

Supplementary Information for

Photo-induced Valence Tautomerism and Polarization Switching in Mononuclear Cobalt Complexes with an Enantiopure Chiral Ligand

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Synthesis and Methods

Materials

(7*S*,14*S*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*SS*-cth) was synthesized according to previously reported procedures¹.

[Co(*SS*-cth)(Phendiox)]PF₆·0.5EtOH & [Co(*SS*-cth)(Phendiox)]AsF₆·0.5EtOH

An equimolar amount of *SS*-cth (1.7 g) was added into an MeOH (10 mL) solution containing Co(OAc)₂·2H₂O (1.5 g), and the mixture was stirred at 70°C for 5 min. An equimolar amount of NaPF₆ and NaAsF₆ was then added into the solution, which was further stirred at 70°C for 5 min. After cooling down to room temperature, the precipitated solid was filtered from the solution and washed with Et₂O. The obtained plum red powder, Co(AcO)(*SS*-cth)AsF₆ and Co(AcO)(*SS*-cth)AsF₆, was dried under reduced pressure and stored at -5°C.

9,10-Phenanthrene-1,10-dione (108 mg) and 9,10-phenanthrene-9,10-diol (110 mg) were added in a molar ratio of 1:1 in EtOH (15 mL), with flowing N₂ gas. After that, NaOH (40 mg) was added into the solution, which was stirred until it became dark red. Co(OAc)(*SS*-cth)AsF₆ and Co(OAc)(*SS*-cth)AsF₆ was poured into the solution immediately and stirred at 70°C until a precipitate started to form. After the solution was cooled down in an ice bath, the desired compound was obtained as a dark brown microcrystalline product.

Recrystallization was performed by dissolving the product in a 1:1 EtOH/H₂O solvent mixture, followed by evaporation in flowing N₂ for 2 days. Tiny flake-like crystals were obtained.

Methods

Magnetic measurements

Magnetic susceptibility measurements were performed on a Quantum Design MPMS-XL

superconducting quantum interference device magnetometer under a 2000 Oe field with a sweeping rate of 5 K min⁻¹. The samples for measurement were prepared by encapsulating the samples into a gelatin capsule. To prevent loss of co-crystallized ethanol molecules, the measurements of the pristine samples were performed from 300 to 5 K, followed by heating up to 400 K. The samples were then maintained at 400 K for an adequate duration of time, and another complete measurement cycle between 400 and 5 K were conducted to determine the magnetic properties of the desolvated samples. The sample for light-induced magnetic susceptibility measurements were performed by attaching a powdered sample to transparent tape. A GLMP-0200A green laser (532 nm) was used as the excitation source, and the samples were irradiated at 5 K for over 40 min.

X-ray diffraction measurements and crystal structural determination

The X-ray crystal structure of [Co(SS-cth)(Phendiox)]PF₆·0.5EtOH was obtained at 78 and 300 K under a cold nitrogen gas stream using a Rigaku Mercury2 CCD detector at BL02B1/Spring-8 (Hyogo, Japan). The wavelength of the incident X-ray was 0.4171 Å. The crystal structures were solved and refined using the OLEX2 program with anisotropic thermal parameters for all nonhydrogen atoms². The hydrogen atoms were geometrically added and refined by the riding model.

Temperature-dependent IR and UV spectrum

Temperature-dependent IR spectra were recorded on an FTIR spectrophotometer (FT/IR-660 Plus, Jasco) equipped with a liquid nitrogen refrigerator cryostat (LT-3-110, Advanced Research System, Ins). The powdered samples were held on a plane CaF₂ plate. The measurements were performed by heating up the sample cabin gradually using a programming temperature controller (331, LakeShore) after cooling down the system to 100 K. Temperature-dependent UV absorption spectra were recorded using a UV-3100PC (Shimadzu) spectrophotometer with a liquid nitrogen refrigerator cryostat (LT-3-110, Advanced Research System, Inc.). The powdered samples were speared evenly on a transparent tape.

Thermogravimetric analysis

Thermogravimetric analysis was performed on a DTU-2A equipment at 293–523 K with a heating rate of 10 K min⁻¹ under air atmosphere. Samples of 10.3 mg of ground powder were prepared to monitor the weight loss during the whole temperature range.

Polarization switching calculation

The polarization switching value is calculated using following function:

$$\Delta P = \frac{2\{\mu_{\alpha(LT)}\cos(\theta_{\alpha(LT)}) + \mu_{\beta(LT)}\cos(\theta_{\beta(LT)})\} - [\mu_{\alpha(HT)}\cos(\theta_{\alpha(HT)}) + \mu_{\beta(HT)}\cos(\theta_{\beta(HT)})]}{V_{cell}}$$

μ_i indicate the dipole moments of each motif in different temperature, and θ_i indicate the angle between each motif and polar *b*-axis of the lattice. V_{cell} refers to the volume of the unit cell.

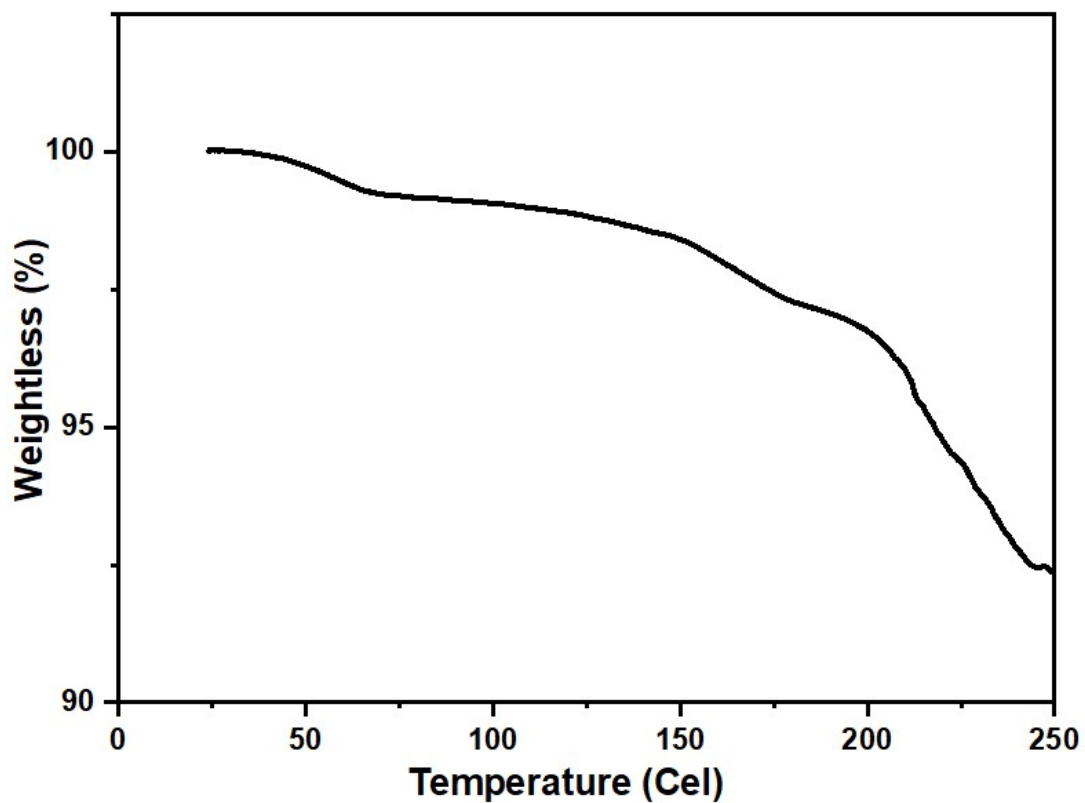


Figure S1. Thermogravimetric analysis of [Co(SS-cth)(phendiox)]AsF₆·0.5EtOH. The measurements were performed using 10.3 mg powder from 20°C to 250°C, temperature at which the sample began to decompose. The TGA result for [Co(SS-cth)(phendiox)]AsF₆·0.5EtOH shows a loss of co-crystallized EtOH molecule at the temperature range from 60°C to 170°C, which is also confirmed in the single crystal structure.

Table S1. Crystallographic data and structure refinement parameters of [Co(SS-cth)(phendiox)]AsF₆·0.5EtOH.

Complexes	[Co(SS-cth)(phendiox)]AsF ₆ ·0.5EtOH	[Co(SS-cth)(phendiox)]AsF ₆ ·0.5EtOH
Formula	C ₆₂ H ₉₀ As ₂ Co ₂ F ₁₂ N ₈ O ₅	C ₆₂ H ₉₀ As ₂ Co ₂ F ₁₂ N ₈ O ₅
Formula weight	1522.139	1522.139
<i>T</i> / K	78	300
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁
<i>a</i> / Å	9.51352(10)	9.57346(16)
<i>b</i> / Å	11.92241(11)	12.02833(19)
<i>c</i> / Å	30.3350(3)	30.3122(4)
<i>α</i> / °	90	90
<i>β</i> / °	93.7791(9)	92.7992(14)
<i>γ</i> / °	90	90
<i>V</i> / Å ³	3433.24(6)	3486.37(9)
<i>Z</i>	2	2
<i>D_c</i> / g·cm ⁻³	1.470	1.450
<i>F</i> (000)	1568.0	1568.0
GOF on <i>F</i> ²	1.050	1.049
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0898, <i>wR</i> ₂ = 0.1873	<i>R</i> ₁ = 0.0817, <i>wR</i> ₂ = 0.1776
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	<i>R</i> ₁ = 0.1218, <i>wR</i> ₂ = 0.2017	<i>R</i> ₁ = 0.1652, <i>wR</i> ₂ = 0.2105
Friedel coverage	0.822	0.811
Flack parameter	0.07(2)	0.01(2)

Table S2. Co-O bond lengths of [Co(SS-cth)(phendiox)]AsF₆·0.5EtOH at 300 K and 78 K

Temperature	<i>α</i> (Å)	<i>β</i> (Å)
300 K	2.050, 2.064	2.084, 2.092
78 K	1.907, 1.898	1.999, 2.017

Table S3. Stretched exponential fitting parameters (*τ*, *β*, *γ*) of the fitting curve at different temperatures.

Temperature (K)	<i>τ</i> (s)	<i>β</i>	<i>γ</i>
5	4015.52	0.67	0.64
15	1429.29	0.56	0.64
20	1197.66	0.91	0.72

Reference

1. A. M. Tait, D. H. Busch and N. F. Curtis, in *Inorganic Syntheses*, 1978, DOI: <https://doi.org/10.1002/9780470132494.ch2>, pp. 10-17.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard and H. Puschmann, *Journal of applied crystallography*, 2009, **42**, 339-341.