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Electrochemically Controlled Self-assembly of Lipophilic Fe^{II} 1,2,4-Triazole Complexes in Chloroform

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Self-assembly of lipophilic, linear Fe^{II} 1,2,4-triazole complexes is electrochemically controllable in organic media. The Fe^{II} complex with chloride counter ion forms gel-like networks in chloroform, which undergoes reversible disassembly upon oxidation of Fe^{II} centers to Fe^{III} species. Counter ions play crucial roles in the electrochemical response of coordination nanowires.

Pseudo one-dimensional (1D) transition-metal complexes have been an important area of research because of their unique electronic,[1] magnetic,[2] and optical[3] properties. Notably, Fe^{II} compounds with 4-alkylated-1,2,4-triazoles have been attracting much interest since their linear coordination structures display spin-crossover (SC) between low-spin (LS, $^1A_{1g}$, $S = 0$, purple) and high-spin (HS, $^5T_{2g}$, $S = 2$, colorless) configurations.[4–6] These 1D structures, however, are inevitably a part of bulk crystals and consequently they have not been considered as building blocks for soluble nanowires. The maintenance of these coordination chains in solution provides a new family of molecular wires, which show unique properties not accessible from solid-state coordination chemistry.[7] We previously reported that modification of 1,2,4-triazole ligand with lipophilic dodecyloxypropyl chains gave unusual heat-set organogels from corresponding Co^{II} and Fe^{II} complexes.[8–11] Remarkable stabilization of LS complexes were observed for lipophilic supramolecular Fe^{II} triazole complexes dispersed in nonpolar solvents[12] and in liquid crystals.[13] Although thermally induced spin-crossover characteristics of alkylchain-derivatized Fe^{II} triazole complexes in solid or in organogels have been also reported by the other researchers,[4–6] isothermal control of the chain morphology and solution properties have been largely unexplored, except for the photoregulation of azobenzene-derived Fe^{II} triazole complexes.[14] We describe herein isothermal, electrochemical control of the coordination structure of Fe^{II} triazole complexes and their influence on self-assembly in organic media.

4-Alkylether derivatized triazole complexes of $[Fe^{II}(\mathbf{1})_3]X_2$ (Chart 1, X = Cl and ClO_4) were employed in this study. We have reported that $[Fe^{II}(\mathbf{1})_3]Cl_2$ formed pale-yellow gel-like networks in chloroform, the color of which is characteristic of high spin (HS) state.[4,10,11]

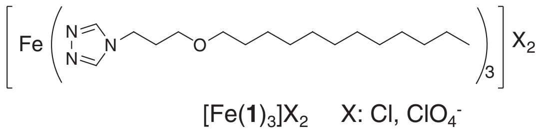

Chart 1. Chemical structure of $[Fe(\mathbf{1})_3]X_2$.

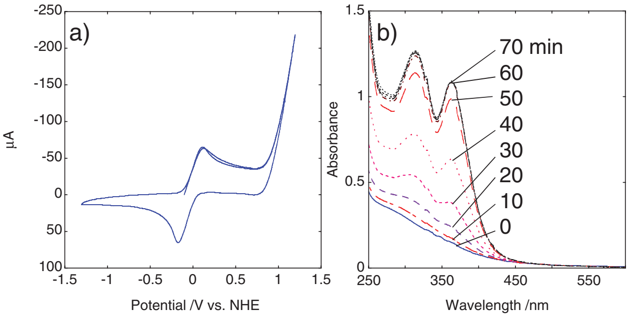

Figure 1. (a) Cyclic voltammogram and (b) time-dependence of UV–vis spectra observed for $[Fe^{II}(\mathbf{1})_3]Cl_2$ dispersed in chloroform. $[[Fe^{II}(\mathbf{1})_3]Cl_2] = 10\,mM$, [tetrabutylammonium chloride] = 0.1 M, 25 °C. UV–vis spectra were obtained at a fixed electropotential of +0.70 V vs. NHE.

Figure 1a shows cyclic voltammometry of $[Fe^{II}(\mathbf{1})_3]Cl_2$ dispersed in chloroform/0.1 M Bu_4NCl. Reduction and oxidation current peaks were reversibly observed at +0.11 and −0.18 V (vs. NHE) respectively, which are ascribed to the couple of Fe^{II}/Fe^{III}. The redox potential was determined to be −0.04 V. On the other hand, $[Fe(\mathbf{1})_3](ClO_4)_2$ showed considerably weaker and positively shifted redox waves at $E = +0.80\,V$ in chloroform/0.1 M Bu_4NClO_4 (Supporting Information, Figure S1).[19] Thus, counter ions exert decisive effect on the electrochemical properties of Fe^{II} triazole complexes. In general, oxidation potentials of six N-coordinated Fe^{II} complexes are observed above +1.0 V vs. NHE. For example, $[Fe(tpy)_2]^{2+}$ (tpy, terpyridine) displays an oxidation potential at +1.1 V vs. NHE.[15,16] The extraordinary lower redox potential of −0.04 V observed for $[Fe(\mathbf{1})_3]Cl_2$, is ascribed to coordination of Cl^- ions to Fe^{III} species produced by the electrochemical oxidation, as supported by the following observations.

UV–vis spectra of $[Fe(\mathbf{1})_3]Cl_2$ in chloroform was obtained by modifying electrochemical method described in the literature.[17] When the chloroform gel of $[Fe^{II}(\mathbf{1})_3]Cl_2$ was subjected to an applied electric potential of +0.70 V vs. NHE, absorption intensities at 330 and 350 nm increased with time (Figure 1b). The observed spectral change was electrochemically reversible, which showed dissolution of the pale yellow gel $[Fe^{II}(\mathbf{1})_3]Cl_2$ to a light brown dispersion containing Fe^{III} species (Figure S2). In contrast, chloroform solution of $[Fe^{II}(\mathbf{1})_3](ClO_4)_2$ showed no color changes under the applied potential of +0.70 V. Instead, the perchlorate complex displayed an electrochemical oxidation wave at higher potential of ca. +0.80 V vs. NHE. Apparently, the presence of chloride anions facilitates oxidation of $Fe^{II}(\mathbf{1})_3$

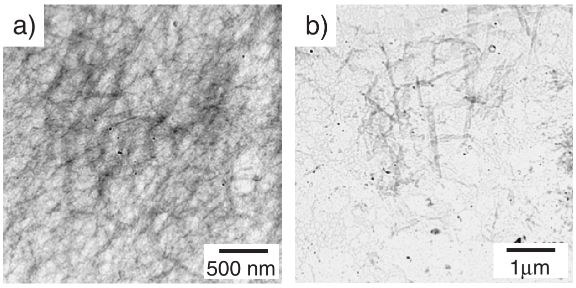

Figure 2. Transmission electron micrographs of [Fe^{II}(**1**)$_3$]Cl$_2$. These samples have been kept in chloroform under the applied potential of (a) −0.3 or (b) +0.7 V vs. NHE for 1–2 h, and were observed without negative staining. [[Fe^{II}(**1**)$_3$]Cl$_2$] = 10 mM in chloroform, 0.1 M tetrabutylammonium chloride. Tempearutre, 25 °C.

complex. As the absorption peaks observed for Fe^{III} species at 330 and 350 nm are not observed for [Fe^{II}(**1**)$_3$]Cl$_2$ or [Fe^{II}(**1**)$_3$](ClO$_4$)$_2$ complexes (Figure S3a),[19] they are reasonably assigned to the ligand to metal charge-transfer (LMCT) absorption band which indicate coordination of Cl$^-$ ions to the Fe^{III} center. It is to note that the intensity of LMCT absorption bands increased sigmoidally with respect to the reaction time (Figure S3b).[19] The coordination of Cl$^-$ ions to Fe^{III} ions requires replacement of the coordinating triazole ligand, which resulted in fragmentation of the polymeric coordination structure. This is consistent with the observed dissolution of chloroform gel. The dissociation of main chains would impair the solvophobic screening by alkylchain layers, which promotes the oxidation and is conducible to the observed sigmoidal response.

Figure 2 shows TEM images of [Fe^{II}(**1**)$_3$]Cl$_2$ specimens transferred on carbon coated copper grids. Below the electrical potential of −0.30 V, networks of fibrous nanoassemblies (widths, 3–5 nm) are abundantly observed in chloroform (Figure 2a). This morphology is similar to that observed for [Fe^{II}(**1**)$_3$]Cl$_2$ before applying electric potential. The observed widths of 3–5 nm correspond to the bimolecular length of **1** (ca. 22 Å estimated by CPK model), indicating that [Fe^{II}(**1**)$_3$]Cl$_2$ is dispersed as molecular wires.

On the other hand, when electric potential of +0.7 V was applied for 2 h, the number of fibrous nanoassemblies decreased. Instead, nanocrystals with lengths of ca. 500–1500 nm and widths of 30–50 nm were abundantly seen (Figure 2b). The observed morphological change is consistent with the dissolution of gel-like phase upon oxidation of [Fe^{II}(**1**)$_3$]Cl$_2$ to the Fe^{III} complexes. It may be that chloride-coordinated Fe^{III} complexes show higher tendency to form nanocrystalline aggregates. A schematic illustration of the electrochemically controlled self-assembly is depicted in Figure 3.

In conclusion, lipophilic Fe^{II} triazole complexes give nanowires in chloroform, which show reversible and electrochemically controlled self-assembly. The oxidation of polymeric Fe^{II} triazole complexes was accompanied by coordination of chloride ions to the Fe^{III} center, which entails dissociation of linear coordination structures and succeeding formation of nanocrystals. The use of coordinating counter ions holds an essential role in the electrochemical transformation, since non-coordinating perchlorate anion did not promote oxidation of [Fe^{II}(**1**)$_3$] complexes. Although redox-active organogels have been formed from low-molecular-weight metal complexes, oxidizing or reducing reagents must be added each time to repeat the cycle.[18] The present coordination of halogen counter anions to higher valence Fe^{III} ions facilitates the electrochemical oxidation both thermodynamically and kinetically, which exempt us from using such additives. It provides a useful strategy in designing electrochemically responsive coordination soft-nanomaterials.

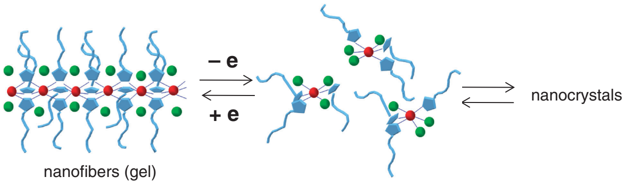

Figure 3. Schematic illustration of electrochemically controlled self-assembly of [Fe(**1**)$_3$]Cl$_2$ in chloroform. Red and green circles represent iron and chloride ions, respectively.

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References and Notes

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