From Supramolecular Functionality to Functional Materials

Victor Borovkov[1,2]
[1]Metek Kitamura Co., Ltd., 1 Warada-cho, Kamitoba, Minami-ku, Kyoto 601-8133, Japan
[2] Department of Applied Chemistry, Osaka University, 2-1 Yamada-oka, Suita 565-0871, Japan

Supramolecular functionality and functional materials have attracted much attention so far due to its direct relevance to many natural assemblies and a number of practical applications in the different fields such as catalysis, nonlinear optics, polymer and materials science, light harvesting and different sensors, molecular and chiral recognition, various supramolecular and chiroptical devices, and absolute configuration determination.

Our functional supramolecular systems are based on simple ethane-bridged bis-porphyrin hosts **1** (M = Zn, Mg, 2H) (Figure 1). The specific mechanism of functionality of this host involves the environmentally assisted syn-anti conformational switching.[1-5] This property can be effectively utilizes in different supramolecular systems and functional materials for various applications. One of the most successful implementations of this approach is the chirality sensing of various enantiomeric guests (L) through formation of stable supramolecular host-guest complexes.[1-6] The sensing mechanism includes noncovalent interactions between **1** and various chiral compounds leading to formation of a unidirectional screw structure in the extended anti conformation of **1**. This generates a noticeable (moderate-to-strong) exciton-coupled circular dichroism (CD) signal in the *B* electronic transition region of **1**. The CD sign correlates uniquely with the direction of induced helicity, thus making it possible to determine straightforwardly the absolute configuration of various chiral guests using **1** as an effective and universal chirality sensor for different types of compounds as in solution and in the solid state.

To expand further the functionality of these systems some thin films and nanoparticles have been consequently obtained on the basis of these supramolecular assemblies. Hence, utilizing the unique syn-anti conformational switching ability of **1** (M = Zn) (Figure 1) an effective sensor for aromatic amines on the basis of Langmuir–Schaefer (LS) thin-films has been developed.[7] In particular, the LS films of **1** are able to sense aromatic amines at the concentrations as low as 20 ppb, whilst exhibiting full reversibility and high specificity. Another type of functional materials on the basis of syn-anti flexibility of **1** (M = Zn) is nanoparticles.[8] It was found that upon encapsulation into the semiconducting poly (9-vinylcarbazole) (PVK) polymer the conformation is switched to the anti form and the subsequent efficient excited energy transfer (up to 96%) from the PVK host to the energy acceptor (**1**) is observed, thus opening further prospects in designing a new class of porphyrin-based functional nanoparticles for the application in effective light harvesting system.

However, porphyrin-based materials have rather limited application prospects in particular from the stability standpoint. Therefore, for more practical applications of the functional systems, particularly in the field of asymmetric catalysis, stable and robust materials are developed. To this end, the chirally modified metal surfaces are considered to be one of the most suitable candidates for such functional materials. Preliminary results show a great promise of this approach. For example, metallic micro- and nano-scaled Ni powders co-modified with (*R*,*R*)-tartaric acid and NaBr exhibit high enantioselectivity (up to 91%) and durability upon hydrogenation of methyl acetoacetate to give (*R*)-methyl-3-hydroxybutyrate as a major product (Figure 2) and maintained the catalytic activity and enantiodifferentiating ability for ca. 3 months under the dry storage condition.[9,10] This enhanced efficiency and remarkable stability make it possible to use the chirally modified nickel powder as a promising material for the robust enantio-differentiating hydrogenation catalyst at the industrial scale. Further details and developments towards chiral materials on the basis of these metal-containing systems will be discussed.

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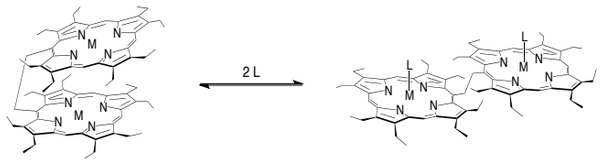

Fig. 1. Structure and syn-anti conformational switching of **1** upon interaction with external guests (L).

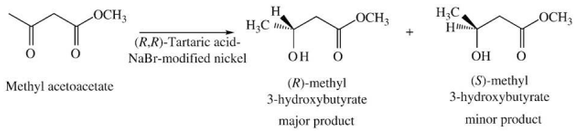

Fig. 2. Enantiodifferentiating hydrogenation of methyl acetoacetate.