Photoresponsive molecular wires of Fe^{II} triazole complexes in organic media and light-induced morphological transformations†

Shoko Kume,‡ Keita Kuroiwa and Nobuo Kimizuka*

A lipophilic linear Fe^{II} 1,2,4-triazole complex containing azobenzene chromophores forms molecular wires in organic solvents; photoisomerization of azobenzene units induced morphological changes that lead to reversible, macroscopic gel-to-sol transition phenomena.

Pseudo one-dimensional (1D) transition metal complexes have been attracting much interest because of their specific electronic,[1] magnetic[2] and optical properties[3] in the crystalline state. These 1D structures usually exist only as basic structural motifs of 3D crystalline solids. Maintenance of these polymeric structures in solution will provide a new family of molecular wires, with functions not accessible from π-conjugated polymers. For example, if the chain conformations or self-assembling properties are regulated, depending on the solvents or environmental stimuli, consequent control of their electromagnetic properties will be expected. To convert 1D inorganic chains into soluble nanowires, amphiphilic packaging strategies have been developed.[4–7] The next challenges will include the development of 1D metal complexes which display morphological changes in response to applied stimuli. We report herein a novel azobenzene-containing iron^{II} triazole complex which shows solvent- and photodependent morphological changes. Their relevance to aggregation and solution properties is also discussed.

An azobenzene chromophore was introduced into triazole ligand **1** *via* ether linkages. The complex [Fe(**1**)$_3$](BF$_4$)$_2$ is soluble in common organic solvents by heating. Fig. 1a shows an atomic force microscopy (AFM) image of [Fe(**1**)$_3$](BF$_4$)$_2$ dropped from a dilute chloroform solution (substrate: highly oriented pyrolytic graphite, HOPG). Flexible, fibrous nanostructures with a uniform width of *ca.* 6.9 nm are observed (Fig. 1a,b). The observed width is nearly twice the length of a ligand molecule **1** (*ca.* 3.5 nm). As Fe^{II} ions generally adopt octahedral coordination structures, observed nanostructures are reasonably assigned to polymeric triazole complexes surrounded by lipophilic alkyloxy-azobenzene groups (Fig. 1c).[8] It appears that BF$_4^-$ counterions are electrostatically associating the cationic coordination main-chain in this non-polar medium.

The length of supramolecular wires in Fig. 1a ranges from 10 to 100 nm, which corresponds to *ca.* 25–250 repeating units, as

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Moto-oka, Nishi-ku 744, Fukuoka 819-0395. E-mail: kimitcm@mbox.nc.kyushu-u.ac.jp
‡ Present address: Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033.

estimated from the reported Fe^{II}–Fe^{II} distance (*ca.* 4 Å for triazole complexes).[9] π–π* absorption of azobenzene chromophores in [Fe(**1**)$_3$](BF$_4$)$_2$ is observed at 359 nm in chloroform. This peak is identical to that of ligand **1** alone (Figure S1†), and thus azobenzene chromophores are well solvated in the lipophilic layer.

On the other hand, upon dissolving [Fe(**1**)$_3$](BF$_4$)$_2$ in chlorocyclohexane, a weak gel was formed in 6–24 hours (Fig. 2a, concentration 20 mM). The observed physical gelation of chlorocyclohexane by [Fe(**1**)$_3$](BF$_4$)$_2$ is indicative of the formation of developed aggregates, as observed by scanning electron microscopy (SEM, Fig. 2e) and transmission electron microscopy (TEM, Figure S3a†). Ultra-thin nanosheets with a minimum thickness of *ca.* 10 nm were observed by SEM for freeze-dried gels. Fig. 2f shows AFM images of [Fe(**1**)$_3$](BF$_4$)$_2$ dropped from dilute chlorocyclohexane solutions. Oriented arrays of linear molecular wires (length: more than 400 nm, height: *ca.* 1 nm from the HOPG surface) are observed, in contrast to the undulating structures in chloroform (Fig. 1a). The average distance between the centers of the molecular wires in Fig. 2f is *ca.* 6 nm, which is smaller by 1 nm compared to those of the undulating molecular wires in Fig. 1. As the AFM-determined height agrees with the minimum thickness of nanosheets observed by SEM, the nanosheets should be formed by
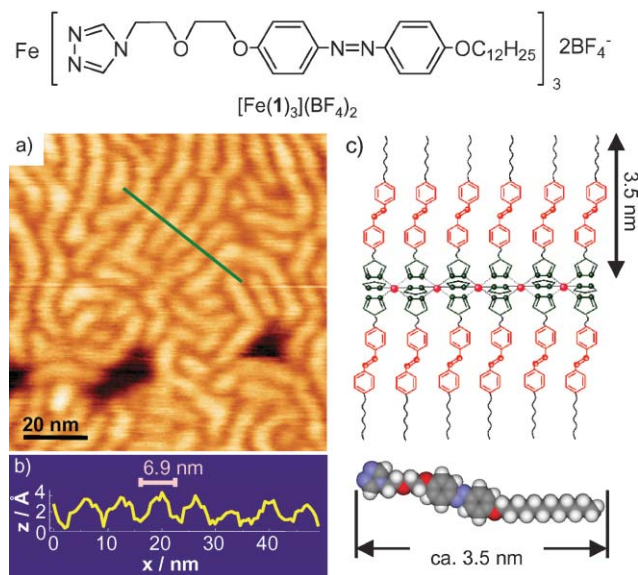
Fig. 1 (a) AFM image of [Fe(**1**)$_3$](BF$_4$)$_2$ dropped from a chloroform solution (1 × 10^{-5} M) onto HOPG. (b) Surface height profile along the green line marked in image (a). (c) Schematic illustration of a molecular wire of [Fe(**1**)$_3$](BF$_4$)$_2$ and a CPK model of **1**. Counterions are omitted for clarity.
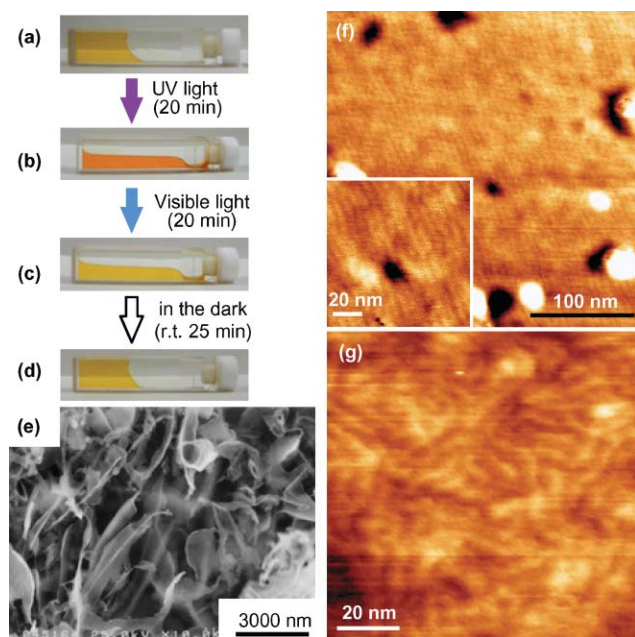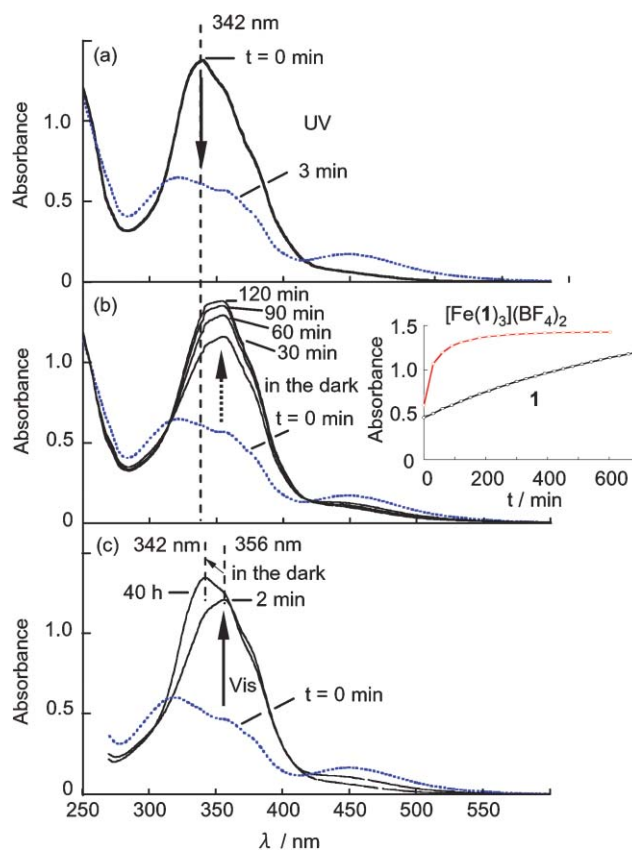
Fig. 2 (a–d) Photographs of $[Fe(1)_3](BF_4)_2$ samples in chlorocyclohexane (10 mM, at room temperature): (a) Before photoirradiation, (b) after irradiation with UV light (365 nm), (c) after irradiating sample b with visible light (546 nm), (d) sample c kept in the dark for 25 min. (e) SEM image of freeze-dried gel. (f,g) AFM images of $[Fe(1)_3](BF_4)_2$ dropped from chlorocyclohexane solutions (1×10^{-5} M): (f) Before photoirradiation, (g) after 2 min irradiation with UV light (365 nm). Substrate: HOPG.

Fig. 3 UV-vis spectral changes of $[Fe(1)_3](BF_4)_2$ upon photoisomerization in chlorocyclohexane (2.1×10^{-5} M). (a) $[Fe(trans\text{-}1)_3](BF_4)_2$ irradiated by UV light for 3 min. (b) UV-irradiated solution stood in the dark at 25 °C. Inset: Peak absorbance recovery with time observed for chlorocyclohexane solutions of $[Fe(cis\text{-}1)_3](BF_4)_2$ and cis-**1**. Samples were irradiated with UV light in advance. The monitored wavelength was 340 nm (for $Fe[(1)_3](BF_4)_2$) and 358 nm (for **1**), respectively. (c) A UV-irradiated $[Fe(cis\text{-}1)_3](BF_4)_2$ solution was progressively irradiated with visible light for 2 min. Subsequent spectral changes in the dark were monitored at 25 °C for 40 h.

two-dimensionally aligned molecular wires. This gives a reasonable account for the thickening and gelation of chlorocyclohexane.

The presence of molecular wires in solution is further supported by UV-Vis and FT-IR spectra. $[Fe(1)_3](BF_4)_2$ in chlorocyclohexane showed a π-π* absorption maximum of azobenzene chromophores at 342 nm (Fig. 3a), which is blue shifted by 17 nm compared to that observed in chloroform. The observed spectral blue shift is typical of excitonic interactions operating among parallel-oriented (H-aggregated) azobenzene chromophores.[10] It is verified that Fe–N coordination bonds of $[Fe(1)_3](BF_4)_2$ are maintained in solution, as C=N stretching vibrations of the triazole unit are observed at around at 1556 cm^{-1}. This peak position is distinct from that of a free ligand **1** (C=N stretching at 1538 cm^{-1}, see supporting information).

The photoisomerization properties of the azobenzene chromophores in $[Fe(1)_3](BF_4)_2$ were then investigated. Interestingly, UV light irradiation of $[Fe(trans\text{-}1)_3](BF_4)_2$ in a yellow chlorocyclohexane gel (10 mM) caused fluidization into an orange-colored solution (Fig. 2, a → b). In the UV-vis spectra, spectral changes typical of trans-to-cis photoisomerization were immediately observed (Fig. 3a). The cis-azobenzene chromophores are obtained in >57% yield within three minutes.[11] The coordination structure of the $Fe(1)_3$ complexes in solution is maintained, even when the azobenzene units are in their cis-form, since the C=N stretching vibrations were observed intact at 1556 cm^{-1}.[12] In AFM, the UV-irradiated sample showed undulating structures similar to those in chloroform (Fig. 2g). Thus, dissolution of organogels is caused by a photoinduced morphological change to the molecular wires. The bent cis-azobenzene unit must hamper the ordered chromophore stacking, resulting in a destabilization of the linear structures.

Upon keeping the chlorocyclohexane solution of $[Fe(cis\text{-}1)_3](BF_4)_2$ in the dark, thermal cis-to-trans isomerization occurred in ca. 2 hours (Fig. 3b). The inset to Fig. 3b compares the recovery in absorption intensities of trans-azobenzene chromophores observed for $[Fe(cis\text{-}1)_3](BF_4)_2$ and cis-ligand **1**. It is notable that thermal cis-to-trans isomerization is significantly promoted in $Fe(1)_3$ complexes compared to monomeric cis-ligand **1**. The acceleration in cis-to-trans thermal isomerization was similarly observed for chloroform solutions. It is natural to assume that the acceleration effect originates from the alleviation of steric crowding among cis-azobenzene chromophores tethered to the linear $Fe(1)_3$ chains.

On the other hand, upon visible light illumination of $[Fe(cis\text{-}1)_3](BF_4)_2$ complexes in chlorocyclohexane (illumination period, 2 min), immediate cis-to-trans photoisomerization occurred (Fig. 2, b → c). A π–π* absorption peak of $[Fe(trans\text{-}1)_3](BF_4)_2$ complexes just after isomerization was observed at 356 nm (Fig. 3d). It showed a gradual shift in the dark to the original blue-shifted peak (at 342 nm) within a period of several minutes to a few hours. The observed spectral shift indicates the recovery of parallel-oriented
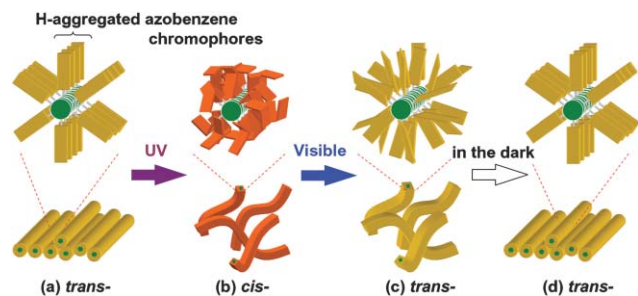
Fig. 4 Schematic illustration of light-induced morphological changes to Fe[(**1**)$_3$](BF$_4$)$_2$.

trans-azobenzene chromophores, and the solution showed regelatinization with the progression of the spectral blue shift (Fig. 2, c → d). The UV- and visible light-induced gel-to-sol transition was totally reversible, and could be repeated many times.

The observed photochromic structural changes of [Fe(*trans*-**1**)$_3$](BF$_4$)$_2$ in chlorocyclohexane are schematically summarized in Fig. 4. In the initial [Fe(*trans*-**1**)$_3$](BF$_4$)$_2$ complex (a), azobenzene chromophores are regularly aligned with a parallel orientation. Formation of organogels at higher concentration indicates that these supramolecular wires aggregate into nanosheets, as shown by SEM. Upon UV-illumination, the *cis*-azobenzene chromophores formed induce morphological changes to give undulating structures (b), and concomitant reduction in inter-nanowire interactions causes dissolution of the gel. Successive visible light irradiation of [Fe(*cis*-**1**)$_3$](BF$_4$)$_2$ readily affords [Fe(*trans*-**1**)$_3$](BF$_4$)$_2$, and photoisomerization of azobenzene chromophores reversibly occurs while maintaining the basic linear coordination structure. Molecular orientation of regenerated *trans*-azobenzene chromophores is initially less ordered (λ_{max} at 356 nm), (c), but successive reorientation of chromophores causes regelatinization of the solvent, (d). It is notable that the photoinduced isothermal gelation process (b → c → d) occurs much faster than the cool-set gelation of [Fe(*trans*-**1**)$_3$](BF$_4$)$_2$. The maintenance of linear coordination structures in [Fe(*cis*-**1**)$_3$](BF$_4$)$_2$ is supported by AFM observations, FT-IR spectra (intact C=N stretching vibrations) and also by the acceleration in *cis*-to-*trans* isomerization.

In conclusion, a photoresponsive molecular wire of a pseudo 1D metal complex has been newly developed. The significance of present study is two-fold. Firstly, this is a first report on metallo-supramolecular gels which show photoresponsive morphological transformations. Azobenzene chromophores attached to polymeric coordination structures display reversible photoisomerization without an appreciable disruption of the molecular wires. This could be due to the absence of other coordinating elements in this non-polar medium, which inhibits chain fragmentation and the release of non-coordinated Fe^{II} ions. Secondly, molecular wires of

Fe^{II} triazole complexes and their solvent- and photoinduced morphological changes were clearly observed by AFM. Changes in molecular wire structure emerged as a macroscopic gel-to-sol transition. It is now possible to photocontrol the morphology and interactions of pseudo 1D metal complexes in solution without losing their polymeric coordination entities. These features draw a clear line between organogels formed from azobenzene-containing, organic low molecular weight gelators[13] and those formed by the aggregation of discrete metal complexes.[14] We envisage that this lipophilic linear coordination system could serve as a useful platform for the development of intelligent molecular wires, in which the regulation of chain conformations plays a decisive role in determining their electromagnetic properties.

Notes and references

1 H. Kitagawa, N. Onodera, T. Sonoyama, M. Yamamoto, T. Fukawa, T. Mitani, M. Seto and Y. Maeda, *J. Am. Chem. Soc.*, 1999, **121**, 10068.
2 (*a*) J. Köber, E. Codjovi, O. Kahn, F. Groliére and C. Jay, *J. Am. Chem. Soc.*, 1993, **115**, 9810; (*b*) R. Clérac, H. Miyasaka, M. Yamashita and C. Coulon, *J. Am. Chem. Soc.*, 2002, **124**, 12837.
3 H. Kisihida, H. Matsuzaki, H. Okamoto, T. Manabe, M. Yamashita, Y. Taguchi and Y. Y. Tokura, *Nature*, 2000, **405**, 929.
4 (*a*) N. Kimizuka, *Adv. Mater.*, 2000, **12**, 1461; (*b*) C.-S. Lee and N. Kimizuka, *Chem. Lett.*, 2002, 1252; (*c*) C.-S. Lee and N. Kimizuka, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4922.
5 K. Kuroiwa, T. Shibata, A. Takada, N. Nemoto and N. Kimizuka, *J. Am. Chem. Soc.*, 2004, **126**, 2016.
6 (*a*) M. Fontana, M. H. Chanzy and A. R. Caseri, *Chem. Mater.*, 2002, **14**, 1730; (*b*) J. Bremi, D. Brovelli, W. Caseri, G. Hähner, P. Smith and T. Tervoort, *Chem. Mater.*, 1999, **11**, 977.
7 O. Roubeau, A. Colin, V. Schmitt and R. Clérac, *Angew. Chem., Int. Ed.*, 2004, **43**, 3283.
8 Specimens prepared by dropping a chloroform solution of ligand **1** did not give such nanostructures.
9 M. Thomann, O. Kahn, J. Guilhem and F. Varret, *Inorg. Chem.*, 1994, **33**, 6029.
10 (*a*) M. Kasha, in *Spectroscopy of the Excited State*, ed. B. D. Bartolo, Plenum Press, New York, 1976, pp. 337; (*b*) M. Shimomura, R. Ando and T. Kunitake, *Ber. Bunsen-Ges. Phys. Chem.*, 1983, **87**, 1134.
11 The ratio of *trans*- and *cis*-azobenzene chromophores was calculated from the UV peak absorption intensity at 342 nm.
12 Magnetic susceptibility measurements of cast films indicate that both [Fe(*trans*-**1**)$_3$] and [Fe(*cis*-**1**)$_3$](BF$_4$)$_2$ complexes have octahedral FeN$_6$ coordination structures. See the ESI†.
13 (*a*) K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda and S. Shinkai, *J. Am. Chem. Soc.*, 1994, **116**, 6664; (*b*) J. Eastoe, M. Sánchez-Dominguez, P. Wyatt and R. K. Heenan, *Chem. Commun.*, 2004, 2608.
14 (*a*) S. Kawano, N. Fujita and S. Shinkai, *J. Am. Chem. Soc.*, 2004, **126**, 8592; (*b*) A. Kishimura, T. Yamashita and T. Aida, *J. Am. Chem. Soc.*, 2005, **127**, 179.