Supporting Information

Heat-Set Gel-like Networks of Linear Co(II) Triazole Complexes in Organic Media and their Thermochromic Structural Transitions

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1. Experimental section

General. 4-(3-(Lauryloxy)propyl)-1,2,4-triazol(1) was synthesized by modifying the literature method.⁹ Chloroform (spectral grade, Kishida) was purchased before use. Content of water in the spectral grade chloroform was less than 0.015 wt% as determined by the Karl Fisher's method (CA-07 moisturemeter). Anhydrous chloroform was obtained by distillation over CaCl₂. Gel permeation chromatography was performed on Shimadzu LC-6A with Shodex KF802-KF803 columns and a SPD-10A UV-detector. Molecular weights (Mw) calculated from GPC was based on using polystyrene standards. Ultraviolet/visible (UV/vis) absorbance spectra were recorded on a JASCO V-550 spectrophotometer. Atomic force microscopy (AFM, non-contact mode) was carried out with a Topometrix explorer 2010). Transmission and Scanning electron microscopies were performed by JEOL JEM-2010 (acceleration voltage, 120 kV) and Hitachi S-5000, respectively. X-ray diffraction (XRD) data of the powdered xerogels were collected on a MacScience Micro-focus X-ray diffractometer M18XHF, Cu K α , $\lambda = 1.54056$ Å). Differential scanning calorimetry (DSC) was conducted on Seiko Electronics SSC-5200 instrument (heating rate, 10 °C hr⁻¹).

Sample preparation. The cobalt complexes were dissolved in spectral grade chloroform or unhydrous chloroform by ultrasonication (Branson 2510). $Co(1)Cl_2$ gelatinizes chloroform and dichloromethane, though the dichloromethane gives more soft, jelly-like assemblies. The gel-like networks are not formed in other solvents such as tetrahydrofuran and chloro-cyclohexane. Specimens for AFM and TEM observations were prepared by using the gel-transfer technique.¹² A freshly cleaved, highly oriented pyrolytic graphite (HOPG, 5 x 5 mm²) was placed on the gel-like phase and their surface layers were transferred by peeling off the substrate.

Rheological Characterization. The oscillatory shear measurement was performed using a stress-controlled rheometer (Carri-MED CSL-100 England) with a parallel plate type geometry (plate diameter, 4 cm). A solvent trap equipped with the rheometer was used to protect the sample from evaporation. The storage modulus G' and the loss modulus G'' were measured at a strain of 0.1 as function of angular frequency from 100 to 0.1 rad/s. Temperature was changed from 22.5 °C to 32.5 °C. It was confirmed that both of the G' and G'' values become independent on the angular frequency and give a plateau at higher temperatures.

Synthesis of triazole ligands. A solution of triethylorthoformate (6.85 g, 45 mmol) and formiylhydrazine (1.8 g; 30 mmol) in 30 mL of anhydrous methanol was refluxed for 3 hrs. Then

3-lauryloxypropylamine (7.43 g, 30 mmol) was added to the solution under the nitrogen atmosphere, and the mixture was further refluxed for 10 hrs. After removing the solvent under reduced pressure, the resulting oil was dissolved in 200 mL of chloroform. The solution was washed with 5% NaHCO₃ aqueous solution (200 mL), water (200 mL), and dried over anhydrous Na₂SO₄. Removal of the solvent afforded oily product and it was purified by silica gel chromatography (eluent, 10/1 (v/v) CHCl₃/CH₃OH). Colorless powder. Yield, 5.7 g (52 %). ¹H NMR (250MHz, CDCl₃) : δ , 0.85-0.90, t, 3H, CH₃, 1.3 (m, 20H, CH₂), 2.0-2.1 (m, 2H, CH₂CH₂O), 3.3-3.5(m, 4H, CH₂O), 4.2 (t, 2H, CH₂N), 8.2 (s, 1.9H, CH=N). IR(KBr): v = 2926 (C-H), 2855 (C-H), 1535 (C=N), 1466 (C=N) cm⁻¹. Elemental Analysis (%) Calcd. for C₁₇H₃₃N₃O: C 69.07, H 11.23, N 14.34. Found C 69.11, H 11.26, N 14.22. 4-(hexadecyl)-1,2,4-triazol(**2**) was synthesized similarly.

Synthesis of cobalt complexes. Cobalt(II) complexes $(Co(1)_3Cl_2 \text{ or } Co(2)_3Cl_2)$ were prepared by mixing methanol solution (5 ml) of compound 1 or 2 (0.31 mmol) with methanol solutions of Co(II)Cl₂ (0.1 mmol, 5 ml) under the nitrogen atmosphere. The pink powders immediately precipitated were corrected by centrifugation. The solids were washed with methanol and dried in vacuum. Yield: 1, 66 mg (65 %) (Blue powder), 2, 91 mg (82 %) (Blue powder). Elemental Analysis (%) Co(1)₃Cl₂, calcd for C₅₁H₉₉N₉O₃Cl₂Co H₂O) C 59.15, H 9.57, N 12.04. Found C 59.23, H 9.84, N 12.19. Co(2)₃Cl₂, calcd. for C₅₄H₁₀₅N₉Cl₂Co 2H₂O) C 61.99, H 10.50, N 12.05. Found C 61.85, H 10.29, N 11.99.

2. Powder X-ray Diffraction



Figure S1. Wide-angle X-ray diffraction pattern of the powdered xerogel of $Co(1)_3Cl_2$. MacScience Micro-focus X-ray diffractometer M18XHF, Cu K α , $\lambda = 1.5418$ Å.

3. Temperature dependence of the absorption intensities at 698 nm (T_d complex)



Figure S2. Temperature dependence of absorption intensity at 698 nm measured in a heating-and-cooling cycle.(a) $Co(1)Cl_2$, (b) $Co(2)Cl_2$. i; in spectral grade chloroform (data from Figure 3, water content, 0.015 wt%), ii; in anhydrous chloroform, iii; in water-enriched chloroform (water content, 0.082 wt%). Water content was determined by Karl Fisher's method.

The decrease in absorption intensity at 698 nm and the gel-to-sol transition upon cooling is retarded in anhydrous chloroform, whereas it is facilitated at higher water concentrations. Therefore, it is apparent that the fragmentation of the polymeric T_d complexes and their transformation to O_h complexes are promoted by the coordination of water molecules. It is interesting to note that the ether-containing complex Co(1)Cl₂ shows coordination structural change even in anhydrous chloroform, whereas that of Co(2)Cl₂ is mostly suppressed. Effect of traces of water molecules on the reological data of organogels has been also noticed for the organogels of metal soaps (ref 15). The sensitivity to water molecules may be a general phenomenon observed for the coordination polymer gels in organic media.

4. Rheological Characterization

The oscillatory shear measurement was performed using a stress-controlled rheometer (Carri-MED CSL-100 England) with a parallel plate type geometry (plate diameter, 4 cm). A solvent trap equipped with the rheometer was used to protect the sample from evaporation. The storage modulus G' and the loss modulus G'' were measured at a strain of 0.1 as function of angular frequency from 100 to 0.1 rad/s. Temperature was changed from 22.5 °C to 32.5 °C. It was confirmed that both of the G' and G'' values become independent on the angular frequency and give a plateau at higher temperatures.



Figure S3. Angular frequency ω dependence of the storage and the loss moduli G', G" at 22.5 °C.



Figure S4. Angular frequency ω dependence of the storage and the loss moduli G', G" at 25 °C.



Figure S5. Angular frequency ω dependence of the storage and the loss moduli G', G'' at 27.5 °C.



Figure S6. Angular frequency ω dependence of the storage and the loss moduli G', G" at 30 °C.



Figure S7. Angular frequency ω dependence of the storage and the loss moduli G', G" at 32.5 °C.