

Supplementary Information

Photo-Responsive Molecular Wires of Fe(II) Triazole Complexes in Organic Media and Light-induced Morphological Transformations.

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1. Experimental

A) Synthesis.

4-(2-(2-hydroxyethoxy)ethyl)-1,2,4-triazol

Triethyl orthoformate (13.3 g, 90 mmol) and formyl hydrazine (3.6 g, 60 mmol) were refluxed for 3.5 h in dry methanol (100 ml) under inert atmosphere. To this mixture, 2-aminoethoxyethanol (5.3 g, 50 mmol) in 10 ml dry methanol was added, and it was refluxed for additional 4 h. Solvent was removed under air, and resulting light brown oil was purified with silica-gel column chromatography. The reaction mixture was first eluted with acetone to remove impurities, and then eluent was changed to methanol to collect the product as pale yellow oil. Yield: 7.39 g (94%) ¹H NMR (DMSO-d₆) δ 8.51 (s, 2H), 4.66 (br, 1H), 4.18 (t, *J* = 5.4 Hz, 2H), 3.66 (t, *J* = 5.4 Hz, 2H), 3.47 (t, *J* = 5.4 Hz, 2H), 3.40 (t, *J* = 6.0 Hz, 2H).

4-(2-(4-(4-dodecyloxyphenylazo)phenoxy)ethoxy)ethyl)-1,2,4-triazol (1)

4-(2-(2-hydroxyethoxy)ethyl)-1,2,4-triazol (393 mg, 2.5 mmol) was dissolved in dry pyridine (5 ml) and cooled to 0 °C. *p*-Toluenesulfonyl chloride (2.86 g, 15 mmol) was added slowly, and the reaction mixture was kept at 4 °C overnight. 50 ml water was added to the reaction mixture, and the product was extracted three times with 50 ml chloroform. The organic layer was dried over with anhydrous sodium sulfate, filtered with Celite plug and concentrated. To residual light brown oil, 4-hydroxy-4'-dodecyloxyazobenzene (956 mg, 2.5 mmol) and potassium carbonate (829 mg, 6 mmol) were added and the mixture was heated at 100 °C in anhydrous DMF for 5 h. Water (50 ml) was added to the reaction mixture, and yellow precipitate was filtered and washed with water. The solid was suspended in 90 ml brine, and extracted with chloroform. The organic layer was dried over with anhydrous sodium sulfate, filtered with Celite plug and the solvent was removed. Crude product obtained was purified with silica-gel column chromatography eluted with chloroform, and recrystallization from toluene gave the product as yellow microcrystal. Yield: 547 mg (42 %)

Anal. Calcd for C₃₀H₄₅N₅O₃: C, 69.07; H, 8.31; N, 13.42. Found: C 68.95; H, 8.31; N, 13.41. ¹H NMR δ 8.17 (s, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* =

8.4 Hz, 2H) 6.99 (d, $J = 9.0$ Hz, 2H), 4.22 (t, $J = 4.8$ Hz, 2H), 4.19 (t, $J = 4.8$ Hz, 2H), 4.03 (t, $J = 6.6$ Hz, 2H), 3.85 (m, 4H), 1.81 (qui, $J = 6.6$ Hz, 2H), 1.47 (qui, $J = 7.2$ Hz, 2H), 1.30 (m, 16H), 0.88 (t, $J = 7.2$ Hz, 3H). MALDI-TOF-MS (m/z) 522.4 [MH^+].

[Fe(1)₃](BF₄)₂·H₂O

The ligand **2** (522 mg, 1.0 mmol) and Fe(BF₄)₂·6H₂O (113 mg, 0.33 mmol) were stirred at 100°C in 10 ml dry DMF for 3 h under inert atmosphere. After removing the solvent under reduced pressure, dark-brown residue obtained was dissolved in 20 ml dichloromethane and filtered with Celite plug. The filtrate was concentrated to 10 ml, and 30 ml diethyl ether was slowly diffused to form jelly-like dark-orange precipitate. The precipitate was collected with centrifugation, and washed twice with diethyl ether, and dried to give dark-orange glassy solid. Yield: 420 mg (70 %). Anal. Calcd for C₉₀H₁₃₁N₁₅O₁₀B₂F₈Fe: C, 59.64; H, 7.28; N, 11.59. Found: C, 59.72; H, 7.24; N, 11.75. IR (KBr pellet) $\nu_{ring} = 1556\text{ cm}^{-1}$.

B) Photoirradiation and spectral measurement

Photoirradiation was conducted with super-high pressure mercury lamp (USHIO, USH-500D) as a light source. Bright lines of 365 nm (for UV-irradiation) and 436 nm (or 546 nm) (for Vis-irradiation) were selected with monochromator (JASCO, CT-10). The ratio of trans- and cis-azobenzene chromophores was calculated from the UV-peak absorption intensity at 342 nm. UV-Vis Spectra were measured for dispersions in 1 mm-length quartz cell, with V-560 and V-570 spectrophotometer (JASCO).

C) Atomic Force Microscopy.

In Atomic Force Microscopy, samples were prepared by casting chloroform solutions (2 ml, 1×10^{-5} M) on freshly cleaved highly oriented pyrolytic graphite (HOPG, 5 mm × 5 mm) surface, and solvents were evaporated under reduced pressure. All images were recorded in ambient condition in tapping mode with a Nanoscope IIIa (Veeco). The probes are commercially available phosphorous doped silicon tips (Veeco, MPP-11100). All data were corrected with 1st order flatten procedure (WSxM 4.0, Nanotec Electronica) to clarify the minute surface patterns. The height of molecular wires was estimated against the dark domains (surface of HOPG).

D) Transmission Electron Microscopy (TEM).

Chlorocyclohexane solution (1×10^{-4} M) was dropped on carbon-coated TEM grid and dried in vacuo. The sample was subsequently stained with aqueous uranyl acetate, and then dried in vacuo. JEM2010 (JEOL) was used at the acceleration voltage of 120 kV.

E) Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy was conducted with Hitachi S-5000. To dichloromethane solutions (before and after photoirradiation, 0.1ml, 1×10^{-3} M) were added 0.5 ml of *tert*-butanol. The mixtures were immediately immersed in liq. N₂ and freeze-dried under reduced pressure. Dried samples were placed on carbon tape, and a thin layer of platinum was sputtered on them before observation.

F) Magnetic susceptibility measurement.

Yellow cast films of [Fe(*trans*-1)₃](BF₄)₂ were prepared on glass plate. UV-irradiation of the cast film afforded orange-colored [Fe(*cis*-1)₃](BF₄)₂ complexes which were scraped off and were put in gelatin capsules. The magnetic susceptibility of the iron(II) complexes was determined over the 5-350 K range. The temperature dependence of the molar magnetic susceptibility of [Fe(*cis*-1)₃](BF₄)₂ and [Fe(*cis*-1)₃](BF₄)₂ are displayed in Figure S-5 in the form of a $\chi_M T$ vs T plot ($\chi_M T$, the molar magnetic susceptibility corrected for diamagnetic contributions. T , temperature). In the first cycle, the specimen was cooled to helium temperature and magnetic susceptibility of [Fe(*cis*-1)₃](BF₄)₂ complex was measured for heating process to 250 K and then cooling process to helium temperature. In the second run, the sample was heated to 350 K to allow thermal isomerization to [Fe(*trans*-1)₃](BF₄)₂ complex. Magnetic susceptibility of the *trans*-complex was measured by cooling to helium temperature and then heating to 250 K.

1. UV-Vis spectra

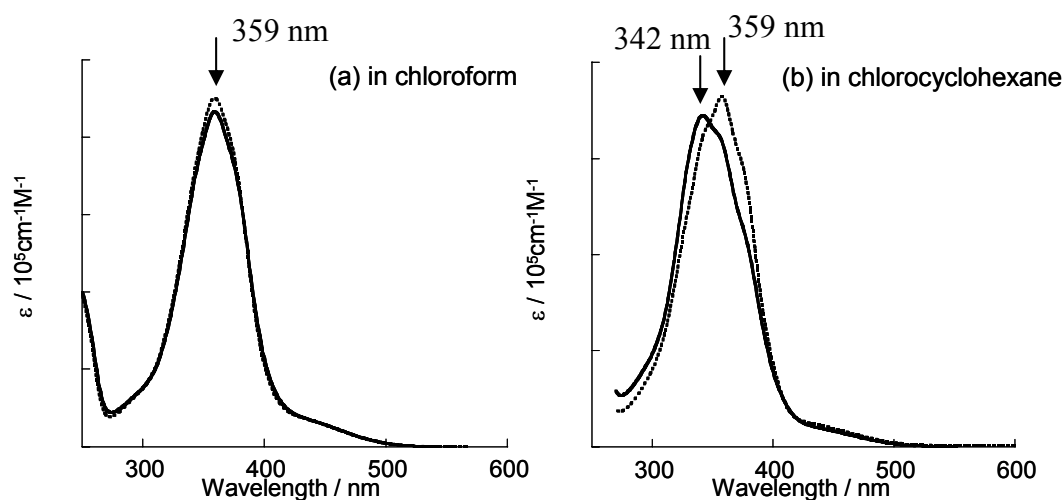


Figure S-1. UV-Vis absorption spectra of **1** (dotted line) and [Fe(**1**)₃](BF₄)₂ (solid line) in chloroform (a) and in chlorocyclohexane (b). Concentration, 2.1×10^{-5} mM, Temperature, 25 °C.

In chloroform, absorption maximum of $[\text{Fe}(\mathbf{1})_3](\text{BF}_4)_2$ is identical with that of the monomeric ligand **1** alone (λ_{max} , 359 nm). It indicates that the azobenzene chromophores are highly solvated by the solvent. On the other hand, $[\text{Fe}(\mathbf{1})_3](\text{BF}_4)_2$ in chlorocyclohexane show spectral blue shift (λ_{max} , 342 nm) compared to the ligand alone. This blue shift is typical of excitonic interactions among parallel-oriented azobenzene chromophores.^{10b}

2. Atomic Force Microscopy.

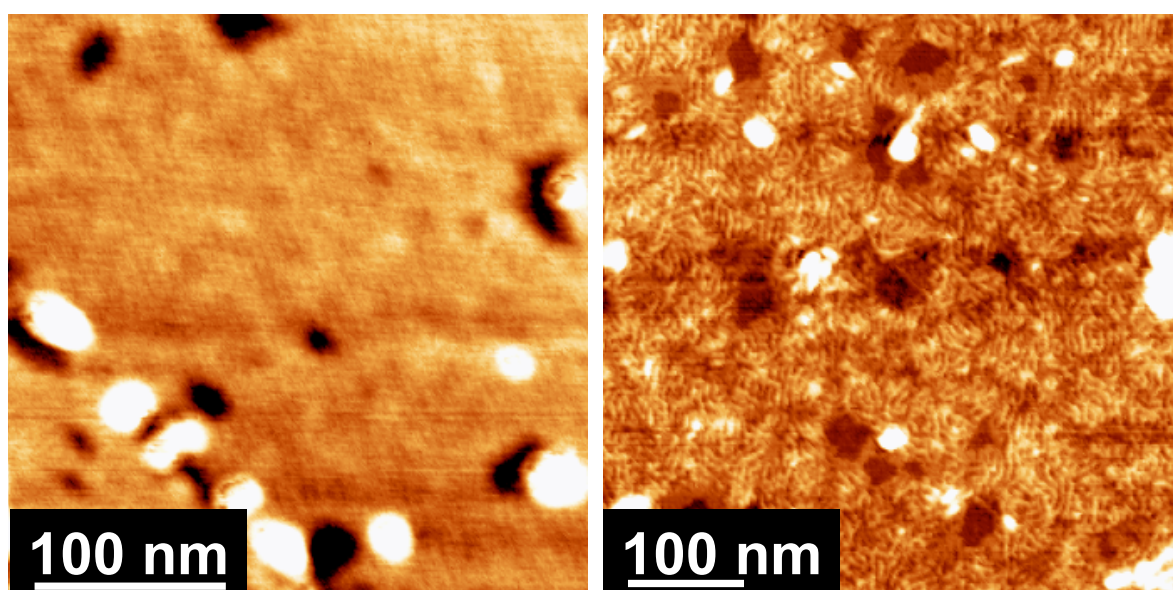


Figure S-2. AFM images of $\text{Fe}[(\mathbf{1})_3](\text{BF}_4)_2$ (1×10^{-5} M) cast from chlorocyclohexane solution on HOPG. Left, before irradiation, Right, after irradiation of the solution with UV light (at 365 nm for 2 min). These specimens are identical to those shown in Fig.2f and Fig.2g, respectively.

The height of supramolecular wires (ca. 1 nm) was estimated by comparing the height between the brightest part of the AFM image and the darkest areas (HOPG surface).

3. TEM and SEM

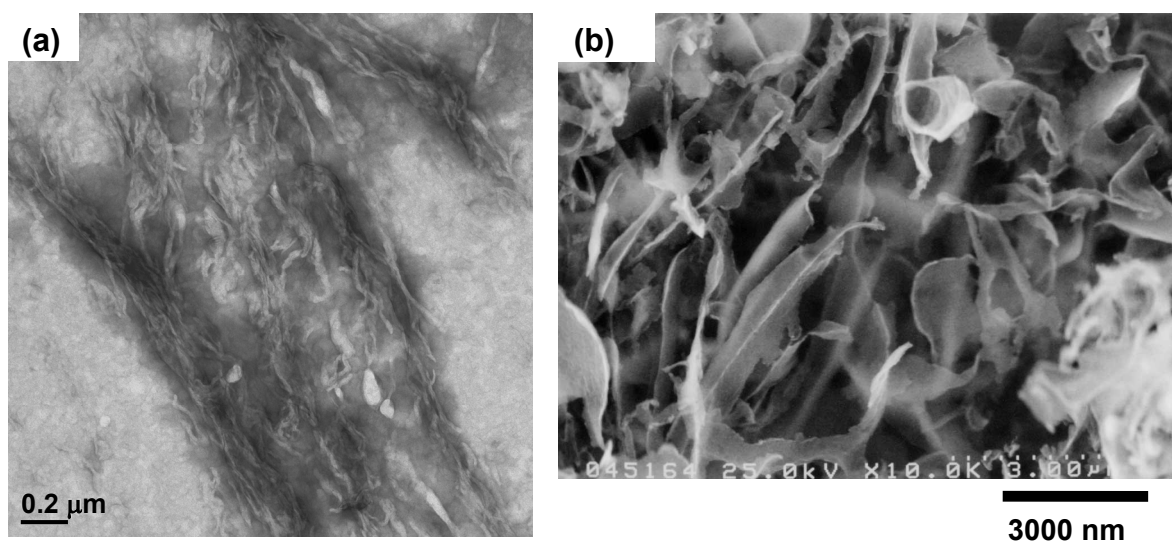


Figure S-3. (a) TEM image of $[\text{Fe}(\text{trans-1})_3](\text{BF}_4)_2$ in chlorocyclohexane. Samples are post-stained with aqueous uranyl acetate after casting $[\text{Fe}(\mathbf{1})_3](\text{BF}_4)_2$ from chlorocyclohexane solution (1×10^{-4} M). (b) SEM image of freeze-dried $[\text{Fe}(\text{trans-1})_3](\text{BF}_4)_2$ from chlorocyclohexane/ *tert*-BuOH (1/5 by vol.) solution (concentration, 1.9×10^{-4} M). Fig.S-3(b) is identical with Fig.2(e).

$\text{Fe}(\text{trans-1})_3$ in chlorocyclohexane tends to form bundles, in consistent with the formation of gels. In the SEM image (b), sheet-like assemblies with a minimum thickness of ca. 10 nm are abundantly seen. This thickness is close to that of single supramolecular wires, and possibly they are comprised of two-dimensionally aligned sheets of supramolecular wires. It gives a reasonable account for the observation of linear oriented structures in AFM (Figure 2f, Figure S-2 left).

4. FT-IR

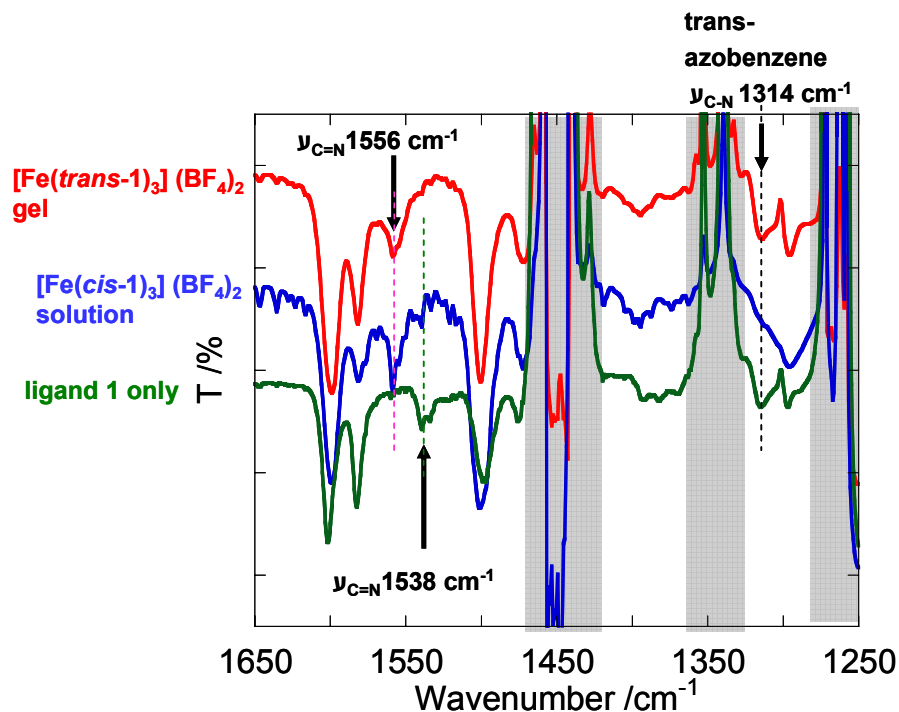


Figure S-4. FT-IR spectra of $[\text{Fe}(\text{trans-1})_3](\text{BF}_4)_2$, $[\text{Fe}(\text{cis-1})_3](\text{BF}_4)_2$, and ligand **1** in chlorocyclohexane. Concentration, 10 mM. NaCl cell.

Both of $[\text{Fe}(\text{trans-1})_3](\text{BF}_4)_2$, $[\text{Fe}(\text{cis-1})_3](\text{BF}_4)_2$ in chlorocyclohexane solutions give C=N stretching band at 1556 cm^{-1} , which is clearly distinct from that observed for the free ligand **1** ($\nu_{\text{C=N}}$ at 1538 cm^{-1}). Therefore, the Fe-N coordination structure is maintained for both of the $\text{Fe}(\text{trans-1})_3$ and $\text{Fe}(\text{cis-1})_3$ complexes in solution.

5. Magnetic susceptibility measurement

To investigate the effect of photoisomerization on spin transition characteristics of $\text{Fe}(\mathbf{1})_3$, magnetic susceptibility was measured for $[\text{Fe}(\text{cis-}\mathbf{1})_3](\text{BF}_4)_2$ and $[\text{Fe}(\text{trans-}\mathbf{1})_3](\text{BF}_4)_2$ in the solid state (Figure S-5).

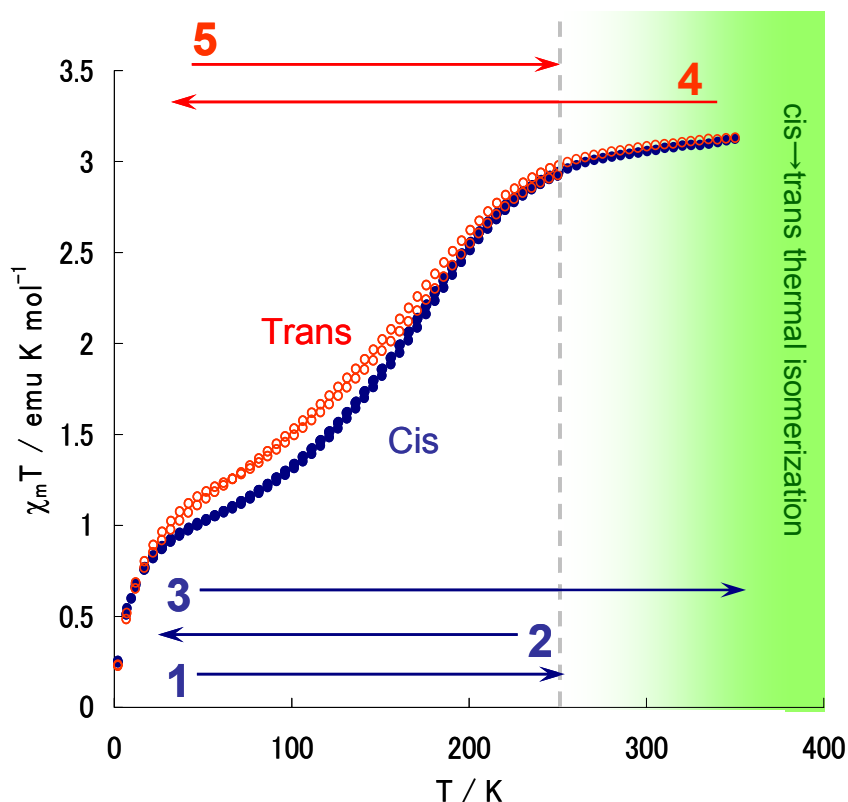


Figure S-5. Temperature dependence of $\chi_M T$ for $[\text{Fe}(\text{cis-}\mathbf{1})_3](\text{BF}_4)_2$ and $[\text{Fe}(\text{trans-}\mathbf{1})_3](\text{BF}_4)_2$, in both the heating and the warming modes.

Compared with previous reports,^[2] spin transitions for these complexes occur very sluggishly at lower temperatures. It seems that the presence of both bulky azobenzene chromophores and large counterions distorts FeN_6 cores and they may lengthen the average Fe-N bonds, leading to destabilization of the LS state.

At 52 K, $\chi_M T$ of $[\text{Fe}(\text{cis-}\mathbf{1})_3](\text{BF}_4)_2$ is equal to $1.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ (low-spin, LS) and it gradually increases to a value of $3.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 260 K (high-spin, HS). Cooling of the sample showed almost no thermal hysteresis and the transition temperature (the temperature at which 50% of LS and HS molecules are present) is 160 K. The fall in $\chi_M T$ below 40 K is due to the zero-field splitting of the HS Fe(II) ions, and the preferred Boltzmann population of the lowest levels with decreasing temperatures.

In the second heating cycle, $[\text{Fe}(\text{cis-1})_3](\text{BF}_4)_2$ sample was warmed to higher temperature of 350 K, to allow thermal cis-to-trans isomerization of azobenzene chromophores. Upon cooling, $[\text{Fe}(\text{trans-1})_3](\text{BF}_4)_2$ showed slightly larger $\chi_{\text{M}}T$ values which are identical in both of the cooling and heating scans. The spin transition temperature for $[\text{Fe}(\text{trans-1})_3](\text{BF}_4)_2$ is ca. 146 K, which is slightly decreased compared to that of the $[\text{Fe}(\text{cis-1})_3](\text{BF}_4)_2$ complex. It is likely that regular packing of trans-azobenzene groups gives larger distortion in the coordination structure. Upon photoisomerization the parallel chromophore packing is lost in the $[\text{Fe}(\text{cis-1})_3](\text{BF}_4)_2$ complex, in which steric restraints arising from H-aggregated azobenzene chromophores may be alleviated.