RESEARCH ACTIVITIES V
Department of Applied Molecular Science

V-A Design of Spin-Functional Nanomaterials through Molecular Programming and Nanostructuring

Metal ions with d^4–d^7 electron configurations can adopt two different magnetic states, *i.e.*, high-spin and low-spin states, which can cross over thermally or by electronic excitation. Spin-crossover phenomena have attracted attention in relation to their potential applications in molecular electronics. A fundamentally important challenge is to synthesize soft spin-crossover materials that can respond to external stimuli such as light and electric/magnetic fields. Up to date, inorganic and crystal engineering approaches have been employed for the synthesis of crystalline spin-crossover solid, which is hardly to process and difficult to use as a component for fabricating nano devices. In contrast to the above approaches, we are developing soft nanomaterials through programmed nanostructuring of metal complexes *via* covalent and non-covalent interactions. We employ one-, two-, and three-dimensional nanoarchitectures to construct well-defined coordination nanospace with spin-active metal complex as building blocks. By altering the size of building blocks, controlling their geometry and orientation, and directing their assembly, it is possible to engineer properties in unprecedented ways. Our strategy is promising for the development of a new family of spin-active nanomaterials whose functionalities and properties are heretofore unavailable in conventional crystalline metal complexes.

V-A-1 Molecular Design and Functions of Spin-Active Dendrimers

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([1]IMS and JST/PRESTO)

Dendrimers are three-dimensional hyperbranched macromolecules that provide well-defined nanoscopic objects at the single molecular level. Unlike ordinary linear polymers, star-shaped polymers, and traditional branched polymers, dendrimers are characterized by their elaborate structure, which allows for precise control of their molecular size, shape, and the numbers and positions of functional groups. Recent studies on dendritic macromolecules have extended the scope of research from synthesis to applications for catalysts, photoactive and electronic materials, medicinal and biomedical materials, and other functional materials.

In this project, we are developing dendrimeric architecture for construction of novel metallodendrimers, whose metal sites are covalently linked in three-dimensional nanospace. By taking advantage of convergent approach, metallodendrimers with different generation numbers, different morphology, and different size are synthesized. These dendrimers provide a platform for the studies on magnetic interactions and cooperativity in spin crossover, among dendritic wedges within confined dendritic nanospace.

V-A-2 Molecular Design and Functions of Spin-Active One-Dimensional Nano-Channels

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In relation to project V-A-1, we are developing spin-active low-dimensional soft materials, in which metal sites are aligned through non-covalent interactions to assemble one-dimensional and two-dimensional arrays. A series of triazole derivatives bearing water-soluble dendritic wedges with different generation numbers were synthesized as a bidentate ligand for coordination polymerization with iron(II). The rod-like rigid polynuclear chain appended with water-soluble dendritic wedges serves as a template for hybridization with mesoporous silicate. The hybrid consists of an iron(II) polynuclear chain that is spatially isolated within mesoporous channel, which thereby enables the investigation of magneto-optical properties at the single molecular level. Hybridized mesoporous silica thin film thus formed, due to its domain structure, functions as novel switching and high-density memory devices based on spin transition.