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Short communication

Incorporation of various alcohol substituents to a metalloporphyrin platform for dramatic changes in morphologies of microcrystals

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ABSTRACT

Micro crystals with various morphologies have been successfully grown from readily accessible molecular platform [10,20-bis(2,6-dibutoxyphenyl)porphyrin]Sn(OH)$_2$. Simple synthetic alteration makes this platform into various molecular building blocks using its axial coordination sites which trigger additional interactions and allow various crystal packing arrangements. We have demonstrated how apparently small modifications to building blocks can initiate significant changes in the morphologies and molecular packings of the corresponding solid state-state materials.

Recently the self-assembly approach has become one of the most widely used techniques for the preparation of many functional materials, due to its potential to translate molecular building blocks into well-defined solid-state systems with relatively facile manner [1–3]. This process is based on the dynamic noncovalent interactions such as van der Waals, π–π, hydrogen bonding, hydrophilic/hydrophobic, electrostatic, donor and acceptor, and metal-ligand coordination between the building blocks [4–6]. In this regard, porphyrins have served as one of the most favorite molecular building blocks for self-assemblies, because of their attractive structural features such as large bulk, rigid planar and highly conjugated framework that can be readily modified with a variety of functional substituents for self-assemblies [7]. In addition, owing to the enormous potentials in catalysis, sensing, optoelectronic, photochemistry and optical device, they have been fascinating building blocks in the emerging field of molecular materials [8,9].

With appropriate functional substituents, porphyrins can stimulate various noncovalent interactions and generate various structures including spheres, rods, wires, ribbons, tubes, and cubics in relatively easy manner [10]. The structural diversities are best relying upon their reaction conditions [11]. One of the most commonly used methods to manipulate their morphologies is to employ the building blocks with certain intermolecular interactions [12]. Furthermore, when they are interacting in highly ordered fashion, the building blocks may allow to adopt crystalline structures. The final morphologies of these crystalline structures are mainly determined by their molecular packing resulted from the substituents of building blocks. Indeed, porphyrins have been extensively used in the construction of molecular materials using their noncovalent interactions with appropriate substituents that are directly bonded to the porphyrin framework [13]. In addition, the utilization of secondary substituents that are not immediately linked to the porphyrin framework has recently attracted much attentions, because they bring additional interactions to control the structural and physical properties of the final structures [14].

We like to demonstrate the use of such secondary substituents to impact the molecular packings, crystal structures, and final morphologies of microcrystals from a (porphyrin)Sn(OH)$_2$ platform. Various alcohols are introduced to allow coordination in place of two hydroxyl groups in (porphyrin)Sn(OH)$_2$ resulting quick generation of various secondary substituents on the porphyrin platform. We are particularly interested in the rational synthesis of porphyrin based unique crystalline structures with various morphologies resulting from the interactions caused by secondary substituents, which may trigger supplementary interactions between the porphyrin molecules in addition to their inherent π-π interactions. Here, we report the synthesis and characterization of various microcrystals from [10,20-(2,6-dibutoxyphenyl)porphyrin]Sn(OH)$_2$ platform in which various alcohols were introduced to generate wide range of bisalkoxy Sn(IV)-porphyrins **1–5** with various alcohol substituents.(Scheme 1) The detailed preparations are described in the Supporting Information section. With a simple precipitation method [15], these porphyrins can easily adopt various micro-sized crystalline objects depending on alcohol substituents which clearly display the additional impact to the crystal growth. When 100 μL of solutions (1 mM) of porphyrins **1–5** in the corresponding alcohols are injected

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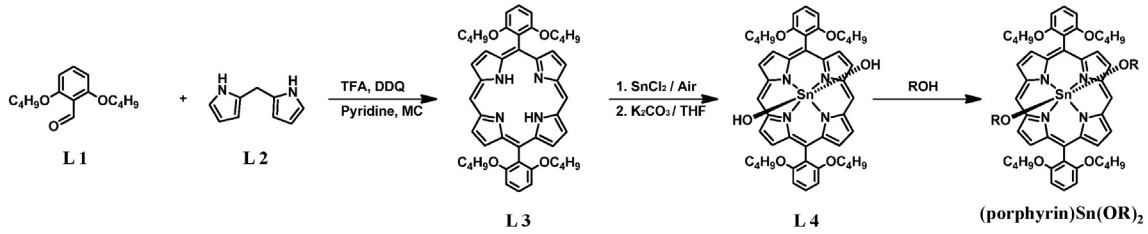

Scheme 1. Preparation of porphyrin building blocks.

into stirring deionized water (5 mL) at room temperature, light brown suspensions were obtained, respectively. Scanning electron microscopy (SEM) analysis revealed these porphyrin suspensions to be collections of fairly uniform microcrystalline objects as described in Fig. 1.

The PXRD patterns for microcrystals and single crystals obtained from the corresponding porphyrins are likewise similar except **4** and **5**,(Fig. S2) suggesting a conservation of the molecular packing arrangement for most of cases. The single crystals were obtained from slow diffusion of solutions of bisalkoxy Sn(IV)-porphyrins in respective alcohols (methanol for (porphyrin)$Sn(OMe)_2$ **1**, ethanol for (porphyrin) $Sn(OEt)_2$ **2**, propanol for (porphyrin)$Sn(OPr)_2$ **3**, isopropanol for (porphyrin)$Sn(O^iPr)_2$ **4** and *t*-butanol for (porphyrin)$Sn(O^tBu)_2$ **5**) over water. The butyl groups on phenyl rings and coordinated alcohols on Sn(IV) core of one porphyrin can interact to those of neighboring molecules to afford highly ordered arrays of porphyrins in solid state [16]. Interestingly, the final morphologies of these microcrystals vary dramatically with the alcohol substituents. For example, **1** produces fairly uniform rectangular plates with ~1.1 ± 0.1 μm in length and **2**

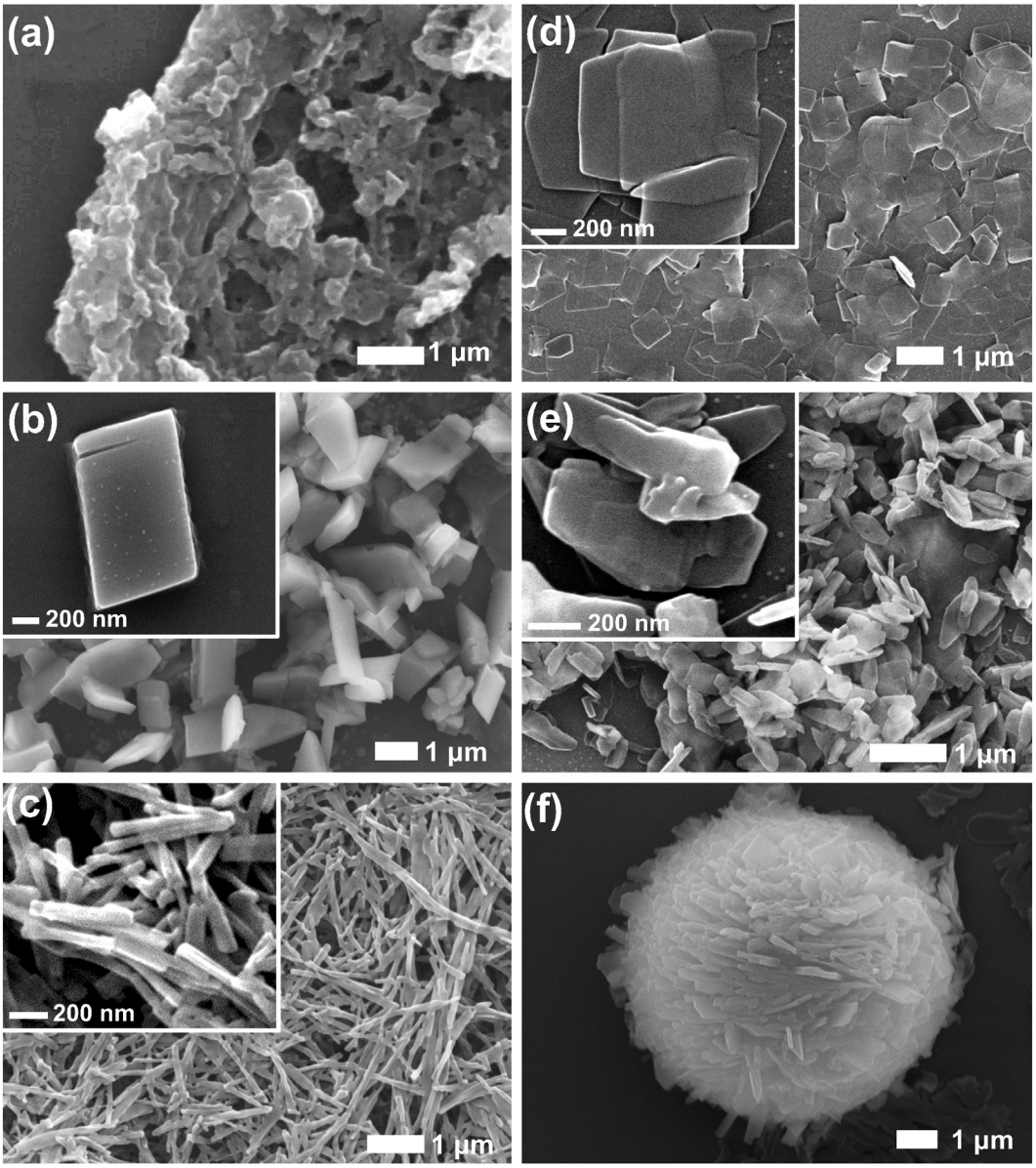

Fig. 1. SEM images of the various micro crystals obtained from porphyrin building blocks **1–5**; (a) (porphyrin)Sn(IV)(OH)2, (b) **1**, (c) **2**, (d) **3**, (e) **4**, and (f) **5**.