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Electronic Supplementary Information (ESI)

Abrupt spin transition in a modified-terpyridine cobalt(II) complex with a highly-distorted [CoN6] core

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EXPERIMENTAL SECTION

Synthesis. All reagents were commercially available and used without further purification. 4'-Hydroxy-2,2':6',2''-terpyridine (HO-terpy) was prepared according to the reported synthetic procedure.[27]

*Naph-C2-terpy (**L1**).* 2-(2-Bromoethoxy)naphthalene (Naph-C2-Br) was prepared by the reaction of 2-naphthol (1.44 g, 10.0 mmol), 1,2-dibromoethane (20.0 mmol) and K_2CO_3 (5.0 g, 36.2 mmol) in dry DMF (100 mL). After stirring overnight, the residue was removed by filtration, and the filtrate was evaporated. The crude powder obtained was purified by column chromatography on silica gel with hexane – ethyl acetate (1/3 = v/v) as eluent (yield, ~40 %). Naph-C2-Br (3.0 mmol) dissolved in DMF (20 mL) was added dropwise to the mixture of OH-terpy (0.5 g, 2.0 mmol) and K_2CO_3 (1.0 g, 7.24 mmol) in DMF (40 mL). The solution was refluxed at 80 ˚C for 15 h, then evaporated. The residue was extracted by $CHCl_3/H_2O$, and the organic layer was dried over $MgSO_4$. After filtering off the $MgSO_4$, the solvent mixture was removed by rotary evaporation to yield the ligand as a crude powder which was purified by column chromatography on a silica gel column with hexane – ethyl acetate (1/4 = v/v) as eluent (yield, ~60 %). ^{1}H-NMR ($CDCl_3$): 9.20 (d, 2H), 8.55 (d, 2H), 8.01 (s, 2H), 7.71-7.45 (m, 6H), 7.35 (m, 2H), 7.19 (m, 3H), 4.72 (t, 2H), 4.33 (t, 2H) ppm.

*R-terpy (R = 2-naphthyl (**L2**), 9-anthracenyl (**L3**))*. 2-Acetylpyridine (1.20 g, 10.0 mmol) and the required π-conjugated aldehyde (10.0 mmol) in MeOH (50 mL) were stirred with mild heating until they had dissolved. Then, aqueous NaOH (10 mL of a 1.5 M solution) was added to the solution. After stirring for 4 h at ambient temperature, the dark yellow precipitate was isolated by filtration and recrystallized from MeOH. This product was used for the next reaction without further purification. 2-Acetylpyridine (0.72 g, 6.0 mmol) was added slowly to a solution of ^{t}BuOK (1.0 g, 6.0 mmol) in dry THF (50 mL). After stirring at ambient temperature under argon for 2 h, the precursor prepared as above (5.78 mmol) was added to the solution. Then, the solution was stirred for 14 h at ambient temperature during which time the color changed to dark red. Excess NH_4OAc in EtOH (20 mL) was added and the solution was heated at reflux for 4 h. Addition of excess water to the solution yielded a precipitate which was filtered off and recrystallized from MeOH to give the corresponding substituted terpyridine ligand (yield, ~50 %). ^{1}H-NMR ($CDCl_3$): **L2**; 9.22-9.11 (s, 4H), 8.55 (d, 2H), 8.22-8.11 (s, 2H), 7.93-7.45 (m, 7H), 7.20 (m, 2H) ppm. ^{1}H-NMR ($CDCl_3$): **L3**; 9.18-9.02 (s, 4H), 8.60-8.45 (m, 3H), 8.22 (d, 2H), 8.05 (s, 2H), 7.80-7.50 (m, 6H), 7.25 (s, 2H) ppm.

*Naph-Cn-terpy (n = 4 (**L4**), 6 (**L5**), 8 (**L6**), 10 (**L7**), 12 (**L8**)).* n-(2-Naphthoxy)-1-bromoalkane (Naph-Cn-Br, n = 4, 6, 8, 10, 12) was prepared by the reaction of 2-naphthol (1.44 g, 10.0 mmol), 1,n-dibromoalkane (20.0 mmol) and K_2CO_3 (5.0 g, 36.2 mmol) in dry DMF (100 mL). After stirring the mixture overnight, the precipitates were filtered off, and the filtrate was evaporated. The crude powder obtained was purified by column chromatography on a silica gel with hexane – ethyl acetate (1/3 = v/v) as eluent (yield, ~40 %). Naph-Cn-Br (3.0 mmol) dissolved in DMF (20 mL) was added dropwise to the mixture of OH-terpy (0.5 g, 2.0 mmol) and K_2CO_3 (1.0 g, 7.24 mmol) in DMF (40 mL). The solution was refluxed at 80 ˚C for 15 h, then evaporated. The residue was extracted by $CHCl_3/H_2O$, and the organic layer was dried over $MgSO_4$. After filtering off the residue of $MgSO_4$, the solvent was removed by rotary evaporation to yield the ligand as a

crude powder which was purified by column chromatography on a silica gel column with hexane – ethyl acetate (1/4 = v/v) as eluent (yield, ~60 %). ^{1}H-NMR ($CDCl_3$): **L4**; 9.01 (d, 2H), 8.53 (d, 2H), 7.98 (s, 2H), 7.75-7.36 (m, 8H), 7.25 (d, 2H), 7.19 (s, 1H), 4.22 (t, 2H), 4.03 (t, 2H), 1.92 (d, 4H) ppm. ^{1}H-NMR ($CDCl_3$): **L5**; 8.99 (d, 2H), 8.51 (d, 2H), 8.01 (s, 2H), 7.74-7.32 (m, 8H), 7.23 (d, 2H), 7.15 (s, 1H), 4.21 (t, 2H), 4.11 (t, 2H), 1.72 (q, 4H), 1.55 (d, 4H) ppm. ^{1}H-NMR ($CDCl_3$): **L6**; 9.22 (d, 2H), 8.49 (d, 2H), 8.05 (s, 2H), 7.71-7.30 (m, 8H), 7.23 (d, 2H), 7.17 (s, 1H), 4.20 (t, 2H), 4.08 (t, 2H), 1.74 (q, 4H), 1.45-1.30 (m, 8H) ppm. ^{1}H-NMR ($CDCl_3$): **L7**; 9.18 (d, 2H), 8.55 (d, 2H), 7.95 (s, 2H), 7.79-7.35 (m, 8H), 7.23 (d, 2H), 7.10 (s, 1H), 4.31 (t, 2H), 4.10 (t, 2H), 1.74 (q, 4H), 1.43-1.26 (m, 12H) ppm. ^{1}H-NMR ($CDCl_3$): **L8**; 8.63 (d, 2H), 8.55 (d, 2H), 7.97 (s, 2H), 7.81-7.29 (m, 8H), 7.23 (d, 2H), 7.07 (s, 1H), 4.18 (t, 2H), 4.01 (t, 2H), 1.74 (q, 4H), 1.43-1.26 (m, 16H) ppm.

*[Co(Naph-C2-terpy)$_2$](BF$_4$)$_2$ (**1**)*. Naph-C2-terpy-terpy (0.36 mmol) was dissolved in $CHCl_3$ (20 mL) and $Co(BF_4)_2{\cdot}6H_2O$ (0.068 g, 0.20 mmol) in MeOH (10 mL) was added to the solution. The color immediately changed to brown, and the solution was stirred for 30 min. The solution was concentrated and the precipitate that formed was filtered off to give the crude brown powder. Single crystals of **1**·2MeOH were obtained by recrystallization from MeOH/acetone (3/1 = v/v). Anal. Calcd for $C_{56}H_{46}CoN_6B_2F_8O_6$ (**1**·2MeOH): C, 59.23; H, 4.44; N, 7.40. Found: C, 59.56; H, 4.03; N, 7.85.

*[Co(R-terpy)$_2$](BF$_4$)$_2$ (R = 2-naphthyl (**2**), 9-anthracenyl (**3**))*. R-terpy (0.36 mmol) was dissolved in $CHCl_3$ (20 mL) and $Co(BF_4)_2{\cdot}6H_2O$ (0.068 g, 0.20 mmol) in MeOH (10 mL) was added to the solution. The color immediately changed to brown and the solution was stirred for 30 min., concentrated, and the precipitate was filtered off to give a crude brown powder. Single crystals of **2**·2$CHCl_3$ were obtained following ether diffusion in to a $CHCl_3$ solution of **2**. Single crystals of **3**·2.5MeOH were obtained by recrystallization of the initial product of **3** from MeOH/acetone (4/1 = v/v). Anal. Calcd for $C_{52}H_{36}CoN_6B_2F_8Cl_6$ (**2**·2$CHCl_3$): C, 55.70; H, 3.42; N, 7.48. Found: C, 55.95; H, 3.41; N, 7.43. Anal. Calcd for $C_{60.5}H_{48}CoN_6B_2F_8O_{2.5}$ (**3**·2.5MeOH): C, 64.21; H, 4.28; N, 7.43 Found: C, 64.57; H, 4.50; N, 7.22.

*[Co(Naph-Cn-terpy)$_2$](BF$_4$)$_2$ (n = 4 (**4**), 6 (**5**), 8 (**6**), 10 (**7**), 12 (**8**))*. Complexes **4** – **8** were prepared by similar procedure to that used for complex **1**. Complexes **4** – **8** were solely characterized by elemental analysis because suitable single crystals of **4** – **8** for XRD measurement were not obtained. Anal. Calcd for $C_{59}H_{58}CoN_6B_2F_8O_7$ (**4**·2H_2O·MeOH): C, 59.27; H, 4.89; N, 7.03. Found: C, 59.57; H, 4.60; N, 7.22. Anal. Calcd for $C_{63}H_{62}CoN_6B_2F_8O_5$ (**5**·MeOH): C, 62.24; H, 5.14; N, 6.91. Found: C, 62.57; H, 5.50; N, 7.02. Anal. Calcd for $C_{67}H_{70}CoN_6B_2F_8O_5$ (**6**·MeOH): C, 63.27; H, 5.55; N, 6.61. Found: C, 63.57; H, 5.40; N, 6.92. Anal. Calcd for $C_{70}H_{74}CoN_6B_2F_8O_4$ (**7**): C, 64.88; H, 5.76; N, 6.47. Found: C, 64.67; H, 5.50; N, 6.22. Anal. Calcd for $C_{74}H_{82}CoN_6B_2F_8O_4$ (**8**): C, 65.74; H, 6.11; N, 6.22. Found: C, 65.27; H, 6.16; N, 6.07.

Physical measurements. ^{1}H-NMR spectra were measured with a JEOL (500-ECX) instrument operating at 500 MHz (using the deuterated solvents as the lock and residual solvent tetramethylsilane as the internal reference). Elemental analyses (C, H, N) were carried out at the Instrumental Analysis Centre of Kumamoto University. X-ray diffraction data for the single crystals were collected with a Rigaku R-AXIS

RAPID 191R diffractometer, R-AXIS RAPID II diffractometer and XtaLAB mini II diffractometer. The structures were solved by direct methods (Sir 2004) and refined by full-matrix least-squares refinement using the SHELXL-2014 computer program 44. Hydrogen atoms were refined geometrically using a riding model. Thermogravimetric analysis (TGA) was performed at 10 K min^{-1} using a Rigaku Instrument Thermo plus TG8120 in a nitrogen atmosphere. Differential scanning calorimetry (DSC) thermal analysis was carried out at 10 K min^{-1} on a SHIMADZU DSC50. Magnetic susceptibilities were measured with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-XL). Samples were put into a gelatin capsule, mounted in-side a straw, and then fixed to the end of the sample transport rod. Cooperativity was estimated from the measured $\chi_m T$ versus T curves (χ_m; molar magnetic susceptibility, T; temperature) by applying the regular solution model (eq. 1), where ΔH, ΔS and Γ are the enthalpy and the entropy variations and the parameter accounting for cooperativity based on SCO, respectively. The HS molar fraction, γ_{HS}, is shown as a function of the magnetic susceptibility via (eq. 2), where $(\chi_m T)_m$ is the $\chi_m T$ value at any temperature, $(\chi_m T)_{HS}$ and $(\chi_m T)_{LS}$ are the pure LS and HS states, respectively. R is the gas constant unit, 8.314 J K^{-1} mol^{-1}. The cooperativity value, C, is given by eq. 3.

$$\ln[(1-\gamma_{HS})/(\gamma_{HS})] = [\{\Delta H+\Gamma(1-2\gamma_{HS})\}/RT]-\Delta S/R \qquad \text{(eq. 1)}$$

$$\gamma_{HS} = [(\chi_m T)_m-(\chi_m T)_{LS}]/[(\chi_m T)_{HS}-(\chi_m T)_{LS}] \qquad \text{(eq. 2)}$$

$$C = \Gamma/(2RT_{1/2}),\ T_{1/2} = \Delta H/\Delta S \qquad \text{(eq. 3)}$$

Table S1 Crystal parameters for **1**·2MeOH at 100 K and 273 K, and desolvated **1** at 93 K and 200 K.

	1·2MeOH@100K	**1**·2MeOH@273K	**1**@93K	**1**@200K
CCDC number	1589733	1589729	1589730	1589731
T/K	100	273	93	200
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1 (#2)	*P*-1 (#2)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a / Å	8.9230 (6)	9.0394 (12)	16.515 (10)	16.379 (8)
b / Å	14.2250 (8)	14.364 (2)	9.411 (5)	9.513 (5)
c / Å	20.5165 (11)	20.975 (3)	30.737 (18)	31.272 (15)
α / ˚	82.411 (4)	82.269 (4)	90	90
β / ˚	79.044 (5)	78.279 (5)	92.621 (14)	92.546 (13)
γ / ˚	87.210 (5)	86.970 (3)	90	90
V / $Å^3$	2533.5 (3)	2641.5 (6)	4773 (5)	4868 (4)
Z	2	2	4	4
D_{calc} / g cm^{-3}	1.49	1.43	1.49	1.46
μ / mm^{-1}	0.428	0.411	0.447	0.438
R1	0.0645	0.1149	0.1289	0.0869
wR2	0.1751	0.3235	0.1810	0.1723

Table S2 Crystal parameters for **2**·2$CHCl_3$ and **3**·2.5MeOH

	2·2$CHCl_3$	**3**·2.5MeOH
CCDC number	1589734	1589732
T/K	100	100
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a / Å	18.6675 (7)	21.7754 (17)
b / Å	13.1102 (5)	12.0778 (8)
c / Å	20.7558 (9)	20.9907 (19)
α / ˚	90	90
β / ˚	94.0428 (13)	110.132 (9)
γ / ˚	90	90
V / $Å^3$	5067.0 (4)	5183.2 (8)
Z	4	4
D_{calc} / g cm^{-3}	1.56	1.45
μ / mm^{-1}	0.729	0.414
R1	0.0967	0.0502
wR2	0.1757	0.1600

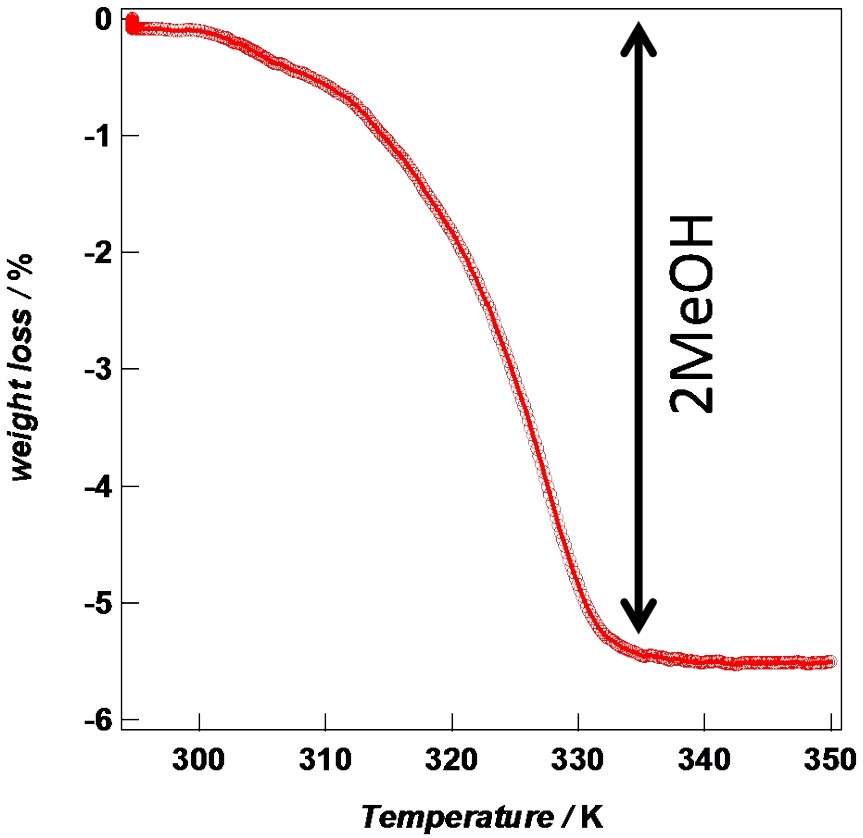

Fig. S1. (a) TGA for complex **1**·2MeOH.

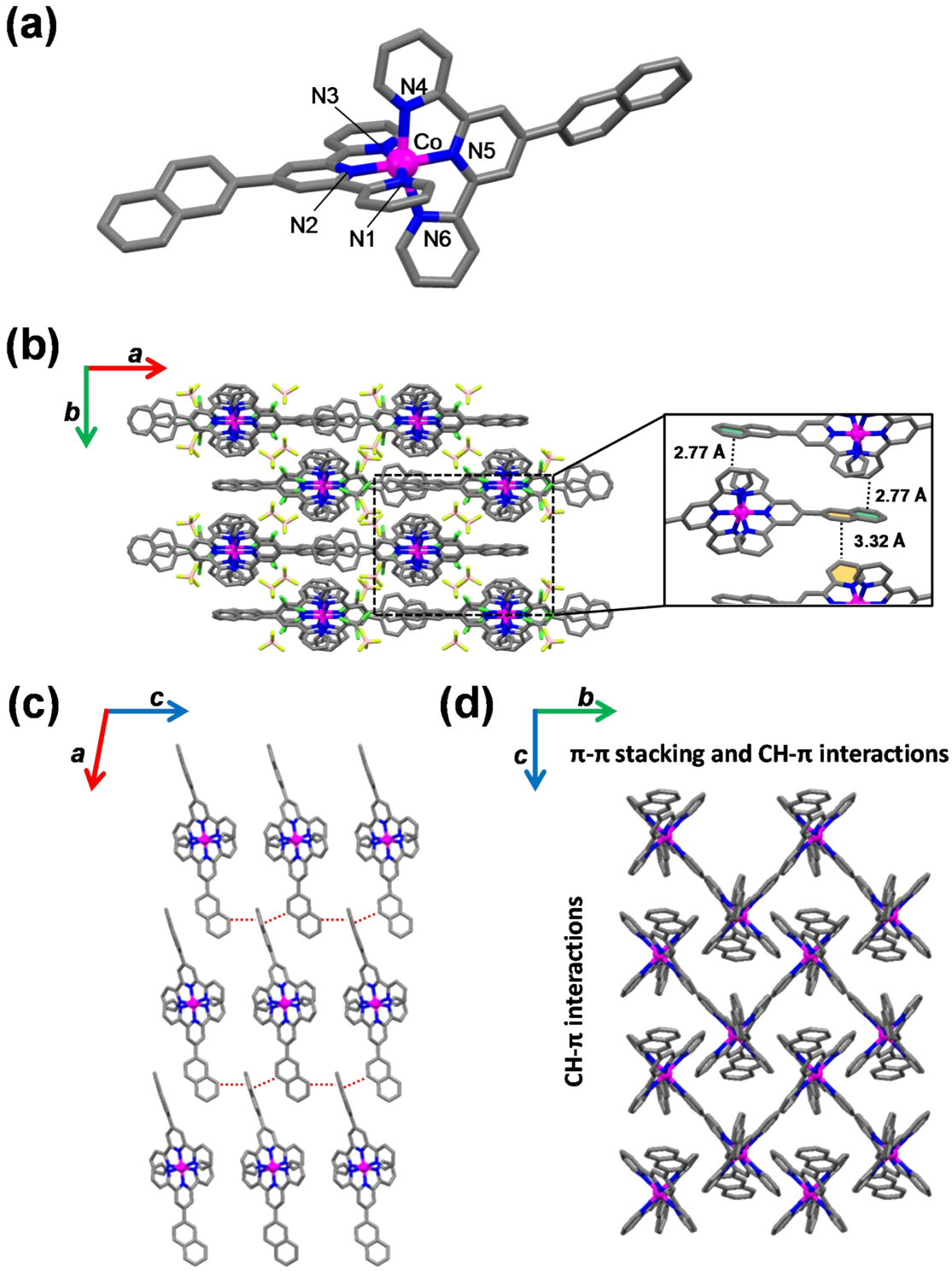

Figure. S2. (a) Molecular structure of **2**·2$CHCl_3$. Hydrogen atoms, counter anions and solvent molecules are omitted for clarity. (b), (c) and (d) Crystal packing structure of **2**·2$CHCl_3$. Pyridine rings in terpyridine ligand contact with naphthalene rings via π–π stacking (3.32 Å) and CH–π interaction (2.77 Å). Colour code: Co, Magenta; N, blue; C, grey; B, pink; F, light-yellow; Cl, green.

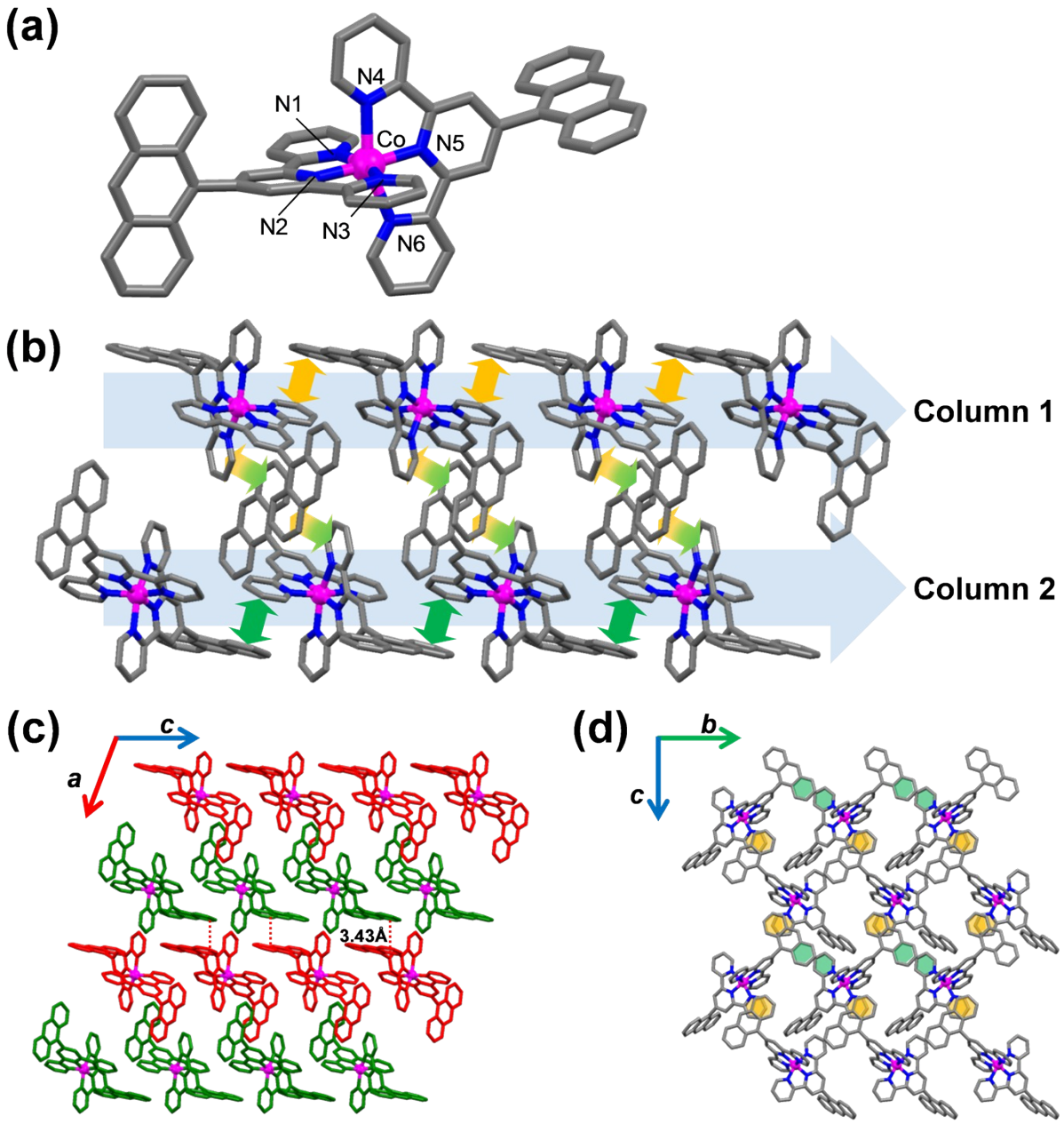

Figure. S3. (a) Molecular structure of **3**·2.5MeOH. Hydrogen atoms, counter anions and solvent molecules are omitted for clarity. Colour code: Co, Magenta; N, blue; C, grey. (b) π–π stacking networks in **3**. The allows between each column show the connection of them by π–π interactions. Crystal packing structure of along (c) the *ac* plane and (d) the *bc* plane. Red; Column 1, Green; Column 2. Orange and green marked aromatic rings show π–π stackings.

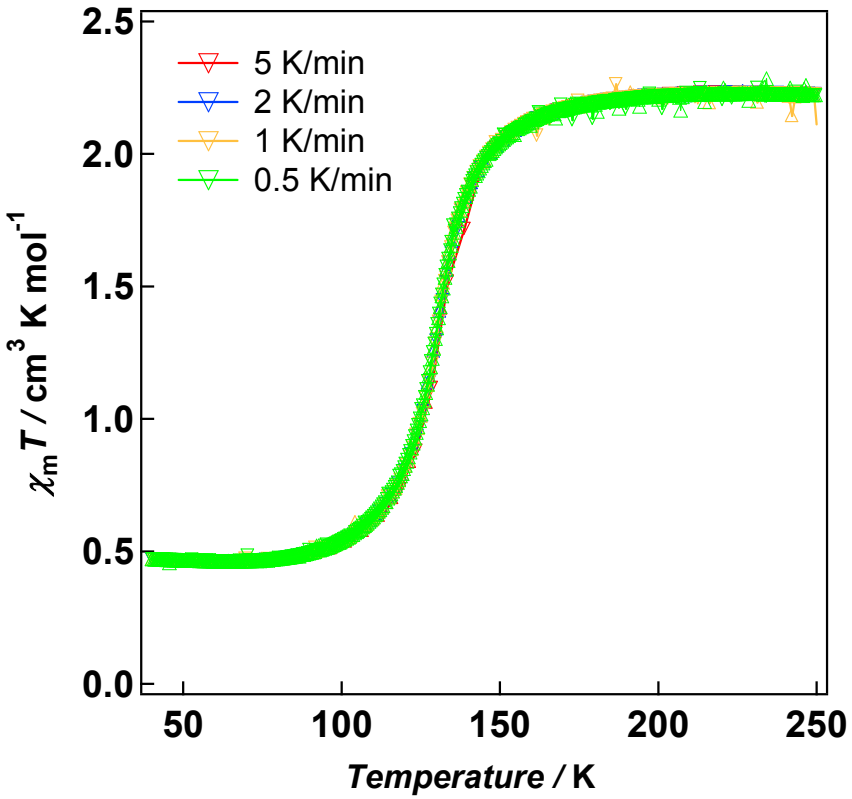

Figure S4. Scan rate dependent SCO behavior of the crystalline sample of **1**.

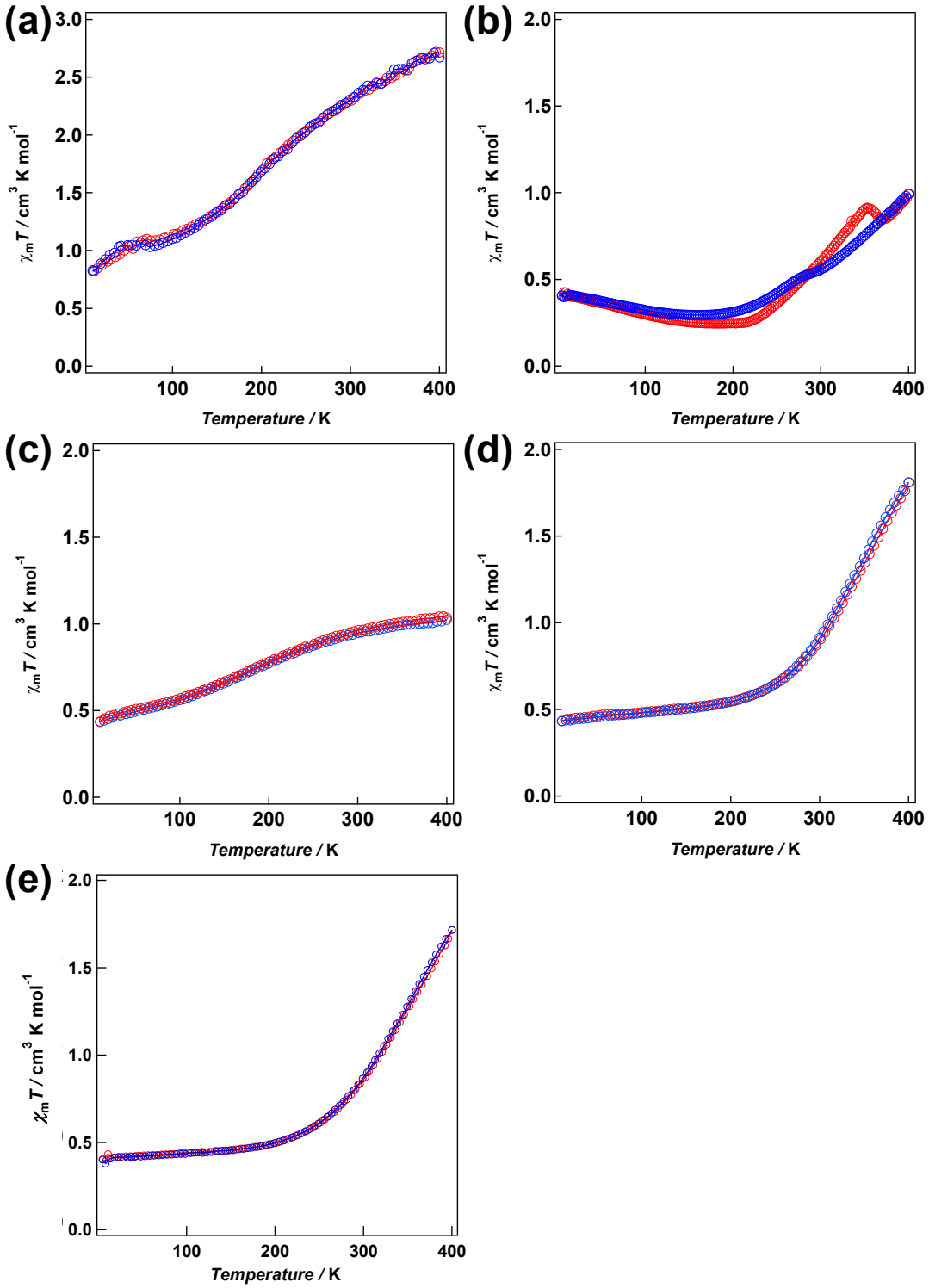

Figure S5. The $\chi_m T$ versus T plots for (a) **4**·2H_2O·MeOH, (b) **5**·MeOH, (c) **6**·MeOH, (d) **7** and (e) **8**. Red and blue coloured plots show heating and cooling process, respectively.

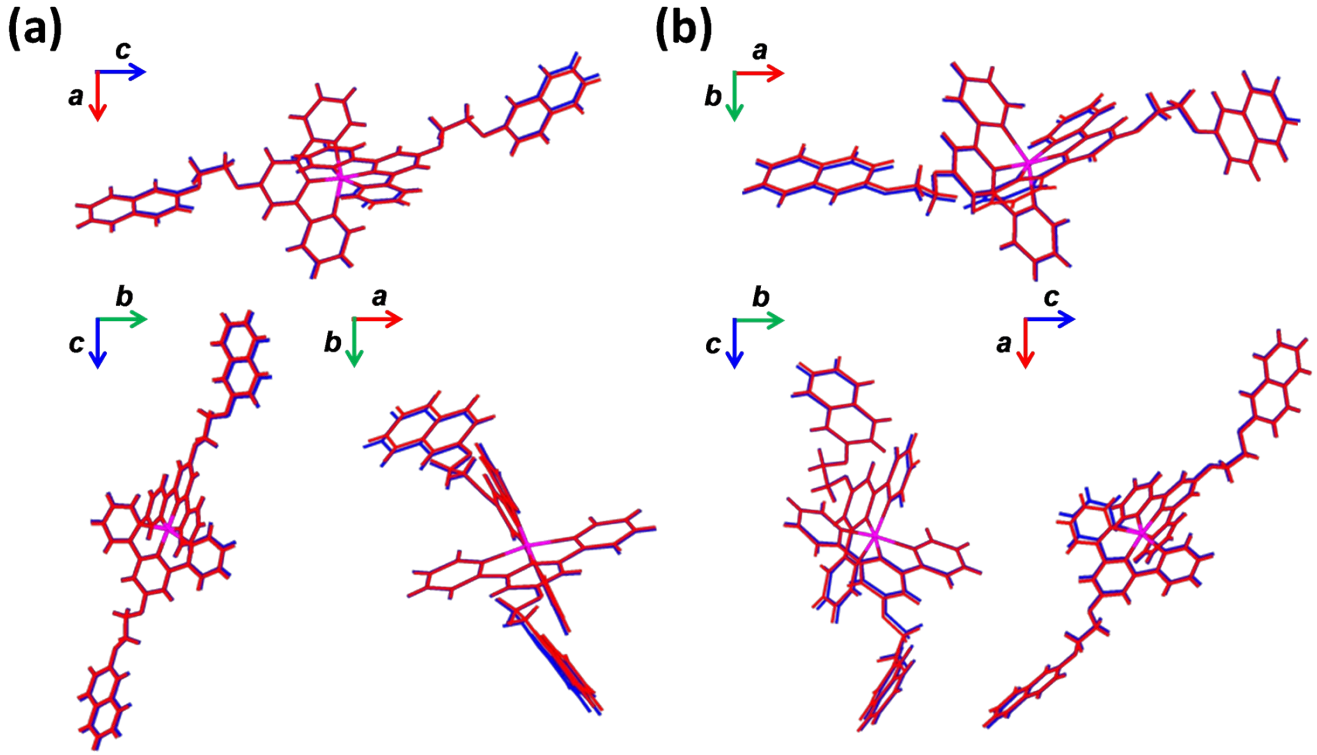

Figure S6. Overlaid structures of (a) **1**·2MeOH and (b) **1** along the respective axis.