Self-assembly-directed Spin Conversion of Iron(II) 1,2,4-Triazole Complexes in Solution and Their Effect on Photorelaxation Processes of Fluorescent Counter Ions

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Lipophilic, linear iron(II) 1,2,4-triazole complexes with 9,10-dimethoxyanthracene-2-sulfonate and 1-pyrenesulfonate counter ions are newly developed. These complexes are dispersed in toluene as nanofibers and display dynamic spin conversion characteristics. Photorelaxation process of 1-pyrenesulfonate accumulated on the complex is regulated depending on the spin state of iron(II) triazole complexes.

The design of self-assemblies with functions regulated by electronic spin states is one of the forthcoming challenges in molecular systems chemistry. One of the possible approaches toward this goal involves coupling of spin-crossover (SC) transition-metal complexes and aromatic fluorophores. 1,2,4-Triazole complexes of Fe^{II} (d^6) are attracting much interest because of their SC characteristics between low-spin (LS, $S = 0$, purple) and high-spin (HS, $S = 2$, colorless) configurations.[1] The SC phenomena are induced by external perturbation such as temperature, and they are accompanied by changes in magnetism and colors. These features provide a basis for developing novel spin–photon communication systems.

As a part of our ongoing research on self-assembling one-dimensional (1D) metal complexes,[2–4] we have developed organogels of lipophilic Co^{II} and Fe^{II} 1,2,4-triazole complexes[3,4] where Fe^{II} centers adopt HS state in solution.[4] The lipophilic surface of 1D metal triazole complexes is capable of accommodating neutral guest molecules by changing molecular orientation of alkyl chains (adaptive molecular clefts).[4b,4d] Though recently SC behavior of Fe^{II} 1,2,4-triazole complexes in dodecane gels were reported,[5,6] regulation of photorelaxation processes based on 1D coordination systems has not been achieved.[7] To evaluate the effect of SC on fluorescence behavior of aromatic chromophores, it is desirable that the whole SC processes occur in dilute solution above room temperature, in order to avoid complexity and limited accuracy inherent to the fluorescence data of condensed gel or solid samples. We herein report self-assembly-directed spin conversion phenomena and their effect on fluorescence of aromatic chromophores which are accumulated on the surface of soluble, lipophilic Fe^{II} 1,2,4-triazole complexes in solution.

As organic chromophores, 9,10-dimethoxyanthracene-2-sulfonate (Anth-SO$_3^-$) and 1-pyrenesulfonate (Py-SO$_3^-$)[8] ions were introduced as counter ions of tris(4-(3-dodecyloxypropyl)-1,2,4-triazole)iron(II) complex (Chart 1). These aromatic counter ions are electrostatically accumulated in the vicinity of cationic Fe^{II} triazole coordination mainchains.

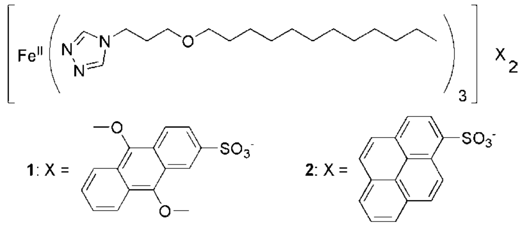

Chart 1.

Complexes **1** and **2** were obtained as pale yellow and purple powders, respectively. These solid samples showed moderate SC at 100–300 K.[10] They are dispersed in toluene by heating and showed purple colors after cooling to ambient temperature. Figure 1 shows temperature dependences of UV–vis spectra for **2**. A peak observed around at 540 nm in Figure 1b is ascribed to ${}^1A_1 \rightarrow {}^1T_1$ transition of the LS complex.[1,4] Upon heating, its intensity decreased and was replaced by a new peak around at 800 nm. The latter peak is assigned to the d–d transition of HS complex (${}^5T_2 \rightarrow {}^5E$), and these data indicate that the SC occurs in solution. An absorption band at 330–400 nm shown in Figure 1a is assigned to the π–π^* transition of pyrene chromophore. This absorbance showed decrease upon heating, which is due to the decrease in absorption intensity of MLCT band (LS complex, Figure S1 in Supporting Information).[10] That is, the absorption intensity of pyrene remained almost unchanged. The complex **1** also showed similar absorption spectral intensity changes in the ${}^1A_1 \rightarrow {}^1T_1$ transition band and at around 300 nm (Figure S2).[10]

Figures 2a and 2b display temperature dependence of fluorescence spectra obtained for **1** and **2**, respectively. Fluorescence intensities of these chromophores in toluene were smaller than those of pure chromophores in water, indicating static quenching by Fe^{II} complexes. Complex **1** gave an emission peak around 448 nm, whose intensity showed gradual decrease when heated beyond ca. 30 °C. Temperature profiles of fluorescence and absorption intensities are depicted in Figure 2c. It is noticeable that fluorescence intensity of Anth-SO$_3^-$ at 448 nm is almost

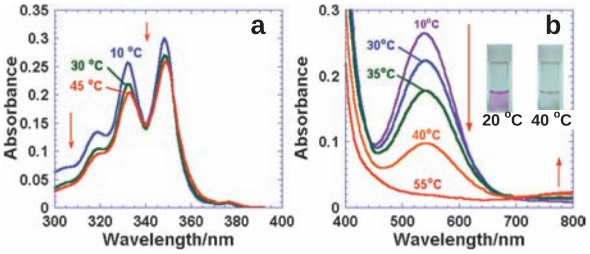

Figure 1. Temperature dependence of absorption spectra obtained for **2** in toluene (heating process). (a) at 0.05 unit mM. (b) at 5 unit mM. Pictures of 5 unit mM dispersions at 20 and 40 °C are shown.

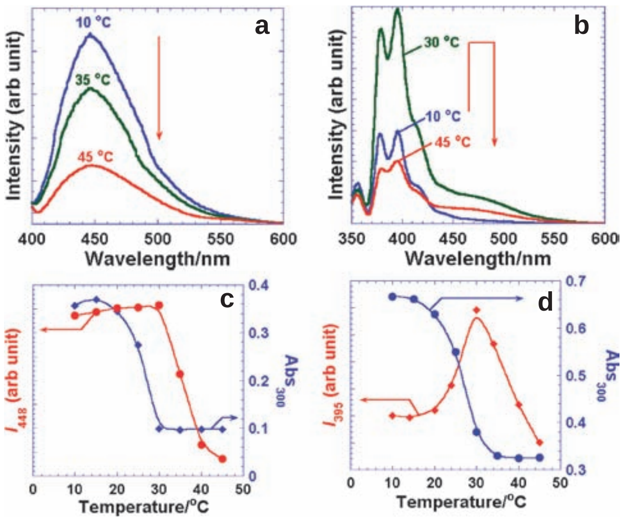

Figure 2. Temperature dependence of fluorescence spectra (a), (b) and fluorescence intensity (c), (d) in heating process. (a) **1**, λ_{ex} at 348 nm. (b) **2**, λ_{ex} at 380 nm. (c) **1**, (d) **2**. Temperature dependence of absorbance at 300 nm is also shown in (c), (d). [**1**] = [**2**] = 0.05 unit mM in toluene.

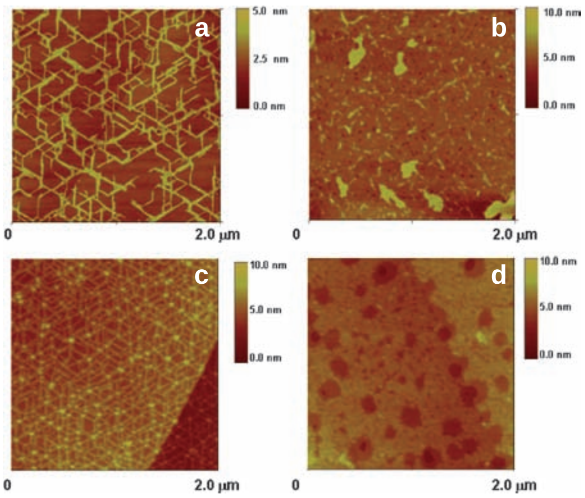

Figure 3. AFM images of **1** and **2** dropped from toluene dispersions ([**1**] = [**2**] = 0.05 unit mM) on freshly cleaved highly oriented pyrolytic graphite (HOPG). (a) **1** at 20 °C, (b) **1** at 40 °C, (c) **2** at 4 °C, (d) **2** at 45 °C.

unchanged below 30 °C, while it starts to decrease after the 300-nm absorption intensity has dropped. In the case of **2**, structured fluorescence is observed at 378 and 395 nm at 10 °C (Figure 2b). To our surprise, fluorescence intensity of Py-SO_3^- showed threefold increase upon heating and reached a maximum at ca. 30 °C. Subsequently, it was followed by a decrease beyond this temperature. A broad emission component around at 480 nm is noticeable above 30 °C (Figure 2b), which is ascribed to pyrene excimer emission.

The unique temperature dependence of fluorescence spectra observed for **2** is in contrast to that observed for **1**. It can be seen that the increase in Py-SO_3^- fluorescence below 30 °C is synchronized with the thermally induced SC, which is depicted by the decrease in absorption intensity at 300 nm (filled circles in blue, Figure 2d). These observations indicate that the excited singlet state of Py-SO_3^- is more effectively quenched by the LS complex, and the fluorescence intensity is recovered with the progress of thermal SC (LS → HS). The observed fluorescence intensity changes are reversible with respect to repeated cycles of heating and cooling (Figure S4).[10] The enhanced quenching of Py-SO_3^- fluorescence by the Fe^{II}_{LS} complex could be ascribed to energy transfer from Py-SO_3^- to the LS complex, since the donor fluorescence and $Fe^{II}(LS) \rightarrow \pi^*$ MLCT absorption show fair spectral overlap (Figure S1).[10] In contrast, spectral overlap between Anth-SO_3^- fluorescence and the MLCT band is poor, resulting in the unchanged fluorescence intensity below 30 °C.

The decrease in fluorescence intensities above 30 °C observed for both samples seems to be related to thermal disintegration of coordination main chains. Figure 3 shows AFM images of **1** and **2** spread from dilute toluene dispersions. Fibrous nanostructures (minimum widths, 20–30 nm, heights, ca. 1.5 nm) are abundantly observed for **1** and **2** in the LS states (Figures 3a and 3c). These nanofibers would consist of bundled supramolecular complexes, as molecular length of the ligand is ca. 2.2 nm (CPK models).[3] In contrast, fragmented irregular structures or dot-like aggregates in porous films are observed for HS complexes (Figures 3b and 3d). These observations indicate that fibrous nanostructures of LS complexes undergo thermal SC and succeeding fragmentation of labile HS complexes. The promoted deactivation of excited chromophores above 30 °C could be ascribed to their enhanced collision with Fe^{II}_{HS} ions in the disintegrated structures. The abrupt changes in the spin states observed in Figures 2c and 2d are distinct from those expected from spin equilibrium which generally occurs in solution more gradually.[9] In the present systems, LS complexes are stabilized in solution, and thermal SC occurs synergistically with the dynamic disintegration process. This unique SC in solution is better described as self-assembly-directed spin conversion.

In conclusion, fluorescence characteristics of fluorophores accumulated on linear Fe^{II} complexes are regulated by self-assembly and dynamic spin conversion in solution. It provides a new perspective in the design of spin–photon communication systems.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.