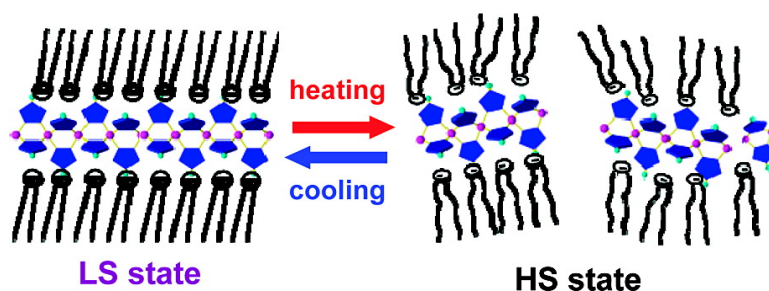


Lipid-Packaged Linear Iron(II) Triazole Complexes in Solution: Controlled Spin Conversion via Solvophobic Self-Assembly

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Lipid-Packaged Linear Iron(II) Triazole Complexes in Solution: Controlled Spin Conversion via Solvophobic Self-Assembly

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Pseudo one-dimensional (1D) metal complexes have been attracting considerable interests due to their unique electronic¹ and magnetic² properties. They exist as basic structural motifs of crystalline solids, and their structural integrity is usually lost when dispersed in solution. The ability to maintain these 1D structures in solution provides a basis to develop functional nanowires, whose properties are not available in the crystalline state. We have developed molecular designs for lipophilic 1D metal complexes which are dispersible in organic media.^{3–5} For example, 1D halogen-bridged, mixed valence platinum complexes are dispersed as nanowires in organic media, by introducing lipid counterions.³ An alternative approach is to employ lipophilic bridging ligands. Co^{II} complexes with 4-dodecyloxypropyl-1,2,4-triazole ligands revealed unique characteristics of forming heat-set physical gels in organic solvents.⁴

In this study, we applied the lipid packaging technique to 1D Fe^{II} 1,2,4-triazole complexes. They are attracting much interest because of the spin crossover (SC) characteristics between low spin (LS, purple, $S = 0$) and high spin (HS, colorless, $S = 2$) configurations.⁶ The changes in magnetism and colors are induced by external perturbation, rendering these complexes powerful candidates for information storage materials. Clérac and co-workers reported that dodecane gels of Fe^{II} 4-octadecyl-1,2,4-triazole complex show thermal spin crossover.⁷ Aida et al. showed that the Fe^{II} complex of double-chained 1,2,4-triazole ligands displays spin crossover which was accompanied by dissolution of the dodecane gel.^{8a} In these systems, however, LS complexes are maintained only in the solid state or in organogels composed of crystalline aggregates. Here we report that application of the lipid packaging technique leads to surprising stabilization of LS complexes in solution and consequent control of spin conversion via dynamic self-assembly of linear coordination chains.

The lipid–Fe^{II} triazole complexes developed in this study are shown in Chart 1. In contrast to the conventional design of 4-alkylated 1,2,4-triazoles, an L-glutamate-derived lipid was introduced as a lipophilic counteranion. 4-Amino-1,2,4-triazole (NH₂trz)^{9,10} and 4-(2-hydroxyethyl)-1,2,4-triazole (HOC₂trz)¹¹ were employed as triazole ligands. The noncovalent introduction of a lipophilic moiety is suitable for 1,2,4-triazole-based spin crossover complexes since covalent modification of triazole ligands with bulky substituents generally causes lengthening of Fe–ligand bonds, resulting in the destabilization of LS states.^{8b}

Triazole complexes with lipid anions (**1**, **2**) were obtained as dihydrate, with faint purple color and no color, respectively (Figure S2). These colors indicate that the solid samples are in the HS configuration at room temperature. The complexes **1** and **2** were then dispersed in toluene by heating (concentrations of 5 or 20 mM). To our surprise, toluene dispersion of **1** showed purple color at room temperature, indicating maintenance of LS complexes in solution. Figure 1a shows temperature dependence of absorption

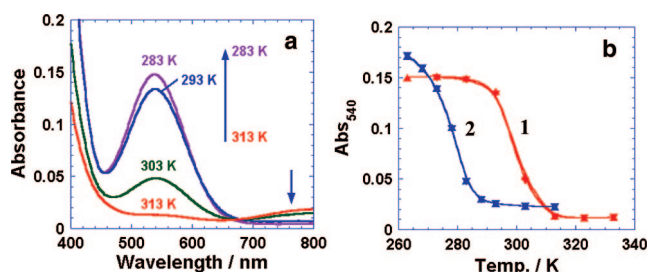
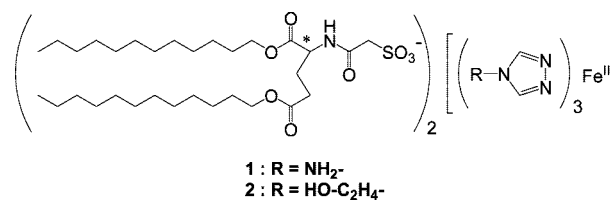


Figure 1. (a) Temperature dependence of UV/vis absorption spectra for complex **1** (5 unit mM in toluene, cooling process). (b) Temperature dependences of peak absorption intensities at 540 nm (LS complex) for **1** and **2**. Absorbance changes in heating and cooling cycles traced the same curves.

Chart 1



spectra obtained for complex **1** (5 unit mM in toluene). Absorption bands around 40 and 800 nm are assigned to d–d transitions of the LS complex ($^1A_1 \rightarrow ^1T_1$) and the HS complex ($^5T_2 \rightarrow ^5E$), respectively.¹² The absorbance at 540 nm (LS state) is decreased upon heating and is accompanied by increase in absorption intensity at 800 nm (HS state). The observed spectral changes are totally reversible with respect to temperature changes (Figure 1b). Lipid complex **2** also showed reversible thermal spectral changes at lower temperature range (Figure S3). T_{sc} , the temperature at which half of the transiting Fe^{II} changed spin, is ca. 300 K for **1** and 278 K for **2**. ΔT_{80} , the smallest temperature range that covers 80% of the spin state changes (which reflects the steepness of the transition),¹² is ca. 17 K for **1** and ca. 18 K for **2** in toluene.

The thermally induced changes in spin state observed for toluene dispersions were compared with those in the solid state. The powdery lipid complexes give T_{sc} values of 280 K for **1** and 170 K for **2** (Figure S5, SQUID data). **1** and **2** in solid samples showed larger ΔT_{80} values of 72 and 164 K. In the case of **1**, T_{sc} in toluene is increased by ca. 20 K compared to that of the solid state, indicating stabilization of the LS state in solution. On the other hand, **2** in toluene showed considerably higher T_{sc} (170 K/solid \rightarrow 278 K/solution) and smaller ΔT_{80} values (164 K/solid \rightarrow 18 K/solution) compared to those of the solid sample (Figure S6). These observations are directly opposite to the general tendency that the LS configuration is destabilized in solution.⁵ In addition, occurrence of more sharp spin state changes in solution is again

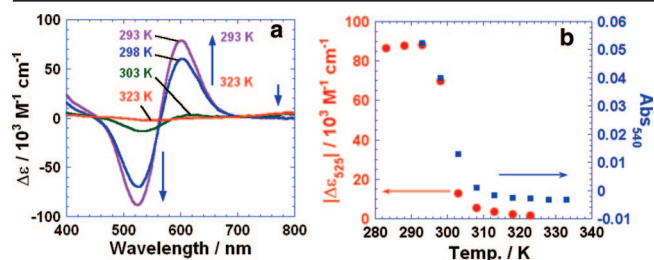


Figure 2. (a) CD spectra of **1** in toluene. (b) Temperature dependence of ICD peak intensity at 525 nm and absorption intensity at 540 nm. [**1**] = 20 unit mM, in cooling process.

extraordinary since, in solutions, changes in spin states are governed by spin equilibrium, and consequently, transitions always occur gradually.¹³

The remarkable stabilization of LS states in solution indicates an increase in the ligand-field splitting energies compared to those in the crystalline states. In toluene, ionic Fe^{II} triazole complexes are dispersed with the help of solvophilic lipid alkyl chains. The solvophobic Fe^{II} triazole complexes would tend to minimize the contact with nonpolar solvent molecules, by contracting Fe–N and/or the nearest neighbor Fe···Fe distances (solvophobic compaction). This is supported by the dependence of SC temperatures on solvent polarity (Figures S10 and S12). On the other hand, such solvophobic interactions do not operate in the solid state. Packing of lipid sulfonate groups in crystalline structures may not be dense enough to stabilize the LS complexes.

Interactions between lipids and Fe^{II} triazole complexes were investigated by circular dichroism (CD) spectra. Temperature dependence of the CD spectrum for **1** is shown in Figure 2. At ambient temperature, negative and positive Cotton effects are observed at 525 and 600 nm in the d–d transition band of the LS complex. As the Fe^{II}(NH₂trz)₃ complex is achiral, observed CD is apparently induced by chiral lipid molecules. It indicates the presence of ordered supramolecular structures in solution. The observed Cotton effects will originate from the splitting of ¹T₁ energy state to ¹E and ¹A₂ states,¹⁴ which allows two d–d transitions (¹A₁→¹E and ¹A₁→¹A₂). It occurs when the O_h symmetry of the Fe^{II}(NH₂trz)₃ complex is changed to D₃ symmetry, which reflects the interaction between Fe^{II}(NH₂trz)₃ and chiral lipid counterions. The intensity of ICD peaks showed abrupt changes at 300 K, which is well correlated with the absorption intensity changes at 540 nm (Figure 2b) and ¹H NMR (Figure S4).

AFM images of complex **1** and **2** spread from dilute toluene dispersions at varied temperatures are shown in Figure 3. Fibrous nanostructures (widths = 20–30 nm, heights = ca. 7 nm) are abundantly observed for **1** and **2** in the LS states (Figure 3a,c). As the bimolecular length of lipid is ca. 4.4 nm (CPK models), the observed nanofibers would consist of bundled supramolecular complexes. In contrast, aggregates of fragmented structures (b) or dots (d) are observed for HS complexes. As specimens (a) and (d) are both prepared at room temperature, these AFM images would reflect the difference in morphology in toluene dispersions. The presence of nanostructures in toluene was also supported by dynamic light scattering (Figure S7). These observations indicate that fibrous nanostructures of LS complexes undergo thermal SC to labile HS complexes and dissociation into fragments. Lipids with enhanced thermal mobility would render the fragments to adopt HS state, as indicated by the abrupt spin state changes. The observations of developed nanofibers after cooling the heat-dispersed samples (Figure 3a,c) and the recovery of LS complexes (Figures 1 and 2) clearly indicate reversible self-assembly of HS fragments into the original, LS nanofibers. This is further supported

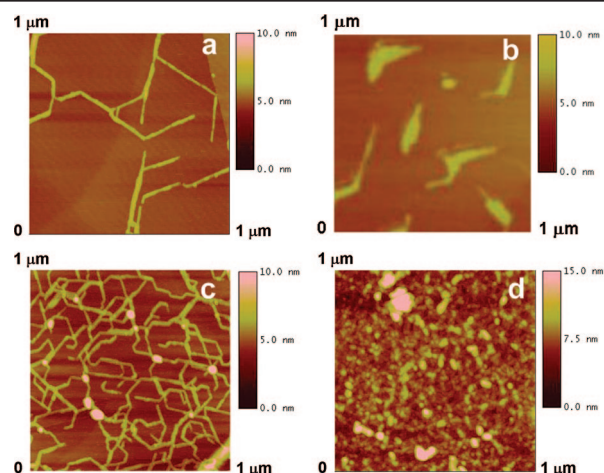


Figure 3. AFM images of complexes **1** (a,b) and **2** (c,d). Samples are cast from toluene dispersions (50 unit μM) on highly oriented pyrolytic graphite (HOPG). (a) **1** cast at ambient temperature (LS state), (b) **1** cast from 313 K solution (HS state), (c) **2** cast at 273 K (LS state), (d) **2** cast at ambient temperature (HS state). Casting and evaporation of toluene were performed at the solution temperature.

by copolymerization of **1** and **2** which occurred after cooling the heat-dissociated mixtures (Figure S13). As spin crossover premises unchanged coordination number at central atoms, the changes in spin state involving disintegration of coordination bonds would be better described as spin conversion directed by self-assembly.

In conclusion, lipid-packaged nanowires of Fe^{II} triazole complexes display spin conversion characteristics in organic media. Abrupt spin conversion is observed due to lipid-assisted solvophobic stabilization of LS complexes, spin crossover, and reversible dissociation of coordination main chains. The solvophobic enhancement of ligand–metal interactions and their synergistic control based on self-assembly push back the boundaries of existing coordination polymer chemistry.

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Supporting Information Available: Synthetic procedures, UV–vis absorption, SQUID, DLS and copolymerization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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