# A Coordination Gelator That Shows a Reversible Chromatic Change and Sol−Gel Phase-Transition Behavior upon Oxidative/Reductive Stimuli

Shin-ichiro Kawano, Norifumi Fujita, and Seiji Shinkai*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Received February 25, 2004; E-mail: seijitcm@mbox.nc.kyushu-u.ac.jp

Stimuli responsiveness promises accessibility for designing and constructing new functional materials such as sensors,[1] actuators,[2] molecular devices,[3] etc. One of the advantages for using low-molecular-weight gels (LMWGs) is their reversibility and sharp sol−gel phase transition as a result of thermal stimuli. Such unique behaviors are due to the fashion of their assembly in that they consist of low-molecular-weight compounds self-assembled into complex three-dimensional networks and that their aggregation into fibrous superstructures is driven by multiple, weak interactions such as dipole−dipole, van der Waals, and hydrogen-bonding interactions.[4−10] Therefore, the stability and the functions of LMWGs strongly reflect the character inherent to the unit component.[11] Although various LMWGs have been reported thus far, the examples using the concept of coordination chemistry are still very limited[12] even though transition metal complexes are useful to impart new chemical and physical properties to the functionalization of organogels. For example, copper−polypyridine complexes in solution show the specific absorption band[13] and the redox activity,[14] which are expected to be applicable to the development of multistimuli responsive LMWGs. Herein, we report a novel class of coordination gelators that exhibit reversible chromatic and sol−gel phase-transition phenomena controlled by the redox state of the metal−ligand complex.

1: R = O·

2: R = O·
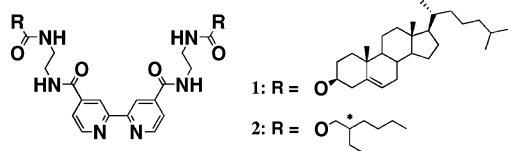
This system features a Cu(I) complex in which the ligand (**1**) is a 2,2′-bipyridine derivative bearing two cholesteryl groups.[15] The Cu(I)·**1**$_2$ complex successfully gels three organic solvents such as benzonitrile, 1-butyronitrile (1-PrCN), and THF/acetonitrile = 1/1 (v/v) among 15 kinds of solvents tested herein. Very interestingly, we have found that the color of the gel including the Cu(I)·**1**$_2$ complex in 1-PrCN is quite different from that of the sol: that is, when the 1-PrCN solution of the Cu(I)·**1**$_2$ complex in the sample vial was cooled to room temperature, the solution of the Cu(I)·**1**$_2$ complex gradually changed into the gel with a clear color change from reddish brown to greenish blue (Figure 1a). As this thermochromic phase-transition behavior is reversible for many times, we can rule out air oxidation of Cu(I) to Cu(II).[16] As far as we know, the Cu(I) complex with such greenish-blue color has never been reported, so that we first focused on this 1-PrCN gel obtained from the Cu(I)·**1**$_2$ complex to clarify the mechanism of the above intriguing phenomenon.

As shown in Figure 1c, the Cu(I)·**1**$_2$ complex gel has the typical MLCT absorption band (λ_{max} = 423 nm), which is attributable to the tetrahedrally coordinated Cu(I)·(2,2′-bipyridine)$_2$ complex.[13] In
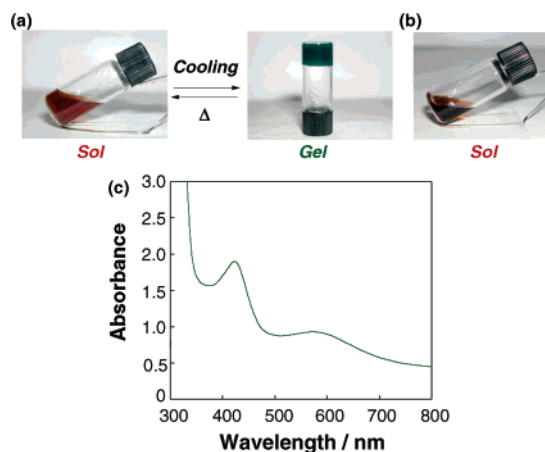

Figure 1. (a) Phase transition and thermochromic behavior of Cu(I)·**1**$_2$ at the sol and the gel phases: **1** + 0.5 equiv of Cu(MeCN)$_4$PF$_6$, [**1**] = 8.7 mmol dm^{-3} in 1-PrCN. (b) Photograph of the solution: **2** + 0.5 equiv of Cu(MeCN)$_4$PF$_6$, [**2**] = 8.7 mmol dm^{-3} in 1-PrCN at 25 °C. (c) UV−vis absorption spectrum of the gel: **1** + 0.5 equiv of Cu(MeCN)$_4$PF$_6$, [**1**] = 8.7 mmol dm^{-3} in 1-PrCN at 25 °C.

addition, the Cu(I)·**1**$_2$ complex gel gives a broad band at 574 nm, which is very unusual as the Cu(I) complexes. Sauvage and co-workers had already reported that this broad band is explicable by the low-symmety in the D_{2h} coordination structure of the Cu(I) complexes.[17] One can propose, therefore, that the Cu(I)·**1**$_2$ complex undergoes some sort of distortion in the confined environment inside the gel fibrils. In contrast, the solution of a Cu(I)·**2**$_2$ complex, which does not gelate 1-PrCN, displays neither the broad band nor the chromatic change, where the color was almost same as that of the solution of the Cu(I)·**1**$_2$ complex (Figure 1b). The CD band at around 420 nm, which appeared in the area of the MLCT band of the complex, was recognized for the 1-PrCN gel sample of the Cu(I)·**1**$_2$ complex at 30 °C (see Supporting Information), whereas the CD band decreased with a rise in the temperature. These results suggest that the molecular packing in the gel fibrils forces the Cu(I) complexes to be distorted in the tetrahedral coordination mode.[18]

We confirmed that the sol−gel phase-transition temperature (T_{gel}) of **1** was influenced by the addition of Cu(MeCN)$_4$PF$_6$. A plot of T_{gel} vs [Cu(I)]/[**1**] gives a maximum at around [Cu(I)]/[**1**] = 0.4−0.5 (see Supporting Information).[19] This maximal molar ratio is consistent with 1:2 stoichiometry as evidenced by the appearance of the MLCT band (λ_{max} = 423 nm).

It is clear, therefore, that the 1-PrCN gel is stabilized by the formation of the 1:2 complex from Cu(I) and **1**.

To obtain visual images of the superstructures constructed from **1** or the Cu(I)·**1**$_2$ complex we took micrographs using transmission electron microscopy (TEM). When the gel was prepared from **1** only, one can observe a well-developed network structure composed
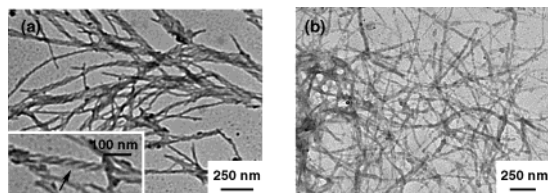
Figure 2. TEM images of 1-PrCN gels prepared from (a) **1** (8.7 mmol dm^{-3}) and (b) **1** (8.7 mmol dm^{-3}) + Cu(MeCN)$_4$PF$_6$ (4.3 mmol dm^{-3}); stained with phosphotungstic acid aqueous solution (20 g dm^{-3}).
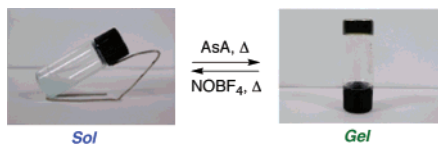

Figure 3. Phase transition and thermochromic behavior of Cu(II)·**1**$_2$: **1** + 0.5 equiv of Cu(OTf)$_2$, [**1**] = 8.7 mmol dm^{-3} in 1-PrCN, [ascorbic acid (AsA)] = [NOBF$_4$] = 6.9 mmol dm^{-3}.

of fibrous aggregates with 13−100-nm diameters (Figure 2a). Surprisingly, it was found that most of the aggregates feature a well-grown left-handed helical motif.[20] On the other hand, well-developed fibrous aggregates with 40−100-nm diameters were still observed with respect to the Cu(I)·**1**$_2$ complex (Figure 2b). Hence, it was suggested that the incipient fibers of the Cu(I)·**1**$_2$ complex are made of the one-dimensional aggregates and then the well-grown fibrous or bundled aggregates form the gel. As the Cu(I) coordination gelator showed the conventional properties of LMWGs, it was expected that this LMWG would exhibit the sharp responsiveness for redox stimuli.

It is very attractive and significant to exploit redox-responsive LMWGs, where the sol−gel phase transition is eventually controllable by redox-conjugated photochemical and electrochemical methods. As far as we are aware, such an example has never been reported. When ascorbic acid was added to the Cu(II)·**1**$_2$ complex and the mixture was then heated until the solid was dissolved completely, the greenish-blue gel was formed after cooling to room temperature. On the other hand, when NOBF$_4$ was added to the Cu(I) complex and the mixture was heated, the deep-green gel turned into the sol with a small amount of pale-blue precipitate. As shown in Figure 3, the sol−gel phase transition can be reversibly induced by addition of the oxidizing and reducing reagents.[21] It is undoubted that the redox state of the Cu ions plays a critical role in the stability of this gel system. To examine whether the gel prepared from the chemically reduced Cu(I)·**1**$_2$ complex has the same properties as the gel prepared from the Cu(I)·**1**$_2$ complex, we used the spectroscopic and electron microscopic methods. As a result, it was confirmed that the UV and CD spectra and TEM image of the chemically reduced gel are consistent with those of the Cu(I)·**1**$_2$ complex gel (see Supporting Information). These results provide clear evidence that the chemically reduced Cu(I)·**1**$_2$ complex is basically the same as the original gel prepared from the Cu(I)·**1**$_2$ complex.

In conclusion, the present work has established the first redox-responsive LMWG using the redox active Cu(I)/Cu(II) of coordination chemistry. This complex has two novel properties: (1) the chromatic change in the Cu(I)·**1**$_2$ complex is induced by the sol−gel phase transition, which is associated with the distortion of the coordination complex in the specific cholesteric gel fibril, and (2)

the tuning of the reversible sol−gel phase transition is possible by changing the redox state of the Cu(I)/Cu(II) complexes by chemical oxidation and reduction. With these achievements in mind, new functions related to photochemical and electrochemical control of sol−gel phase-transition events are currently under investigation.

Supporting Information Available: Synthesis of **1** and **2**; ^{1}H NMR spectra of **1** and **2**; T_{gel} plot vs [Cu(I)]/[**1**]; variable-temperature CD spectra of the Cu(I)·**1**$_2$ complex gel; UV−vis absorption, CD spectra, and TEM image of the Cu(I)·**1**$_2$ complex gel obtained by the reduction of Cu(II); gelation properties of **1** and the Cu(I)·**1**$_2$ complex; EPR spectra of the sol and the gel states of the Cu(I)·**1**$_2$ complex; UV spectra of the oxidized gel of the Cu(I)·**1**$_2$ complex. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537−2574.
(2) Osada, Y.; Okuzaki, H.; Hori, H. *Nature* **1992**, *355*, 242−244.
(3) (a) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−3391. (b) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515−1566.
(4) For recent reviews, see: (a) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133−3159. (b) van Esch, J. H.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2263−2266. (c) Gronwald, O.; Shinkai, S. *Chem. Eur. J.* **2001**, *7*, 4328−4334.
(5) Murata, K.; Aoki, M.; Suzuki, T.; Harada, T.; Kawabata, H.; Komori, T.; Ohseto, F.; Ueda, K.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6664−6676.
(6) Hanabusa, K.; Yamada, Y.; Kimura, M.; Shirai, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1949−1951.
(7) van Esch, J.; Schoonbeek, F.; de Loos, M.; Kooijman, H.; Spek, A. L.; Kellogg, R. M.; Feringa,B. L. *Chem. Eur. J.* **1999**, *5*, 937−950.
(8) Yoza, K.; Amanokura, N.; Ono, Y.; Akao, T.; Shinmori, H.; Takeuchi, M.; Shinkai, S.; Reinhoudt, D. N. *Chem. Eur. J.* **1999**, *5*, 2722−2729.
(9) Kobayashi, H.; Amaike, M.; Jung, J. H.; Friggeri, A.; Shinkai, S.; Reinhoudt, D. N. *Chem. Commun.* **2001**, 1038−1039.
(10) Ishi-i, T.; Ono, Y.; Shinkai, S. *Chem. Lett.* **2000**, 808−809.
(11) (a) Sugiyasu, K.; Fujita, N.; Takeuchi, M.; Yamada, S.; Shinkai, S. *Org. Biomol. Chem.* **2003**, *1*, 895−899. (b) Sugiyasu, K.; Fujita, N.; Shinkai, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1229−1233.
(12) (a) Beck,J. B.; Roman, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 13922−13923. (b) Sohna, J.-R. S.; Fages, F. *Chem. Commun.* **1997**, 327−328. (c) Kawano, S.-i.; Fujita, N.; van Bommel, K. J. C.; Shinkai, S. *Chem. Lett.* **2003**, *32*, 12−13. (d) Kuroiwa, K.; Shibata, T.; Takada, A.; Nemoto, N.; Kimizuka, N. *J. Am. Chem. Soc.* **2004**, *126*, 2016−2021.
(13) Williams, R. M.; Cola, L. D.; Hartl, F.; Lagref, J.-J.; Planeix, J.-M.; Cian, A. D. Hosseini, M. W. *Coord. Chem. Rev.* **1997**, *230*, 253−261.
(14) Livoreil, A.; Sauvage, J.-P.; Armaroli, N.; Balzani, V.; Flamigni, L.; Ventura, B. *J. Am. Chem. Soc.* **1997**, *119*, 12114−12124.
(15) See Supporting Information.
(16) Both the sol and the gel states of the Cu(I)·**1**$_2$ complex are EPR silent, which means that Cu(II) ion does not contribute to this chromatic change.
(17) (a) Ichinaga, A. K.; Kirchhoff, J. R.; McMillin, D. R.; Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J.-P. *Inorg. Chem.* **1987**, *26*, 4290−4292. (b) Phifer, C. C.; McMillin, D. R. *Inorg. Chem.* **1986**, *25*, 1329−1333. (c) Burke, P. J.; Henrick, K.; McMillin, D. R. *Inorg. Chem.* **1982**, *21*, 1881−1886.
(18) Zarges, W.; Hall, J.; Lehn, J.-M. *Helv. Chim. Acta* **1994**, *74*, 1843−1852.
(19) Over the molar ratio [Cu(I)]/[**1**] = 0.5, the gel stability was weakened because the 1:2 complex was not the main species, which was monitored by the relative decrease in the MLCT band intensity.
(20) It is rare that the aggregate of cholesteryl derivative with the (*S*)-configuration at C-3 shows these *left*-handed helical structures. Although we herein could not reveal why this anti-motif was observed, the details of the assembled architecture are being investigated.
(21) The quantitative completions of chemical oxidation and reduction of the Cu·**1**$_2$ complexes were evidenced by UV and EPR spectra; see Supporting Information.

JA048943+