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

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Abstract: A novel class of thermally responsive supramolecular assemblies is formed from the lipophilic cobalt(II) complexes of 4-alkylated 1,2,4-triazoles. When an ether linkage is introduced in the alkylchain moiety, a blue gel-like phase is formed in chloroform, even at very low concentration (ca. 0.01 wt %, at room temperature). The blue color is accompanied by a structured absorption around 580−730 nm, which is characteristic of cobalt (II) in the tetrahedral (T_d) coordination. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) of the gel-like phase confirms the formation of networks of fibrous nanoassemblies with widths of 5−30 nm. The observed widths are larger than a molecular length of the triazole ligand (ca. 2.2 nm) and they are consisted of aggregates of T_d coordination polymers. Very interestingly, the blue gel-like phase turned into a solution by cooling below 25 °C. A pale pink solution is obtained at 0 °C, indicating the formation of octahedral (O_h) complexes. The observed thermochromic transition is totally reversible. The formation of gel-like networks *by heating* is contrary to the conventional organogels, which dissolve upon heating. Temperature dependence of the storage and loss moduli (G' and G'') shows minima around at 27 °C, at which temperature they gave comparable values. On the other hand, G' exceeds G'' both in the gel-like phase (temperature above 27 °C) and in the solution phase (temperature below 25 °C). These observations indicate that T_d complexes are present as low-molecular weight species around at 25−27 °C. They are self-assembled to polymeric T_d complexes by heating and form gel-like networks. Upon cooling the solution below 25 °C, T_d complexes are converted to O_h complexes and they also self-assemble into oligomeric or polymeric species at lower temperatures. The observed unique thermochromic transition (pink solution → blue gel-like phase) is accompanied by an exothermic peak in differential scanning calorimetry (DSC), and is shown to be an enthalpy-driven process. The lipophilic modification of one-dimensional coordination systems provides unique solution properties and it would be widely applicable to the design of thermoresponsive, self-assembling molecular wires.

Introduction

One-dimensional coordination compounds are attracting much interest as scaffolds for designing materials with unique electronic and magnetic properties.[1,2] These low dimensional structures are usually available only as the structural motifs of bulk crystalline materials, and accordingly they have been a subject of solid-state inorganic chemistry and physics. The ability to isolate and maintain such linear complexes in solution would provide a new family of functional molecular wires. We have recently developed an ingenious approach to disperse halogen bridged, mixed valence platinum complexes in organic media as lipid-packaged nanowires.[3,4] The intervalence charge-

transfer absorption characteristics of these complexes are controlled by tuning the chemical structure of lipid counter-anions. These nanowires show solvatochromism[5] and supra-molecular thermochromism,[4,6] the latter occurs as a consequence of reversible dissociation and polymerization of the conjugated wires. Pillared honeycomb stereo-architectures have also been constructed by the water microdroplet-templated self-assembly of the nanowires at solid surfaces.[7]

In this paper, we describe development of a novel class of gel-like networks which are self-assembled from lipophilic Co(II)−1,2,4-triazole (Trz) complexes (Chart 1).[8] 1,2,4-Triazoles are known as bridging ligands and their linear iron(II) complexes have been rigorously studied, because of the spin crossover

[†] Department of Chemistry and Biochemistry.
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(1) (a) Kahn, O.; Martinez, C. J. *Science* **1998**, *279*, 44. (b) Kahn, O. *Acc. Chem. Res*. **2000**, *33*, 647.
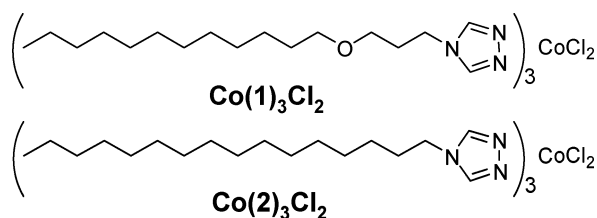(2) Okamoto, H.; Yamashita, M. *Bull. Chem. Soc. Jpn*. **1998**, *71*, 2023 and references therein.
(3) Kimizuka, N.; Oda, N.; Kunitake, T. *Chem. Lett.* **1998**, 695−696.

(4) (a) Kimizuka, N.; Oda, N.; Kunitake, T. *Inorg. Chem.* **2000**, *39*, 2684. (b) Kimizuka, N.; Lee, S.-H.; Kunitake, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 389.
(5) Lee, C.-S.; Kimizuka, N. *Chem. Lett.* **2002**, 1252.
(6) Kimizuka, N. *Adv. Mater.* **2000**, *12*, 1461.
(7) Lee, C.-S.; Kimizuka, N. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4922.
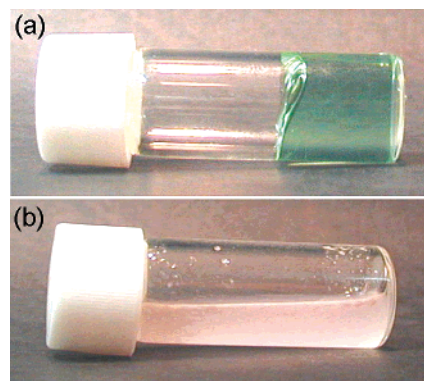
Chart 1. Chemical Structures of Lipophilic Co(II) Triazole Complexes

$Co(1)_3Cl_2$

$Co(2)_3Cl_2$

Figure 1. Pictures of $Co(1)_3Cl_2$ in chloroform: (a) a blue gel-like phase at 25 °C; (b) a pale pink solution at 0 °C.

characteristics.[1,8b,9] However to date, studies of the triazole complexes have been limited to the bulk crystalline samples, and there have been no reports on the maintenance of polymeric structures in solution. To develop soluble triazole complexes, we introduced a solvophilic, dodecyloxypropyl chain in the ligand. When a cobalt(II) complex of the lipophilic triazole ligand **1** ($C_{12}OC_3Trz$) is dissolved in chloroform, a blue gel-like phase is formed at room temperature. Interestingly, it turns into a pale pink solution upon cooling, and the gel-like phase is regenerated by heating. This is a first example of reversible, heat-set gel-like networks formed in organic media. The unusual thermal transition characteristics of the chloroform solutions was characterized by UV−vis spectra, AFM, TEM, scanning electron microscopy (SEM), DSC, and rheology measurements.

Results and Discussion

The lipophilic triazole ligands **1** ($C_{12}OC_3Trz$) and **2** ($C_{16}Trz$) were synthesized by modifying the literature method.[9] A flexible ether linkage is introduced in **1**, since it enhances the solubility in organic media and improves the packing of alkyl chains in the supramolecular assemblies.[10a,b] The complexes of $Co(1)_3Cl_2$ and $Co(2)_3Cl_2$ were obtained as blue powders by mixing each ligands with $CoCl_2$ in methanol.

Very interestingly, when $Co(1)_3Cl_2$ is dissolved in spectral grade chloroform, a blue gel-like phase is formed at room temperature (Figure 1a; concentration, 5 unit mM).[11] A minimum concentration required for the gelation was very low, (ca. 0.1 unit mM, 0.007 wt %) and much harder gel-like phase is obtained at higher concentrations (above ca. 20 unit mM). On the other hand, $Co(2)_3Cl_2$ requires considerably higher concentration (ca. 10 wt %) to gelatinize chloroform. These gel-like structures are stably maintained over a period of one month. Gel permeation chromatography (GPC) was conducted for the freshly prepared chloroform solution of $Co(1)_3Cl_2$ (concentration, 1 unit mM) after passing the solution through a membrane filter (Advantec Toyo Co. Ltd. I3JP050AN, pore diameter, 0.5 μm). It was found that the most of blue complex is remained on the membrane filter, and a chromatogram of the filtrate showed presence of the oligomers with an average molecular weight of ca. 9000 (data not shown). It seems that the blue

complex left on the filter is consisted of higher molecular weight polymers.

Atomic force microscopy (AFM) was conducted to investigate their nanostructures. Figure 2a shows an AFM image of $Co(1)_3Cl_2$ transferred on highly oriented pyrolytic graphite (HOPG).[12] Networks of fibrous nanoassemblies with widths of 5−30 nm are abundantly seen. As the observed widths are larger than a molecular length of **1** (ca. 22 Å, estimated by CPK model), they must be aggregates of the linear complexes. Developed networks of fibrous assemblies were also observed in transmission electron microscopy (TEM, Figure 2b). In contrast to $Co(1)_3Cl_2$, chloroform solution of $Co(2)_3Cl_2$ gives crystalline nano-aggregates with lengths of ca. 500−1500 nm and widths of 30−50 nm (Figure 2c). Apparently, developed networks are not formed from $Co(2)_3Cl_2$, and this is consistent with the observed lower ability to form gel-like phase. Scanning electron microscopy (SEM) of the freeze-dried gel of $Co(1)_3Cl_2$ afforded thicker entwined fibers (Figure 2d, width, ca. 100 nm), and these thicker structures must be formed during the drying process.[12] Wide-angle X-ray diffraction measurement (WAXD) of the powdered blue xerogel of $Co(1)_3Cl_2$ showed an intense (001) peak and weak (002), (003) peaks at $2\theta = 2.5°$, $5.2°$, and $7.1°$ respectively. These diffractions indicate that the xerogel fibers are formed from lamella structures with a long spacing of 35.4 Å, which corresponds to a tilt bilayer structure of $Co(1)_3Cl_2$.

UV−vis absorption spectra of $Co(1)_3Cl_2$ and $Co(2)_3Cl_2$ in chloroform are shown in Figure 3. Structured absorptions are observed at 25 °C (peaks at 639, 673 and 698 nm), which are characteristic of the tetrahedral cobalt(II) complex (T_d, $^4A_2 \rightarrow$ $^4T_1(P)$).[13] As the lipophilic ligand **1** without cobalt(II) is freely dissolved in chloroform, van der Waals forces alone cannot provide the nano-fibrous networks in Figure 2. The developed nanofibers observed in Figure 2 must rely on the additional intermolecular interactions which will be provided by the polymeric coordination. A possible model for the tetrahedral polymers is shown in Figure 4a. The presence of polymeric structures is further supported by rheological studies described later.

(8) (a) Parts of this study were presented at the 49th SPSJ Annual Meeting: Kimizuka, N.; Shibata, T. *Polymer Preprints Jpn*. **2000**, *49*, 3774. (b) Cast films of related lipophilic Fe(II)-1,2,4-triazole complexes display reversible spin transition characteristics: Shibata, T.; Kimizuka, N.; Kunitake, T. *The 76th CSJ National Meeting*; 4F137, Yokohama, 1999.
(9) Armand, F.; Badoux, C.; Bonville, P.; Teixier, A. R.; Kahn, O. *Langmuir* **1995**, *11*, 3467.
(10) (a) Kimizuka, N.; Kawasaki, T.; Hirata, K.; Kunitake, T. *J. Am. Chem. Soc.* **1995**, *117*, 6360. (b) Kimizuka, N.; Kawasaki, T.; Hirata, K.; Kunitake, T. *J. Am. Chem. Soc.* **1998**, *120*, 4094. (c) Kawasaki, T.; Tokuhiro, M.; Kimizuka, N.; Kunitake, T. *J. Am. Chem. Soc.* **2001**, *123*, 6792.
(11) Samples of this kind are usually referred as "organogels", but we avoid it since the storage and loss moduli measured were dependent on angular frequency ω. See Supporting Information.

(12) Kimizuka, N.; Shimizu, M.; Fujikawa, S.; Fujimura, K.; Sano, M.; Kunitake, T. *Chem. Lett.* **1998**, *10*, 967.
(13) (a) Cotton, F.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980. (b) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1968; p 318. The $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ transition of O_h complexes in the visible region near 500 nm is in admixture with spin forbidden transitions (ϵ, 5−40 M^{-1} cm^{-1}). This absorption is considerably weaker than $^4A_2 \rightarrow ^4T_1(P)$ transitions of T_d complexes, which acquire some intensity by means of spin−orbit coupling.
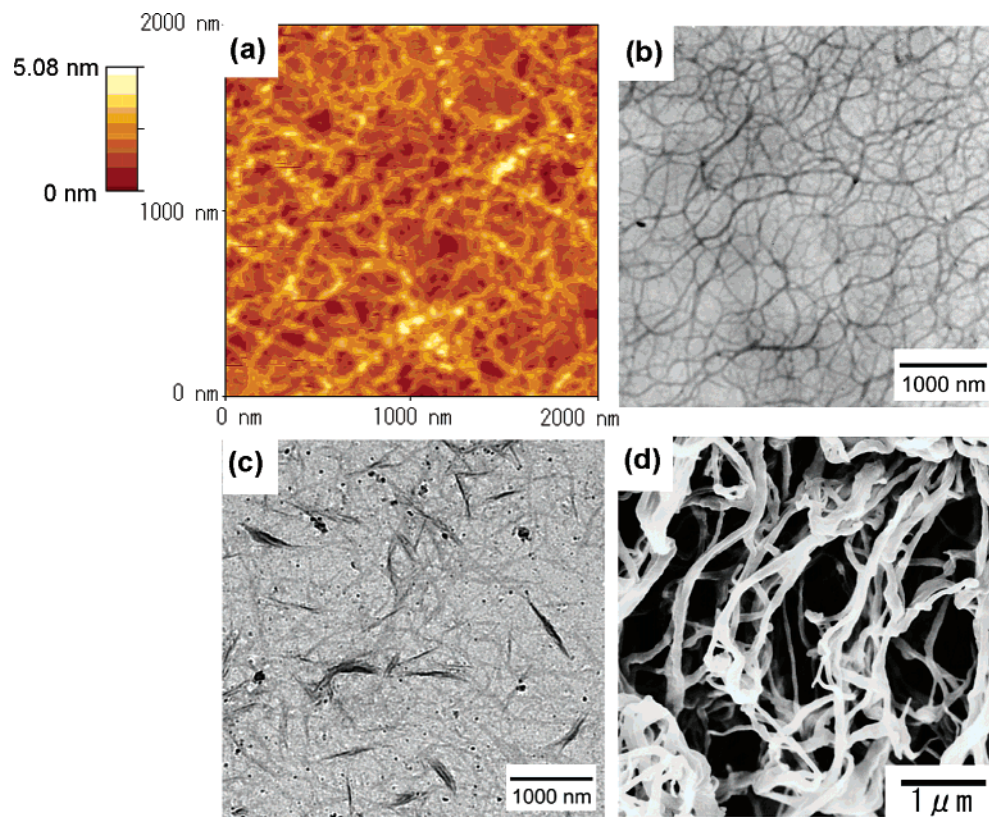
Figure 2. (a) AFM image of Co(**1**)$_3$Cl$_2$ (1 unit mM) transferred on HOPG. (b) TEM image of Co(**1**)$_3$Cl$_2$ (1 unit mM) transferred on a carbon-coated TEM grid. Samples are not stained. (c) TEM image of Co(**2**)$_3$Cl$_2$ (1 unit mM). (d) SEM micrograph of a freeze-dried gel Co(**1**)$_3$Cl$_2$.

To our surprise, when the gel-like phase is cooled below 25 °C, absorption intensity of the T_d complex is weakened and it became a solution. A pale pink solution is obtained at 0 °C, which color indicates the formation of octahedral (O_h) complexes.[13] Figure 5a displays the absorption intensity at 698 nm (T_d complex) measured in a heating-and-cooling cycle. The absorption intensity of Co(**1**)$_3$Cl$_2$ changes almost monotonically with the temperature changes (range, 0−23 °C). The 698 nm-absorption intensity reaches a maximum above 25 °C and slight increase in scattering is observed upon further heating. As the T_d complexes coexist with the O_h complexes in the solution phase (below 25 °C), the dissolution of the gels by cooling seems to occur as a consequence of decreased junctions (contacts and interactions) between the bundled tetrahedral polymers. This may be caused by the fragmentation process discussed below. The temperature at which the heat-set sol-to-gel transition occurs was almost invariable even for the higher concentration samples (ca. 100 mM). In addition, the sol-to-gel transition is totally reversible with subsequent temperature cycles.

In contrast to Co(**1**)$_3$Cl$_2$, chloroform solution of Co(**2**)$_3$Cl$_2$ (1 unit mM) showed smaller temperature dependence and considerable fraction of T_d complex (ca. 60%) is maintained even at 0 °C (Figures 3b and 5a). Thus, introduction of the ether-linkage in alkyl chains not only promotes the formation of gel-like nanoassemblies, but also gives the higher thermal responsiveness.

The heat-set gel-like network formation observed for Co(**1**)$_3$Cl$_2$ is in marked contrast to the conventional low molecular mass gelators[14] and metal soap organogels,[15] which undergo dissolu-

tion by heating. Mixtures of Pd(II) ion and multidentate ligands were reported to gelatinize dimethyl sulfoxide,[16] however formation of such 3D gel networks is irreversible and they are insoluble in common organic solvents.

To further investigate the nature of thermal transition in chloroform, temperature dependences of the storage and the loss shear moduli, G' and G'' were measured for Co(**1**)$_3$Cl$_2$ (Figure 5b). The cross over point where $G' = G''$ provides a measure for the gel-like network formation, marking the transition from predominantly viscous to elastic properties.[17a] It is to note that G' and G'' show minima, which is a quite unusual temperature dependence. G' value becomes almost comparable to G'' at the temperature range of 25−27 °C, and it indicates that the complexes are present as nonpolymerized species. Upon heating above 27 °C, G' value shows increase and it exceeds G'' at higher temperatures. This is consistent with the observed formation of polymeric T_d complexes and their physical cross-linking. Fragmentation of the polymeric complexes occurs by cooling the gel-like phase around at 27 °C, which is accompanied by the dissolution and decrease in the absorption intensity (Figure 3a). The fragmentation is promoted by water molecules slightly present in the solution (less than 0.015 wt %), since they are retarded in anhydrous chloroform (see Supporting Information). Upon cooling the solution below 27 °C, G' value is started to increase again and becomes almost temperature-independent at lower temperatures. It is noteworthy

(14) (a) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133. (b) Abdallah, D. J.; Weiss, R. G. *Adv. Mater.* **2000**, *12*, 1237.
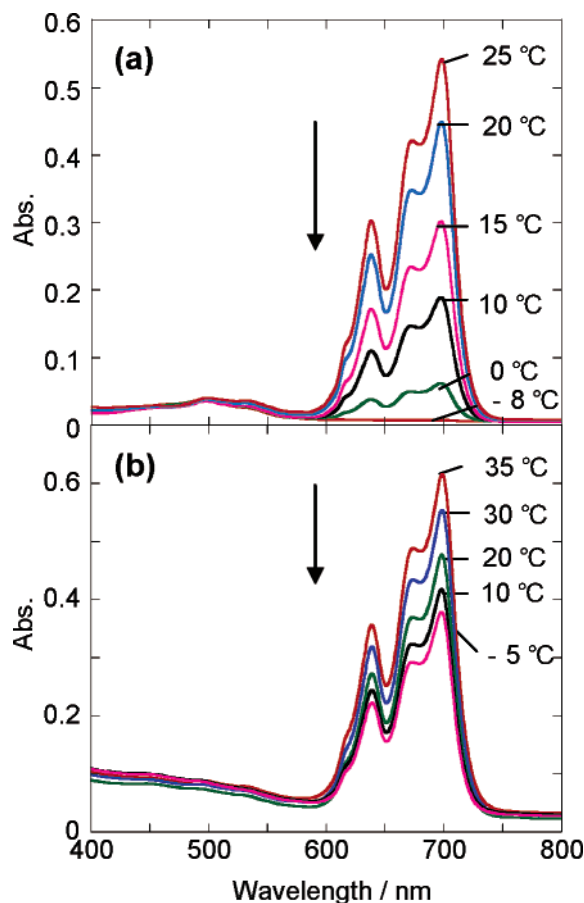
(15) (a) Pilpel, N. *Chem. Rev.* **1963**, *63*, 221. (b) Fukasawa, J.; Tsutsumi, H. *J. Colloid Interface Sci.* **1991**, *143*, 69.
(16) Xing, B.; Choi, M.-F.; Xu, B. *Chem. Eur. J.* **2002**, *8*, 5028.
(17) (a) Nowak, A. P.; Breedveld, V.; Pakstis, L.; Ozbas, B.; Pine, D. J.; Pochans, D.; Deming, T. J. *Nature* **2002**, *417*, 424. (b) Shikata, T.; Hirata, H. *Langmuir* **1989**, *5*, 398.

Figure 3. Temperature dependence of UV−vis spectra: (a) Co(**1**)$_3$Cl$_2$; (b) Co(**2**)$_3$Cl$_2$ in chloroform (1 unit mM).
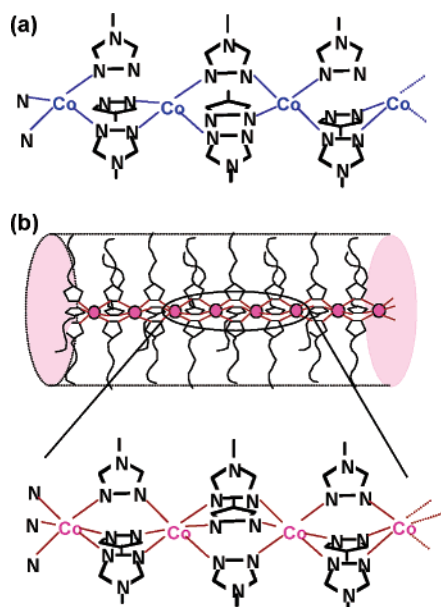

Figure 4. Schematic illustrations of (a) polymeric T_d complex and (b) polymeric O_h complex. The polymeric T_d complexes form fibrous nano-assemblies that give gel-like networks. It is possible that coordination of water molecules to the O_h complexes causes disruptions in the coordination structure and in the degree of polymerization.

that G' exceeds G'' also in the liquid phase (below 25 °C). This indicates that the fragmented octahedral complexes are re-assembled into oligomers or polymers.[17b]
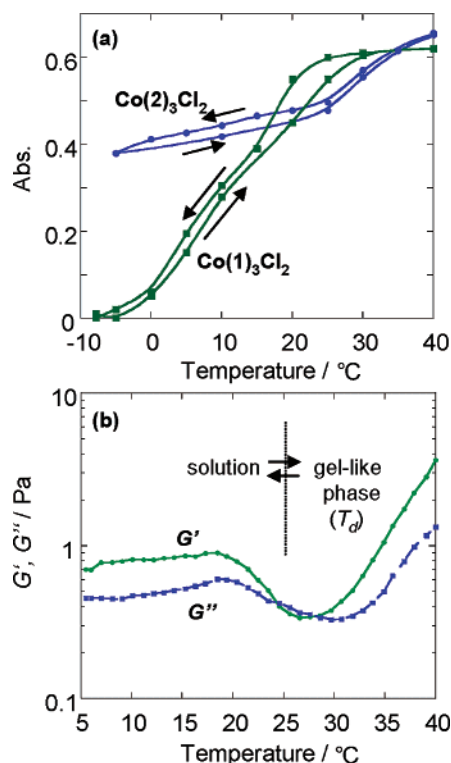

Figure 5. (a) Temperature dependences of absorption intensity at 698 nm in a heating-and-cooling cycle. (b) Temperature dependence of the storage modulus G' and the loss modulus G'' for Co(**1**)$_3$Cl$_2$ at angular frequency ω = 10 rad s^{-1}. Concentrations, 1 unit mM in chloroform.

We presume that the octahedral oligomers or polymers observed in the solution phase possess a rodlike structure with alkyl chains radially oriented from the main chains, as schematically shown in Figure 4b. This triple N1, N2 bridged coordination structure has been suggested for Fe(II)(trz)$_3$ complexes[1,18] and was also reported for Fe(II)(pz)$_3$ and Co(II)(pz)$_3$ complexes (pz, pyrazolate).[19] The rodlike structure seems to be highly lipophilic and would be well dispersed in chloroform, since no aggregate structures were observed in TEM. Though the O_h complexes are possibly fragmented by water molecules and it may cause the distribution in both the molecular weight and ligand compositions, the reversible thermal transition (O_h polymers or oligomers (below ca. 25 °C) ↔ dissociated complexes (at. 25−27 °C) ↔ gel-like networks of T_d polymers (above 27 °C)) clearly indicates the unique self-assembling properties of the molecular wires.

The thermodynamic stability of the present coordination polymers would be determined mainly by the following factors: (i) thermal stability of the coordination structures, (ii) interactions of solvent molecules and alkyl chains (solvation related interactions), (iii) interactions between the alkyl chains in a molecular wire (van der Waals forces), (iv) interactions between the aggregates, and (v) electrostatic interactions between polymeric complexes and counteranions. The configurational equilibrium between octahedral and tetrahedral structures of Co(II) ion is affected by several effects, including crystal-field stabilization, properties of ligands (chemical struc-

(18) Haasnoot, L. G. In *Magnetism: A Supramolecular Function*; Kahn, O., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996; p 299.
(19) Masciocchi, N.; Ardizzoia, G. A.; Brenna, S.; LaMonica, G.; Maspero, A.; Galli, S.; Sironi, A. *Inorg. Chem.* **2002**, *41*, 6080.
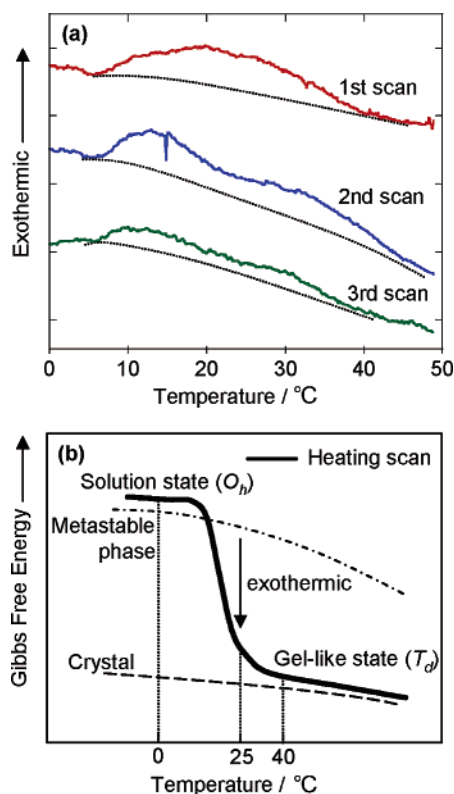
Figure 6. (a) DSC thermograms of Co(**1**)$_3$Cl$_2$, concentration, 1 unit mM in chloroform. (b) Schematic temperature dependence of Gibbs free energy for Co(**1**)$_3$Cl$_2$ in chloroform.

ture, polarizability, π-acceptor capacity) as well as crystal packing.[20] In the case of monomeric Co(II) complexes in solution, octahedral coordination is favored at lower temperatures.[21] The equilibrium shifts to tetrahedral coordination at higher temperatures, and this process is entropically driven.[20,21] The observed temperature dependence, i.e., O_h complexes at 0 °C and T_d complexes at room temperature, is consistent with these observations.

On the other hand, the formation of gel-like networks as a whole is enthalpically driven, as shown by the following differential scanning calorimetry (DSC) data. Figure 6a shows DSC thermograms obtained for Co(**1**)$_3$Cl$_2$ in chloroform. The formation of gel-like networks is accompanied by an exothermic peak between 5 °C and 40 °C and the peak was reproducibly observed ($\Delta H = -33$ kJ mol^{-1}, $\Delta S = 111$ J K^{-1}mol^{-1}) though the peak structure is slightly altered in the repeated scans.

The exothermic peak (negative ΔH) indicates an enthalpy driven process that is in line with the transition from a metastable solution state to a more stable gel-like state. A schematic plot of the temperature dependence of the Gibbs free energy is shown in Figure 6b. The exothermic transition upon heating arises primarily from the greater thermodynamic stability of the nano-fibrous networks (tetrahedral complexes) versus the octahedral complexes in solution. The octahedral complexes in lower temperature solutions are transformed to the tetrahedral complexes that afford gel-like state (solid line, above 25 °C). As the tetrahedral complexes are maintained also in the lamellar

xerogels and in the crystalline samples (broken line), they are compatible to the regularly oriented ligand molecules. The observed negative enthalpy change is reasonably ascribed to the ordering process of ligand alkylchains possibly to the lamellar structures and interactions between the fibrous aggregates. They would have balanced the free energy increase accompanied by the reductions in translational and rotational freedom of motion. Similar heat-induced mesophase to crystal phase transition has been reported for liquid crystalline polymers.[22] Formation of organogels from crystalline fibrous aggregates has been also widely observed.[23]

It is interesting to compare the present heat-set gel-like network formation with heat-set hydrogels formed by globular proteins,[24] peptides,[25] or synthetic polymers.[26] Formation of these heat-set hydrogels are known as entropy driven (positive ΔS) process which is in line with the hydrophobic interactions.[24-26] The heat-set hydrogels of proteins are associated with denaturation which proceeds irreversibly. In organic liquids, hydrophobic interactions are either not operative or of secondary importance, and renders enthalpic stabilization responsible for the heat-set phase transition.

Conclusion

Described herein is a first example of thermally reversible, heat-set gel-like networks in organic media. It is developed by combining the elements of the one-dimensional metal complexes and mesoscopic supramolecular assemblies.[3-8,10] There are several appealing features in these self-assembling molecular wires. The first is impartment of lipophilic nature to the one-dimensional coordination complexes. The lipophilic modification of bridging ligands gives an alternative strategy to the electrostatic binding of lipid molecules to the oppositely charged linear complexes we reported previously.[3-7] Introduction of ether group in the 4-alkylated triazole Co(II) complex is important, since it promotes the formation of developed gel-like networks in chloroform. Second, fibrous nano-assemblies of tetrahedral complexes in the gel-like state are thermally responsive and they are transformed to the metastable, octahedral complexes in solution by cooling. This self-assembly is reversible and the heat-set transition (from the O_h complexes in solution to the T_d complexes in gel-like phase) is enthalpically driven. These features give a clear distinction from the conventional organogels that dissolve upon heating. In addition, it is also contrast to the heat-set polymer hydrogels which formation is entropy driven. The amphiphilic one-dimensional coordination systems thus provide unique self-assembling properties which are not accessible from the conventional inorganic or polymer chemistry. We foresee that the heat-set organogels will find wide range of applications as new thermoresponsive materials.

(20) King, H. C. A.; Körös, E.; Nelson, S. M. *J. Chem. Soc.* **1963**, 5449.
(21) (a) Sunamoto, J.; Hamada, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3130. (b) Aizawa, S.; Iida, S.; Matsuda, K.; Funahashi, S. *Inorg. Chem.* **1996**, *35*, 1338. (c) Aizawa, S.; Funahashi, S. *Inorg. Chem.* **2002**, *41*, 4555.

(22) (a) Papadimitrakopulos, F.; Sawa, E.; MacKnight, W. J. *Macromolecules* **1992**, *25*, 4682. (b) Cheng, S. Z. D.; Yandrasits, M. A.; Percec, V. *Polymer* **1991**, *32*, 1284.
(23) (a) Terech, P.; Allegraud, J. J.; Garner, C. M. *Langmuir* **1998**, *14*, 3991. (b) Lescanne, M.; Colin, A.; Mondain-Monval, O.; Fages, F.; Pozzo, J.-L. *Langmuir* **2003**, *19*, 2013.
(24) (a) Valstar, A.; Vasilescu, M.; Vigouroux, C.; Stilbs, P.; Almgren, M. *Langmuir* **2001**, *17*, 3208. (b) Croguennoc, P.; Nicolai, T.; Kuil, M. E.; Hollander, J. G. *J. Phys. Chem. B* **2001**, *105*, 5782.
(25) (a) Pochan, D. J.; Shneider, J. P.; Kretsinger, J.; Ozbas, B.; Rajagopal, K.; Haines, L. *J. Am. Chem. Soc.* **2003**, *125*, 11802. (b) Wright, E. R.; McMillan, A.; Cooer, A.; Apkarian, R. P.; Conticello, V. P. *Adv. Funct. Mater.* **2002**, *12*, 149.
(26) (a) Aoshima, S.; Sugihara, S. *J. Polym. Sci. Part A* **2000**, *38*, 3962. (b) Okabe, S.; Sugihara, S.; Aoshima, S.; Shibayama, M. *Macromolecules* **2002**, *35*, 8139.

Supporting Information Available: Experimental section, powder X-ray diffraction pattern of the xerogel, temperature dependence of UV−vis absorption intensities measured in anhydrous chloroform and in water-containing chloroform (water content 0.015 wt % and 0.082 wt %), and rheological data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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