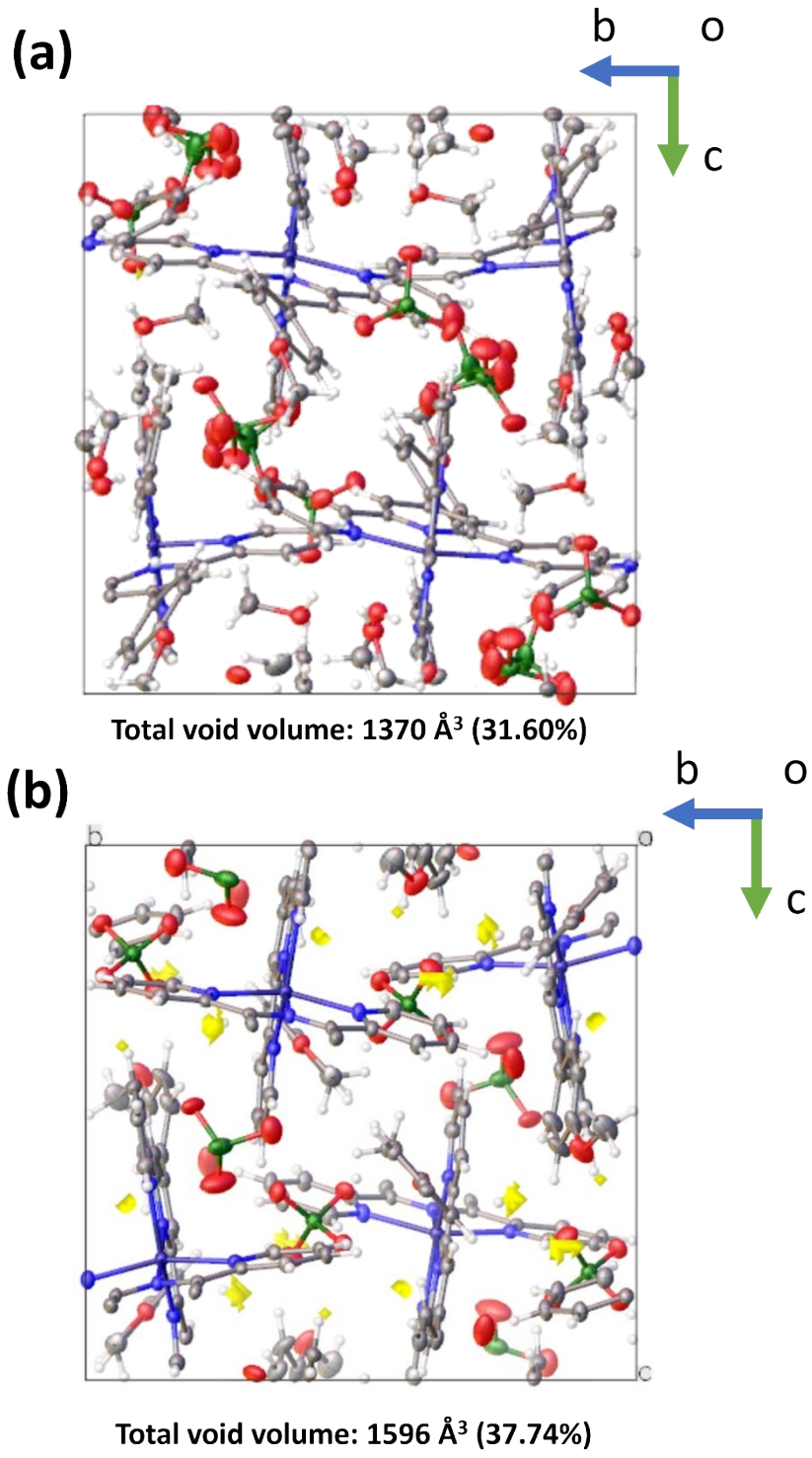

Fig. S8. Single crystal void volumes for (a) **1**·1.5MeOH, (b) **1** at 110 K. Yellow "fog" represents the voids

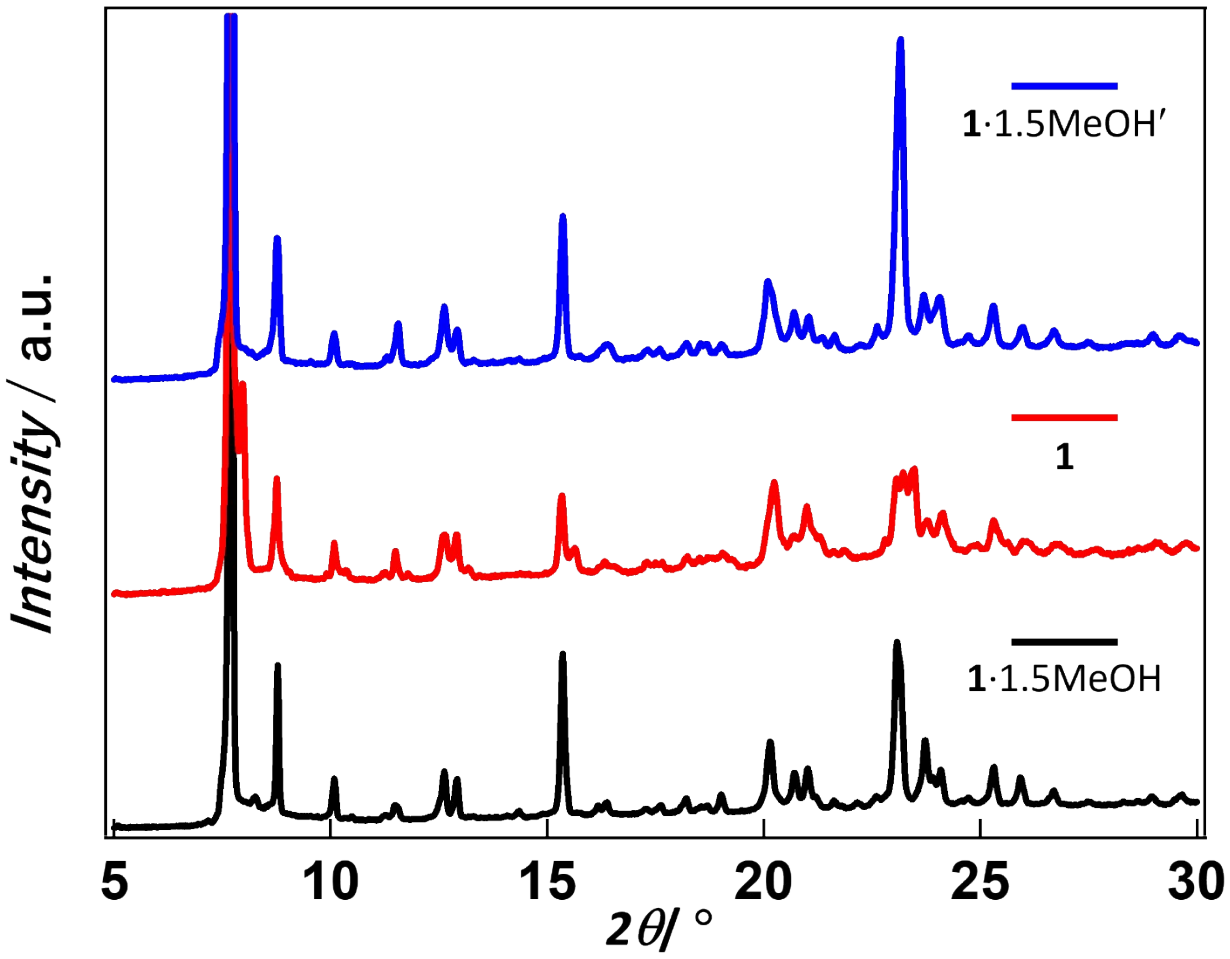

Fig. S9. PXRD patterns for **1**·1.5MeOH (black), **1** (red), and **1**·1.5MeOH′ (blue) at 300 K

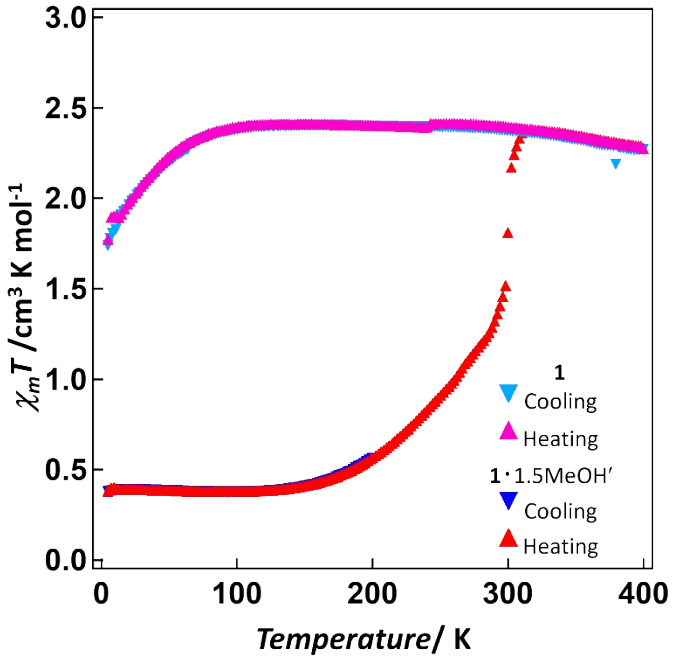

Figure S10. $\chi_m T$ versus T plots for **1**, **1**·1.5MeOH′ in the range 2–400 K (▲: heating mode, pink:**1**, red: **1**·1.5MeOH′, ▼: cooling mode, light blue:**1**, bule: **1**·1.5MeOH′), where $\chi_m T$ is the molar magnetic susceptibility, and T is the temperature

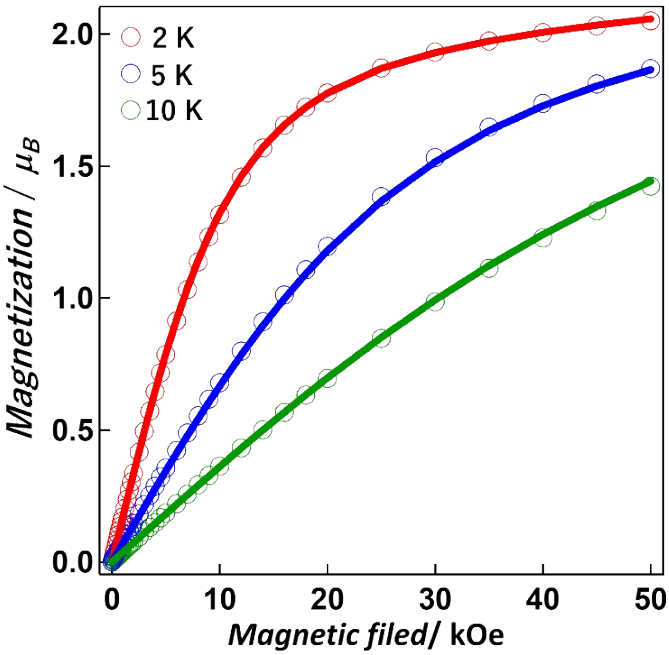

Figure S11. M versus H plots for **1**. The plots show the experimental values (red: 2 K, blue: 5 K, green: 10 K, solid line: fitting)

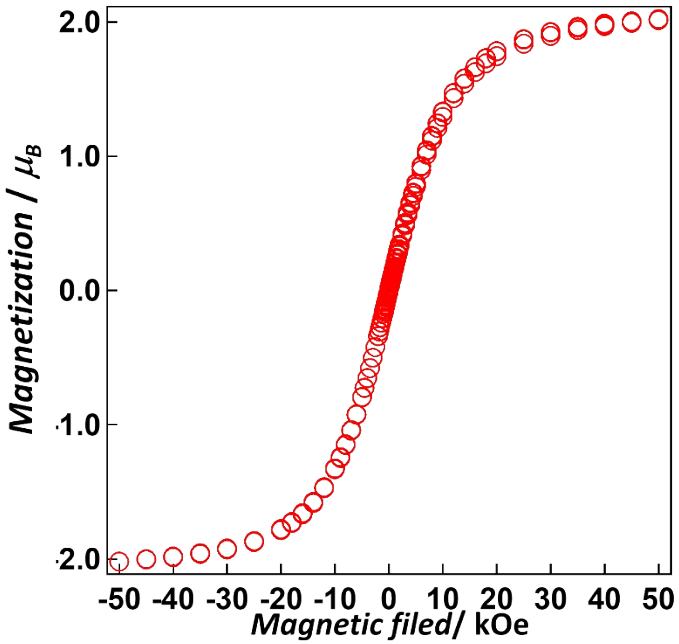

Figure S12. *M* versus *H* plots at 2 K for **1**

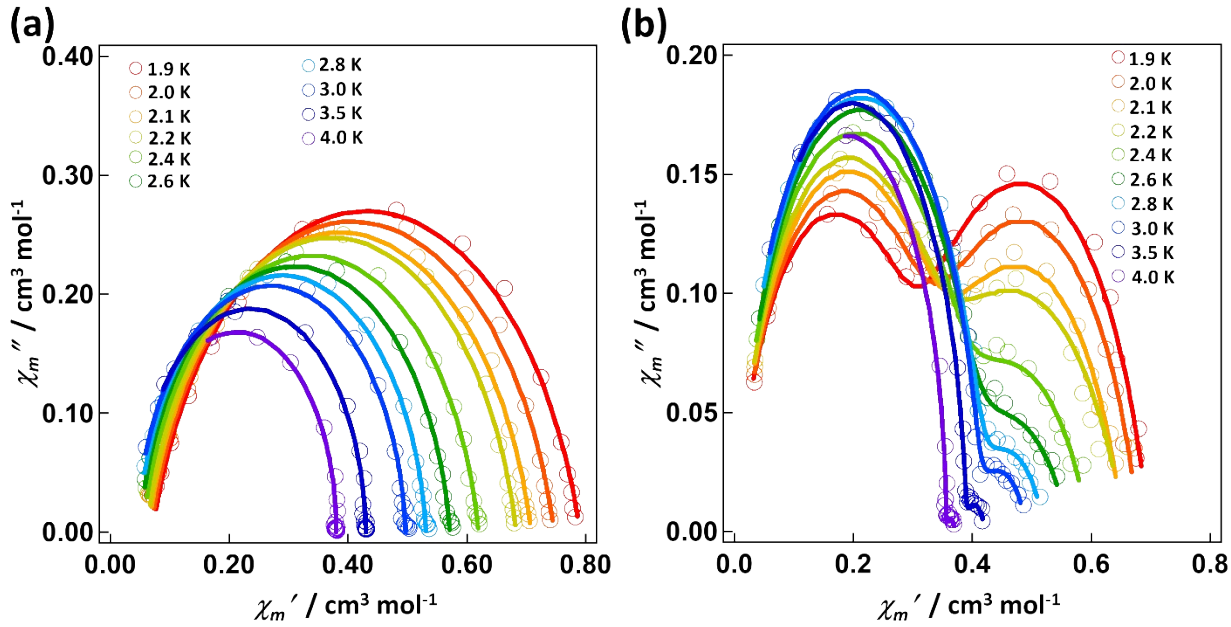

Figure S13. Cole-Cole plots for **1** under an applied dc field of (a) 1000 Oe and (b) 3000 Oe. Solid lines represent the best fits for the generalized Debye and two processes model

Table S5. Fitted parameters for the Cole-Cole plots for **1** under applied field of 1000 Oe as determined within the generated Debye model (τ : magnetic relaxation time, α : distribution of relaxation times).

	1000 Oe	
T (K)	τ (s)	α
1.9	1.25×10^{-2}	0.181
2.0	1.03×10^{-2}	0.165
2.1	8.49×10^{-3}	0.156
2.2	7.20×10^{-3}	0.145
2.4	4.47×10^{-3}	0.124
2.6	2.82×10^{-3}	0.0986
2.8	1.78×10^{-3}	0.0748
3.0	1.16×10^{-3}	0.0577
3.5	4.58×10^{-4}	0.0204
4.0	2.14×10^{-4}	1.02×10^{-15}

Table S6. Fitted parameters for the Cole-Cole plots for **1** under applied field of 3000 Oe as determined within the two processes Debye model (τ : magnetic relaxation time, α : distribution of relaxation times).

	3000 Oe			
	Low frequency		High frequency	
T (K)	τ (s)	α	τ (s)	α
1.9	5.68×10^{-2}	0.228	8.08×10^{-4}	0.130
2.0	5.41×10^{-2}	0.246	8.44×10^{-4}	0.130
2.1	5.31×10^{-2}	0.271	8.47×10^{-4}	0.124
2.2	4.86×10^{-2}	0.360	7.91×10^{-4}	0.0832
2.4	5.67×10^{-2}	0.378	7.73×10^{-4}	0.0930
2.6	6.87×10^{-2}	0.448	6.97×10^{-4}	0.0729
2.8	1.08×10^{-1}	0.381	6.03×10^{-4}	0.0728
3.0	1.34×10^{-1}	0.371	4.93×10^{-4}	0.0507
3.5	1.87×10^{-1}	0.271	2.83×10^{-4}	0.0296
4.0	2.00×10^{-1}	0.214	1.64×10^{-4}	1.02×10^{-20}

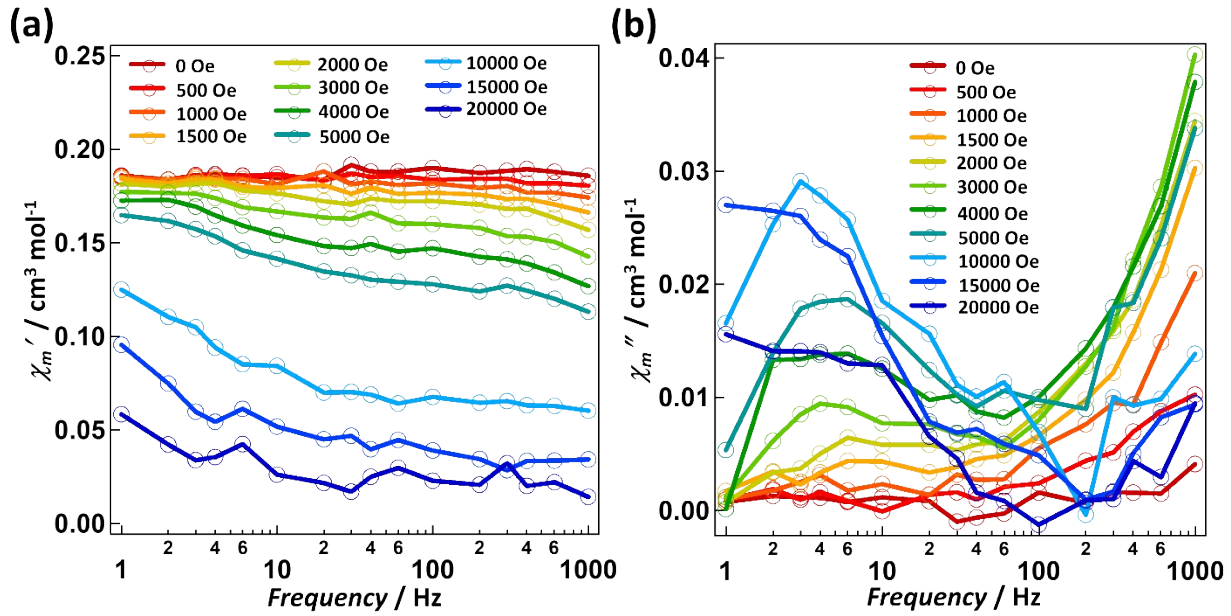

Figure S14. Variable-frequency AC magnetic susceptibility data of **1**·1.5MeOH collected under an applied field bias from 0 to 20000 Oe. The solid lines serve as a guide for the eyes

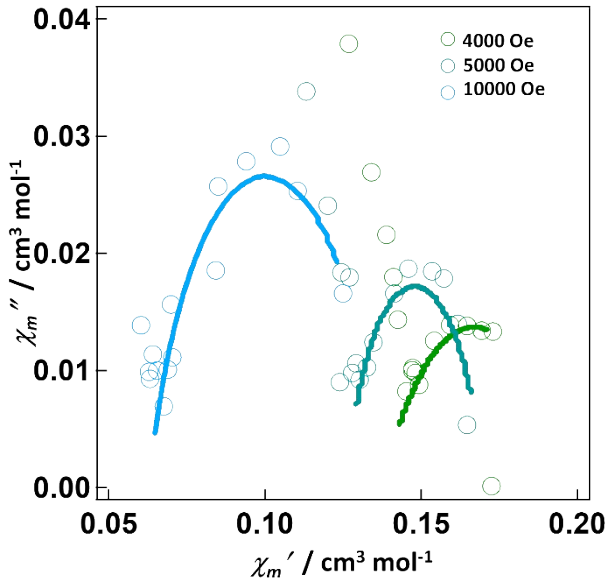

Figure S15. Cole-Cole plots for **1**·1.5MeOH at 2 K. Solid lines represent the best fits for the generalized Debye processes model

Table S7. Fitted parameters for the Cole-Cole plots for **1**·1.5MeOH at 2 K as determined within the generated Debye model (τ: magnetic relaxation time, α: distribution of relaxation times).

Field (Oe)	τ (s)	α
4000	5.15×10^{-2}	0.445
5000	2.62×10^{-2}	0.244
10000	4.71×10^{-2}	0.212