Supplementary Information of

Modulable Cooperativity in a Valence Tautomeric Complex Functionalized with

Branched Alkyl Chains

Daisuke Kiriya,^a Kohei Nakamura^a, Susumu Kitagawa^a and Ho-Chol Chang*^b

^a Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan,

^b Division of Chemistry, Graduate School of Science, Hokkaido University, North 10 West 8, Kita-ku, Sapporo, 060-0810, Japan.

chang@sci.hokudai.ac.jp

Contents

1. Experimental details.

2. Figure S1. Temperature dependent IR spectra of CoC8,10Opy.

3. Figure S2. Temperature and time dependent XRD patterns of CoC8,10Opy.

4. Figure S3. Temperature-dependent magnic susceptibility in the range of 10–400 K.

5. Figure S4. In situ crystallization of CoC8,10Opy in SQUID magnetometer.

6. Movie. Crytallization process of CoC8,10Opy around room temperature (ESI4.avi)

1. Experimental Details

1.1. Materials. Sodium hydride (NaH, Wako), 3,5-dichloropyridine (Tokyo Chemical Industry Co., TCI), 2-octyl-1-dodecanol (Aldrich), and $Co_2(CO)_8$ (Lancaster Synthesis Ltd.) were used without further purification. 3,6-di-*tert*-butyl-benzoquinone (DTBBQ) were prepared under nitrogen atmosphere using standard schlenk techniques according to the published procedures.^{1,2}

1.2. Syntheses for ligand C8,10Opy. To an anhydrous 75 mL dimethylformamide suspension of NaH (60–72% in oil) (1.5 g, 40 mmol) in a 300 mL three-neck flask equipped with a magnetic stirrer and a rubber septum, was added 2-octyl-1-dodecanol (41 mmol) at 273 K. Gas evolved and the gray suspension was stirred for 125 min at room temperature, and then 3,5-dichloropyridine (0.74 g, 5.0 mmol) was added. On further stirring at 358 K for 60 h a brown suspension was produced. The reaction was quenched by adding H₂O, and the organic material was extracted with CH₂Cl₂. The combined organic layers were washed with water, dried with Na₂SO₄ and MgSO₄, and concentrated under reduced pressure to give a brown-yellow liquid. Purification by column chromatography (silica gel, hexane/ethyl acetate = 28/1, *Rf* = ca. 0.4) yielded the product as a light yellow oil, 15% yield. ¹H NMR (500 MHz, CDCl3) δ 0.84–0.87 (t, 12H), 1.24–1.45 (m, 64H), 1.74–1.77 (m, 2H), 3.83–3.85 (t, 4H), 6.70 (t, 1H), 7.89 (d, 2H).

1.3. Syntheses for CoC8,10Opy. $Co_2(CO)_8$ (0.11 mmol) was dissolved in 18.7 mL of toluene, and 3,6-di-*tert*-butyl-benzoquinone (0.435 mmol) and C8,10Opy (0.422 mmol) were added at room temperature under N₂ atmosphere. The mixture was stirred for 3 h at 353 K, and then acetonitrile was added and the mixture was left at room temperature for several days. Dark purple oil was obtained. [Co(C8,10Opy)₂(3,6-DTBQ)₂] (**CoC8,10Opy**). Anal. Calcd for C118H210CoN2O8: C, 76.86; H,11.48; N,1.52. Found: C, 76.53; H, 11.58; N, 1.77.

1.4. Physical measurements. Elemental analysis was performed on a Flash EA 1112 series (Thermo Finnigan instrument). Microscopic analysis was carried out on the samples between two glass slides using a BX51 microscope (Olympus) with an LK-600 hot stage (Linkam) under N_2 atmosphere. Different scanning calorimetric measurements were measured on a DSC 822e (Mettler) under N_2 atmosphere. Variable temperature X-ray

diffraction measurements were carried out with Cu K α radiation equipped with a RINT-2000 diffractometer (Rigaku). IR spectra were carried out on samples between two BaF₂ glass slides using a Nicolet Continuum microscope fitted to a Thermo Electron Nicolet 6700 FT-IR spectrometer with an LK-600 hot stage (Linkam) under N₂ atmosphere. Magnetic susceptibilities were recorded at 1 T with a super conducting quantum interference device (Quantum Design). All values were corrected for diamagnetism using Pascal's constants.³

[References]

¹ Kiriya, D.; Chang, H.-C.; Kitagawa, S. J. Am. Chem. Soc. 2008, **130**, 5515-5522.

² (a) Belostotskaya, I. S.; Komissarova, N. L.; Dzhuaryan, É. V.; Ershov, V. V. Izvestiya.

Akademii. Nauk. SSSR 1972, 7, 1594-1596. (b) Karpyuk, A. D.; Starosel'skaya, L. F.;

Petrov, É. S.; Beletskaya, I. P. Izvestiya. Akademii. Nauk. SSSR 1985, 1, 218-220.

³ Kahn, O. *Molecular Magnetism*; Wiley-VCH: Weinheim, Germany, 1993.



Figure S1. Temperature-dependent IR spectra of **CoC8,10Opy** on the cooling process from 393 to 313 K. (a) Bands around 1280 and 1450 cm⁻¹ was assigned to the C–O vibration modes, and (b) a band around 3700 cm⁻¹ was assigned to a IVCT (intervalence charge transfer) band indicative of the contribution of the *ls*-[Co^{III}] with mixed-valence 3,6-DTBSQ and 3,6-DTBCat. These spectroscopic variations indicate the VT shift from the *hs*-[Co^{III}] to the *ls*-[Co^{III}] tautomer.⁴

[Reference] ⁴ (a) C. G. Pierpont, *Coord. Chem. Rev.*, 2001, 216, 99-125. (b) M. W. Lynch,
M. Valentine, and D. N. Hendrickson, *J. Am. Chem. Soc.* 1982, 104, 6982.



Figure S2. Temperature- and time-dependent XRD patterns of **CoC8,10Opy** on the heating and cooling processes. The melt obtained by cooling kept the molten state at 298 K for 470 min.



Figure S3. (a) Temperature-dependent magnetic susceptibility of **CoC8,10Opy** in the range of 5-400 K and (b) the scan rates in the magnetic measurements (red dots; 1^{st} heating of crystalline phase, blue dots; 1^{st} cooling, green dots; 2^{nd} heating, and black dots; 2^{nd} cooling).



Figure S4. (a) Crystallization process of **CoC8,10Opy** in SQUID magnetometer at 295 K during the 2^{nd} heating process and (b) the time-dependent magnetic susceptibility in this process (1^{st} heating; red dots, 1^{st} cooling; blue dots, and 2^{nd} heating; green dots).

6. Movie

Crystallization process of CoC8,10Opy around room temperature (ESI4.avi).

Sample: CoC8,10Opy

Process: kept the temperature at r.t. after heating from glass phase

Playback: at 300 times speed