Macromolecular and Supramolecular Approaches to Spin-Functional Soft Materials

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The first-row transition metal ions of d^4–d^7 electronic configuration are of interest, due to their possibility for the coexistence of two spin states, *i.e.* low-spin and high-spin states. Under certain conditions, the two spin states are known to switch in response to external perturbations caused by changes in temperature and pressure or photoexcitation. This phenomenon, referred to as spin transition or spin crossover, leads to changes in the magnetic and optical properties of the materials and has great potential for memory, display, and sensor applications. Solid or crystalline inorganic materials have been studied most extensively so far as potential spin-crossover materials, and some show reversible spin transition in a narrow temperature range. On the other hand, recent attention has been focused on soft materials with spin-crossover properties, as these materials can be processed easily by casting and tuned by molecular design. However, because of a larger freedom of molecular ordering, one may anticipate a possible loss of long-range cooperativity among the spin-transition sites, with the result of non-abrupt spin crossover, as often observed in solution.

Recently, we have designed a series of dendritic triazole derivatives, which serve as bidentate ligands that covalently bridge the iron(II) centers to form rigid coordination polymers, whose spin-transition properties are controlled by the dimensions of the dendritic ligand.[1,2] Herein, we review our recent work on macromolecular and supramolecular approaches to the synthesis of newly designed spin-functional soft materials, with a focus on the possibility for the control of spin state and spin–spin interaction.

1. Synthesis and Functions of Multi Metallosalen Wheels

Salen units, due to their high binding affinity for various metal ions, are useful building blocks for the construction of functional materials such as spin-crossover crystalline solids, components of molecular magnet, and catalysts for organic transformation and polymerization.

By appending dendritic metallosalen complexes with different generation numbers to di-, tri-, and hexakis-substituted benzene cores, a series of multi metallosalen wheels having different geometry and numbers of salen units on the exterior surface were synthesized (Figure 1) and unambiguously characterized by NMR and MALDI-TOF MS measurements. These molecular wheels are unique in that their metal sites are located on the identical single layer of the dendritic framework and thus allows for a clear correlation between function and structure. Studies on spin and catalytic functionalities are in progress.

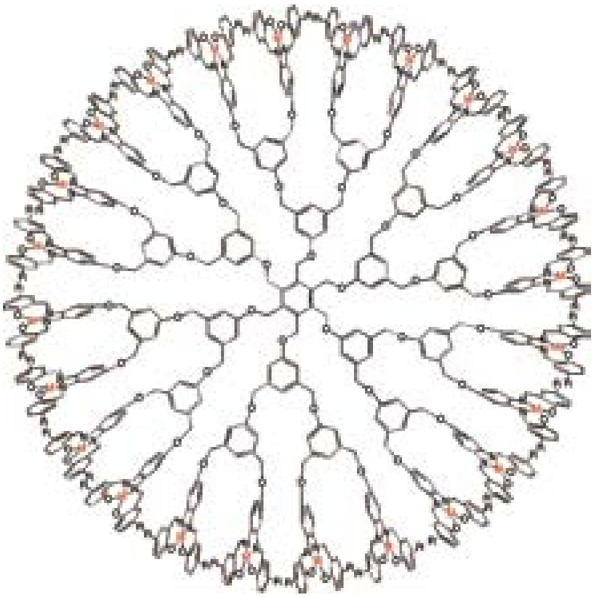

Figure 1. Schematic Representation of Multi Salen Wheels bearing 24 Metal Ions On the Exterior Surface.

2. Synthesis and Functions of TEG-Tethered Iron–Triazolate One Dimensional Chain

A series of newly designed Fe(II)-triazolate coordination polymers with TEG-tethered dendritic wedges $(\mathrm{G}n^m\mathrm{trz})\mathrm{Fe}$ (Figure 2; n = number of the generation of benzyl ether dendritic wedge; m = number of TEG chains) were synthesized and their spin-crossover properties were investigated both in solution and solid.

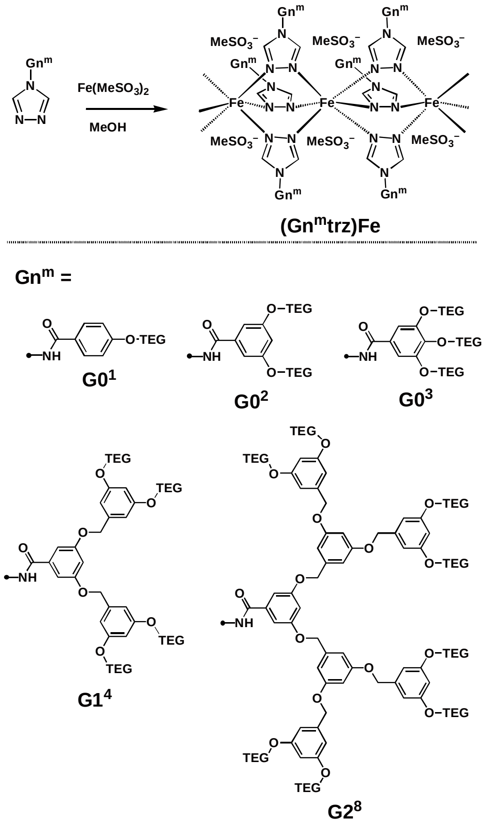

Figure 2. Schematic Representation of TEG-tethered Dendritic Iron–Triazolate Polymers.

TEG-tethered dendritic triazoles $(\mathrm{G}n^m\mathrm{trz})$ with different numbers of TEG chains on the exterior surface were synthesized by convergent method and unambiguously characterized by NMR, MALDI-TOF-MS, IR measurements. Polymerization of $\mathrm{G}n^m\mathrm{trz}$ with $\mathrm{Fe(MeSO_3)_2}$ in MeOH at room temperature afford a series of coordination polymers $(\mathrm{G}n^m\mathrm{trz})\mathrm{Fe}$ with iron–triazolate backbone encapsulated in TEG-tethered dendritic wedges. These dendritic polymers are highly soluble in THF, MeOH, EtOH, *n*-propanol to give a stable solution over a long period. Since the ‘naked’ iron–triazolate polymer is not soluble, TEG-tethered dendritic wedges not only enhanced solubility but also prevented the polynuclear chain from decomposition in solution.

A MeOH solution of $(\mathrm{G0^2}$-trz)Fe at room temperature was colored violet, characteristic of low-spin state, and discolorated upon heating at 30 °C, whilst after cooling at 20 °C, the solution turned to violet again. This thermally induced coloration-discoloration process is reversible without any deterioration for many times. The above color change suggests that thermal spin crossover takes place even in MeOH. In fact, temperature variable electronic absorption spectroscopy display a heating profile with a decrease at 450-nm absorption band, originated from *d–d* absorption band of the low-spin state, together with the appearance of a new peak centered at 750 nm, characteristics of the high-spin state. The spin transition temperature was thus estimated to be 25 °C. This is also the case for $\mathrm{G0^1trzFe}$ with one TEG chain on the dendritic surface, to show a spin transition temperature at 25 °C. On the other hand, $\mathrm{G0^3trzFe}$ with three TEG chains on the surface of the dendritic wedges although displayed a reversible spin crossover in MeOH but with a much low transition temperature at 6 °C.

$(\mathrm{G1^4trz})\mathrm{Fe}$ and $(\mathrm{G2^8trz})\mathrm{Fe}$ bearing large dendritic wedges were highly soluble in MeOH but displayed a colorless solution at room temperature, indicating a high-spin state of the focal metal chain. Upon cooling at 0 °C, the solution turned to violet, as a result of spin transition to low-spin state. The spin transition temperature in MeOH were estimated to be 8 and 5 °C, respectively. Therefore, when the size of dendritic wedge becomes large, the temperature for spin transition in MeOH decreased. In sharp contrast to the case of $(\mathrm{G0^2trz})\mathrm{Fe}$, solid samples of $(\mathrm{G1^4trz})\mathrm{Fe}$ and $(\mathrm{G2^8trz})\mathrm{Fe}$ retain high spin state even upon cooling at –78 °C. All these observations indicate that the TEG-tethered dendritic wedges play an important role in spin transition of the focal iron-triazolate chain.

XRD measurements of $(\mathrm{G0^2trz})\mathrm{Fe}$, $(\mathrm{G1^4trz})\mathrm{Fe}$, and $(\mathrm{G2^8 trz})\mathrm{Fe}$ exhibit that these dendrimers form hexagonal columnar structures. TEG-tethered dendritic wedges in the solution likely adopt stretched conformation, therefore, the decrease of spin transition temperature in solution is predominately affected by the size of the dendritic wedges. A large dendritic wedge causes steric hindrance between the neighboring metal sites and thus decreases the polymerization degree of the focal iron-triazolate chain. As a result, the spin transition temperature decreased. On the other hand, in solid state, the TEG chains become shrink to give a global conformation. Such a conformational change result in further increment of the steric hindrance between the two neighboring dendritic wedges, and eventually the focal iron-triazolate chain becomes distort, especially in the case of high-generation $(\mathrm{G1^4trz})\mathrm{Fe}$ and $(\mathrm{G2^8trz})\mathrm{Fe}$. Therefore, the TEG-tethered dendritic wedges not only greatly improved the solubility of rigid coordination polymer chain, but much importantly *through* conformational change enables magneto-optical switching of the focal iron-triazolate chain.

References

1) T. Fuigaya, D. Jiang and T. Aida, *Chem. Asian J.* **2**, 106 (2007).
2) Z. He, T. Ishizuka and D. Jiang, *Polym. J.* in press (2007).

Award

JIANG, Donglin; SPSJ Wiley Award 2006.