

FOCUS REVIEW

Self-assembly and functionalization of lipophilic metal-triazole complexes in various media

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An aspect of nanochemistry, which has attracted significant attention, is the formation of one-dimensional (1D) nanofibers from the self-assembly of metal complexes. The fabrication of nanoarchitectures from such complexes, based on the design of compounds, which show cooperative functionalities, is currently seen as one of the important goals within the field of nanomaterials. In this review, we describe methods that allow the tuning of the intermolecular interactions between metal-triazole complexes, whether in solution, thin films or liquid crystals. The lipophilic triazole ligand **1** (C₁₂OC₃Trz) has been designed such that an ether linkage exists in the alkyl chain moiety. This flexible ether linkage enhances the solubility of various complexes of this ligand (including [Co^{II}(1)₃]Cl₂ and [Fe^{II}(1)₃]Cl₂) in organic media and also improves the packing efficiency of the alkyl chains. Such lipophilic modifications of 1D coordination systems can result in dynamic structural transformations leading to unique solution properties, including heat-set gel-like networks, guest-induced structural changes, electrochemical transformations and spin crossover state switching. The supramolecular chemistry of 1D metal complexes is unprecedented in its scope and potential applications, and it is hoped that the studies presented herein will provide new information to promote further investigation of dynamic supramolecular devices.

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INTRODUCTION

One-dimensional (1D) metal complexes have attracted significant interest as scaffold structures in the design of materials with unique nanoarchitectures and properties.^{1–8} These low-dimensional structures typically occur as structural motifs within bulk crystalline materials, and accordingly they have traditionally been studied within the fields of both solid-state inorganic chemistry and physics. The ability to isolate and assemble such linear complexes in solution could potentially lead to a new family of functional molecular wires. We have developed a creative approach to disperse halogen-bridged, mixed-valence platinum complexes in organic media as lipid-packaged nanowires.^{9–19} These nanowires exhibit supramolecular thermochromism,^{12–14} solvatochromism^{16,17,19} and nano assembly into pillared honeycomb stereo architectures.¹⁸

On the other hand, 1,2,4-triazoles are known to act as bridging ligands and their linear metal complexes have been actively investigated because of their polymeric structures and magnetic interactions between linearly aligned metal ions.^{1,2,6,7,20,21} For example, a series of oligonuclear compounds based on Mn, Fe, Co, Ni and Zn has been prepared, all of which have been found to undergo antiferromagnetic interactions.^{22–24} The most interesting feature of these compounds is their characteristic spin crossover switching between low spin (LS, purple, $S=0$) and high spin (HS, colorless, $S=2$).^{1,2,6,7,20–22}

In addition, their magnetic properties have rendered these complexes to be obvious candidates for use as information-storage materials. In particular, Fe^{II}-1,2,4-triazole complexes have the advantages of ease of synthesis and the ready formation of bridged structures, although they are generally only obtained as powders; thus, the challenge remains to process them into ultrathin films and other delicate structures in preparation for device applications. To date, preliminary studies of the triazole complexes have been limited to the study of bulk powdery samples, and there has been no general methodology developed for the conversion of these materials into nanostructures. One aspect of the development of such complexes, which should ideally be possible, is the tuning of their magnetic properties, based on supramolecular control of the spatial arrangement of the metal ion and triazole ligand, resulting in magnetic cooperation between metal complexes.

Working towards the development of supramolecular triazole complexes, we initially introduced a solvophilic dodecyloxypropyl chain within the ligand (Scheme 1).^{25,26} These dodecyloxypropyl chains make it possible to dissolve the metal complex of the lipophilic triazole ligand **1** in organic media. To date, several lipophilic triazole complexes have been reported by supramolecular and coordination chemists.^{27–33} However, it is noteworthy that LS complexes of these compounds are destabilized in the solid state or organogels, because

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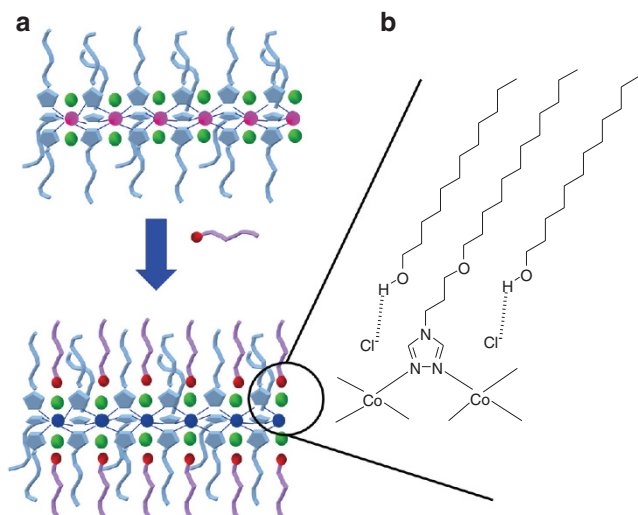


Figure 2 Schematic illustration of coordination structural changes induced by guest molecules (long-chain alcohols) binding on the surface of $[\text{Co}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ (a). It occurred as a consequence of ionic hydrogen-bond formation between long-chain alcohols and chloride ions (b).

increase in lamellar long spacing from 35.6 to 44.3 Å, indicating that the alkyl chains adopt a more perpendicular orientation with respect to the coordination structure of main chains. Thus, the binding of alcohol molecules to the surface of $[\text{Co}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ induces the formation of T_d coordination structures, in which ligand alkyl chains and alcohols are aligned in an ordered fashion. The lipophilic $[\text{Co}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ complex can therefore accommodate guest-alcohol molecules by changing both its coordination structure and the orientation of its alkyl chains. The binding space thus created on the surface of such 1D complexes is referred to as an adaptable molecular cleft.³⁵

Supramolecular control of spin crossover phenomena associated with Fe-triazole complexes in various media

The interactions between alcohols and the surfaces of linear triazole complexes have been applied as a means of controlling the spin crossover phenomenon of the $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ complex.³⁷ The Fe^{II} complex is a purple powder when in its solid ambient temperature form, which is a characteristic of complexes in their LS state. However, it is transformed into a pale-yellow organogel (its HS state) when dissolved in chloroform.³⁷ Such gels are the result of the formation of nanofiber aggregates, as confirmed by transmission electron microscopy. The casting of such chloroform solutions onto solid substrates produces transparent purple films, where the complex is once again in the LS state. These cast films exhibit sluggish spin crossover ($\text{LS} \rightleftharpoons \text{HS}$) phenomena in response to temperature changes, without thermal hysteresis (Figure 3a). In contrast, the co-casting of equimolar quantities of dodecanol or tetradecanol with $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ forms composite films, in which alcohol molecules are bound to the complex by ionic hydrogen bonding between the hydroxyl group of the alcohol and the chloride ion, as well as by van der Waals interactions. At room temperature, the cast films consist of regular lamellar structures both before and after doping with alcohol, as determined by estimations from wide-angle X-ray diffraction measurements. Interestingly, binary films made from $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ and long-chain alcohols (containing 12 or 14 carbons) exhibit reversible abrupt spin crossover with thermal hysteresis (Figure 3a). The

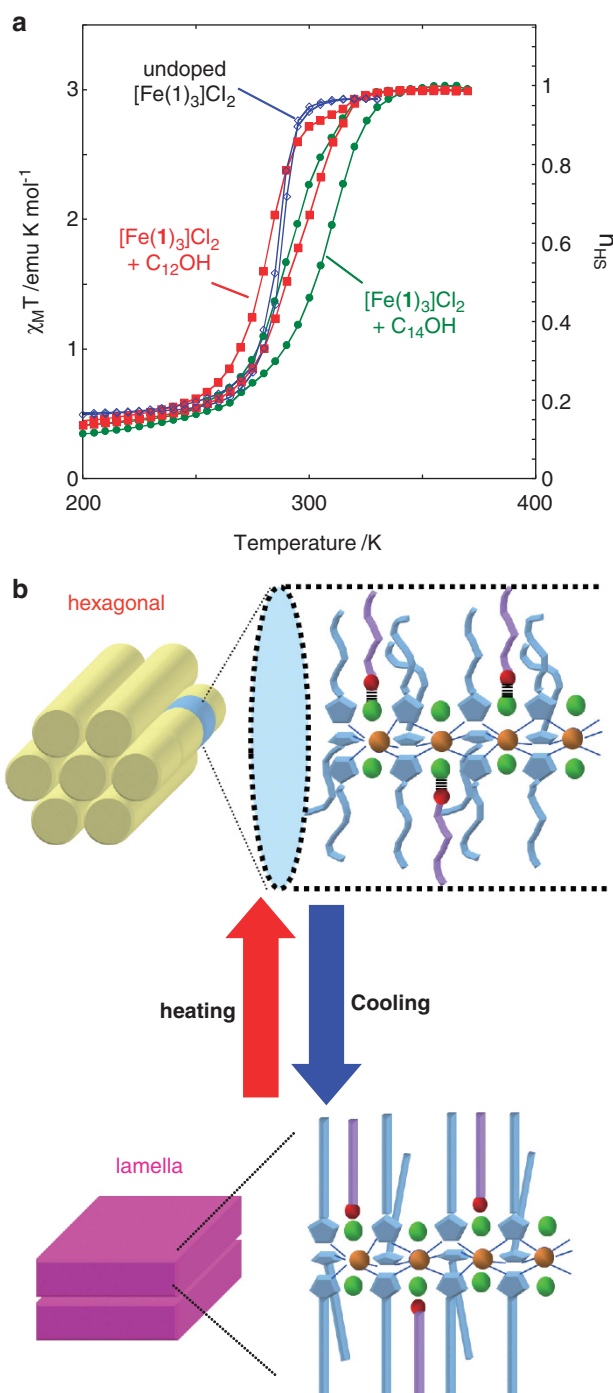
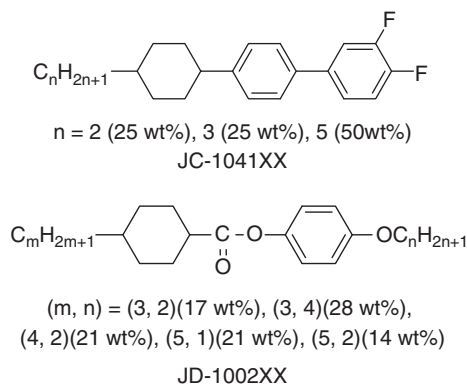


Figure 3 (a) Temperature dependence of the magnetic susceptibility of $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2/\text{C}_n\text{OH}$ samples ($n = 12$ and 14). (b) Schematic illustration of the supramolecular unit structures in the cast films. $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2/\text{C}_{14}\text{OH}$ display the dynamic structural transformation between lamellar (at 298 K) and hexagonal structures (at 373 K).

observed bistability of these films is closely related to dynamic structural transformations between lamellar and hexagonal structures, leading to a novel supramolecular strategy for controlling the bistability of spin crossover phenomena (Figure 3b).³⁷

In order to derive functional systems through imparting spin-based functionality to guest molecules, we have demonstrated the formation



Scheme 2 Chemical structure of liquid crystals, **JC-1041XX** and **JD-1002XX**.

of liquid-crystal gels from linear Fe^{II} -1,2,4-triazole complexes and nematic liquid crystals.³⁸ Both **JC-1041XX** and **JD-1002XX** are employed as the liquid crystals, because they display nematic liquid-crystal phases over a wide temperature range (T/K of phase transitions: K 291.1 N 365.2 I (**JC-1041XX**) and K 276.8 N 347.9 I (**JD-1002XX**), Scheme 2). The purple color of the resulting gels indicates that the $[Fe^{II}(1)]_3Cl_2$ complex adopts the LS configuration in either **JC-1041XX** or **JD-1002XX**, in contrast to the HS gels formed in chloroform.³⁸ At elevated temperatures, the macroscopically homogeneous gel structure is preserved, although the color changes from purple to pale yellow. The observed color changes are thermally reversible, as shown by the temperature dependence of reflectance spectra. In addition, the temperature dependence of the magnetic susceptibility demonstrates that the liquid-crystal gel composed of $[Fe^{II}(1)]_3Cl_2$ and **JC-1041XX** exhibits spin crossover at elevated temperatures with the appearance of thermal hysteresis. The spin crossover temperature in the heating cycle (for LS \rightarrow HS, $T_{sc}\uparrow$) is approximately 334 K, which is higher than that observed in the cooling cycle (for HS \rightarrow LS, $T_{sc}\downarrow$, 324 K, Figure 4a). Similarly, a combination of $[Fe^{II}(1)]_3Cl_2$ and **JD-1002XX** exhibits higher spin crossover temperatures during heating as opposed to cooling ($T_{sc}\uparrow$ at 324 K and $T_{sc}\downarrow$ at 319 K). The binary $[Fe^{II}(1)]_3Cl_2$ /liquid-crystal composites therefore exhibit sluggish spin crossover transitions with thermal hysteresis within a higher range of temperatures as compared with pure $[Fe^{II}(1)]_3Cl_2$, for which both $T_{sc}\uparrow$ and $T_{sc}\downarrow$ are at 300 K.³⁷ To date, the behavior of 1D $Fe(II)$ complexes of 4-substituted 1,2,4-triazoles and their spin crossover characteristics have been studied solely for the solid state or as organogels.^{27–33} In these forms, however, LS complexes are destabilized, because van der Waals interactions between the rigid alkyl chains lead to increased Fe-to-Fe distances and hence promoted conversion to the HS state. In contrast, the system formed from the combination of lipophilic Fe^{II} complexes and hydrophobic liquid crystals has several advantages because of the considerable effects of the liquid-crystal environment on either solvophobic compaction of the N–Fe coordination bonds or destabilization of the HS complex (Figure 4b).³⁸ Advantages of composites between liquid crystal and organic (and/or polymeric) molecules have been reported because of their unique interaction, which arise from their bicontinuous phase-separation structures.^{44,45} These bicontinuous structures are formed when organic components exhibit substantial miscibility with liquid crystals. Molecular assemblies of functional low-molecular-weight gelators have been also shown to give liquid-crystal gels.^{46,47}

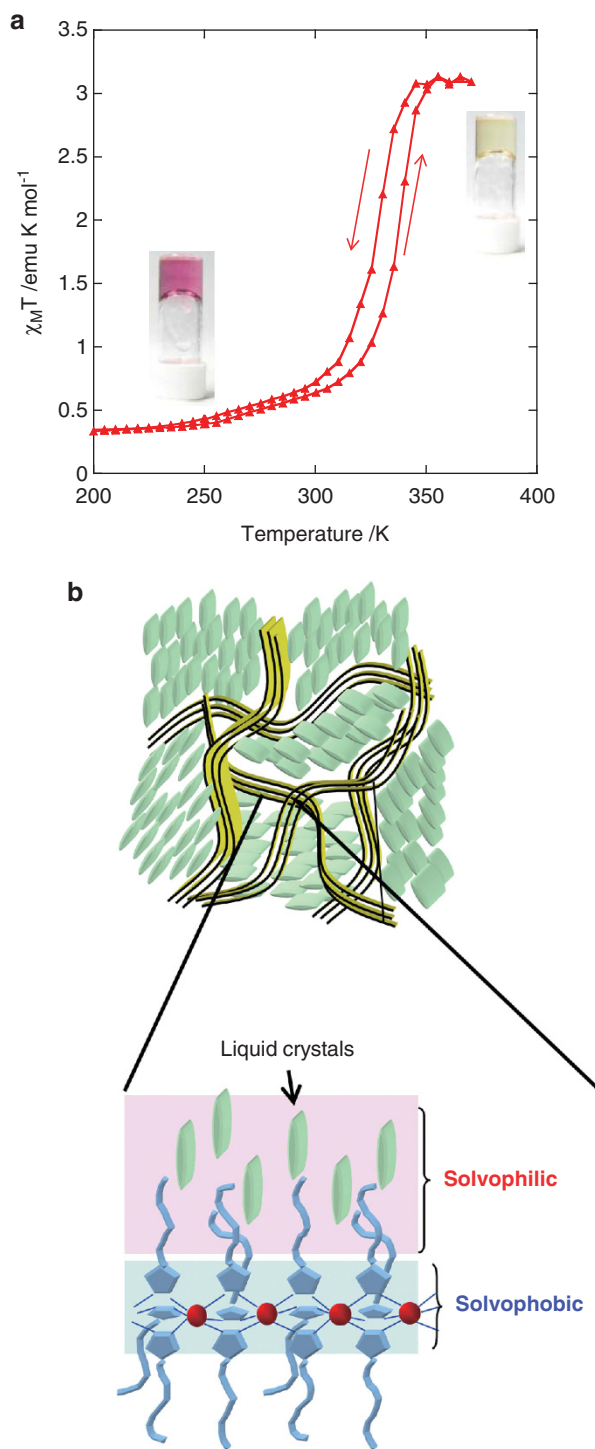


Figure 4 (a) Temperature dependence of the magnetic susceptibility of $[Fe^{II}(1)_3]Cl_2$ /**JC-1041XX** liquid-crystal gels. Inner photographs are of $[Fe^{II}(1)_3]Cl_2$ /**JC-1041XX** liquid-crystal gels at 293 K (left) and 363 K (right). (b) Schematic illustration of $[Fe^{II}(1)_3]Cl_2$ /liquid crystals.

Therefore, in liquid-crystal hybrids, the functional components, such as lipophilic triazole complexes, will take on a specific role in the design and development of intelligent soft materials by imparting spin-based functionalities and solvophobic interaction.

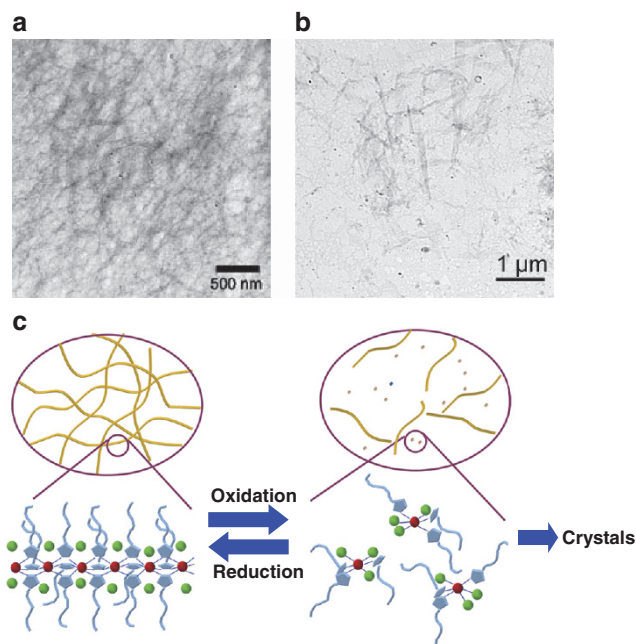


Figure 5 (a, b) Transmission electron micrographs of $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$. These samples have been kept in chloroform under the applied potential of (a) -0.3 or (b) $+0.7$ V vs NHE for 12 h. (c) Schematic illustration of electrochemically controlled self-assembly of $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ in chloroform (left, reduction and right, oxidation).

Supramolecular control of the nanofiber morphology of Fe-triazole complexes via external stimuli

The structural dynamism of Fe^{II} -triazole complex nanofibers in response to temperature and guest-molecule interactions has inspired us to develop a technique to allow electrochemical regulation of their nanostructures. As described above, $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ forms pale-yellow gel-like networks in chloroform, the color of which is a characteristic of the HS state.³⁷ Interestingly, $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ is found to be electrochemically active, and reversible reduction and oxidation current peaks are observed at $+0.11$ and 0.18 V (vs normal hydrogen electrode (NHE)), respectively, attributed to the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ transition (redox potential: 0.04 V).³⁶ In addition, when the chloroform gel of $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ is subjected to an applied electric potential of $+0.70$ V (vs Normal Hydrogen Electrode (NHE)), absorption by the gel at both 330 and 350 nm increases over time. This spectral change is electrochemically reversible and is accompanied by dissolution of the pale-yellow gel based on $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ to a light-brown dispersion containing Fe^{III} species.³⁶

Transmission electron microscopy imagery shows that $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ in chloroform, below an electrical potential of 0.30 V, exists as a series of abundant networks of fibrous nanoassemblies (with widths 3–4 nm, Figure 5a). The observed width of 3–4 nm corresponds to the bimolecular length of **1** (ca. 2.2 nm estimated by the Corey-Pauling-Koltun (CPK) model), indicating that $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ is dispersed as molecular wires. Alternately, when an electric potential of $+0.7$ V is applied for 2 h, the number of fibrous nanoassemblies decreases and numerous nanocrystals with lengths in the range 500–1500 nm and widths 30–50 nm are observed (Figure 5b). This observed morphological change is consistent with the dissolution of the gel-like phase upon oxidation of $[\text{Fe}^{\text{II}}(\mathbf{1})_3]\text{Cl}_2$ to the Fe^{III} complex. It is thus evident that lipophilic Fe^{II} -triazole complexes in chloroform tend to form nanowires, which show reversible and electrochemically

controllable self-assembly. The oxidation of polymeric Fe^{II} -triazole complexes are accompanied by the coordination of chloride ions to the Fe^{III} center, which entails dissociation of the linear coordination structures and the subsequent formation of nanocrystals (Figure 5c).³⁶

CONCLUSION

In this review, novel research concerning lipophilic transition metal-triazole complexes has been described. In particular, this summary covers the solution chemistry, spin crossover characteristics and structural transformations of triazole complexes modified with an ether linkage. Studies of such complexes demonstrate that the soluble nanowire complexes formed in various media or as a result of interaction with guest molecules exhibit characteristics and properties very different from those found in the bulk crystals. The structural dynamism of Fe^{II} -triazole complexes has been shown to offer a mean of investigating the electrochemical regulation of such species, and as such, there has been a growing interest in their photochemical characteristics^{48,49} and the spin conversion⁵⁰ via the self-assembly of these complexes. These findings provide a basis for the potential design of flexible nanometal complexes, where the structure and properties of coordination chains are affected by their interactions with external stimuli. Moreover, the self-assembly characteristics of these nanometal complexes may be exploited in order to exert dynamic control over their physical properties. The dynamism of these systems should allow the development of novel nanomaterials exhibiting synergistic properties, enabling the fabrication of supramolecular devices and machines.

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