Preparation of Self-Assembled Crystalline Microparticles with Bispyridyl Zn-Porphyrin

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Well-defined solid-state microcrystalline structures from bispyridyl Zn-porphyrin have been successfully synthesized. The coordinative interactions between pyridine and Zn are main responsible for this translation of porphyrin molecular building blocks to crystalline microscopic objects. The hexagonal plates are obtained from acetonitrile and rhombus plates are grown from toluene solution. With a simple manipulation during the microcrystal growth, such as growth temperature and time, the morphologies can be controlled by adopting different molecular packing. Consequently, morphologies of microcrystals have been diversified.

Key Words : Porphyrin, Building block, Pyridine, Crystalline, Morphology

Introduction

Due to their potential applications in solar cells, electronics, sensors and catalysis, self-assembled nanostructures have attracted much attention.[1] Specially, porphyrins have received a great deal of interest because they show unique properties in photonic and electronics[2] and are proven to be good building blocks to construct self-assembled nanostructures.[3] Since much attention has been recently focused on solar energy conversion, electron transfer and artificial photosynthesis,[4] great efforts are focused on the fabrication of porphyrin based functional nanostructures.[5] In fact, porphyrins can promote multiple inter- and/or intra-interactions such as hydrogen bonding, π-π stacking, electrostatic interactions and metal-ligand coordination with synthetic modifications on the porphyrin framework,[6] and well-defined nanostructures such as spheres, fibers, rods, ribbons, plates, sheets, cubes, wheels, rings and grids are accessed by introducing functional moieties on the porphyrin frameworks.[4,7]
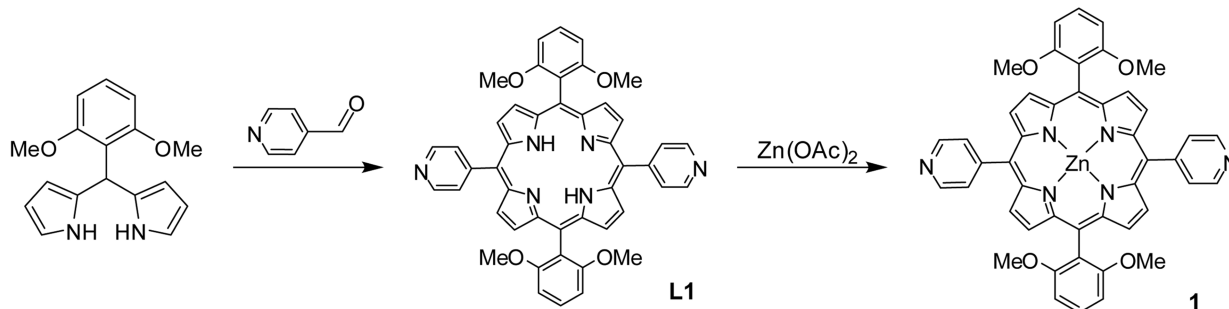
After Shelnutt and others have demonstrated a relatively simple method to grow nano- or micro crystals of porphyrin,[7] a number of reports has been focused on crystalline particles based on the interaction such as hydrogen bonding between pyridine and Sn(OH)$_2$. In their study a reprecipi-

tation method is mainly employed to produce crystalline particles. This method is based on quick injection of a solution of porphyrin into a bad solvent in which the corresponding porphyrin building block shows very low solubility. Therefore, the size and morphology of crystals are highly relying on the molecular packing during the crystallization process that would be promoted by the interactions between the functional groups provided by building blocks. However, ligand to metal coordinative interaction, such as coordination bonding between pyridine and zinc has not been fully demonstrated. So, we have envisaged that coordination driven self-assembly of porphyrin nano- or microcrystalline objects would be feasible by introducing coordination bonding between pyridine and Zn.

Herein, we like to report on the synthesis of porphyrin microscopic crystalline particles from the pyridine substituted Zn-porphyrin (Scheme 1).

Experimentals

General. 2,6-Dimetoxybenzaldehyde and [2,6-dimethoxyphenyl]dipyrromethane were synthesized by according to modified literature procedures.[8] All other chemicals were obtained from commercial sources and used without further purification. All of the reactions and manipulations were

Scheme 1

carried out under N_2 with the use of standard inert-atmosphere and Schlenk techniques unless otherwise indicated. Solvent used in inert-atmosphere reactions were dried and degassed using standard procedures. Flash column chromatography was carried out with 230-400 mesh silica-gel from Aldrich using wet-packing method. All deuterated solvent were purchased Aldrich. NMR spectra were recorded on a Varian AS400 (399.937 MHz for ^{1}H and 100.573 MHz for ^{13}C) spectrometer. [1]H chemical shifts are referenced to the proton resonance resulting from protic residue in deuterated solvent and ^{13}C chemical shift recorded downfield in ppm relative to the carbon resonance of the deuterated solvents. Absorbance and emission spectra were obtained using an Agilent UV-Vis-NIR spectrophotometer and Hitachi F-7000 fluorescence spectrophotometer using quartz cells. All scanning electron microscopy (SEM) images were obtained using a Jeol JSM-7001F. Powder X-ray diffraction measurements were recorded with a Rigaku D/MAX-Ultima III diffractometer using nickel-filtered Cu Kα radiation (λ = 1.5418 Å) over a range of 2° < 2θ < 40° and an X'Celerator detector operating at 40 kV and 40 mA.

Synthesis.

[5,15-Bis(4-pyridyl)-10,20-bis[2,6-dimethoxyphenyl]-porphyrinato]zinc(II) (1).[9] To a solution of 5,15-bis(4-pyridyl)-10,20-[2,6-dimethoxyphenyl]porphyrin, **L1** (565 mg, 0.767 mmol) in DCM (42 mL) was added a solution of zinc acetate dihydrate (Zn(OAc)$_2$(H$_2$O)$_2$, 1.18 g, 5.37 mmol) in methanol (15 mL). The reaction mixture was allowed to stir for overnight. After evaporation of solvent, the solid was re-dissolved in DCM and the resulting solution was filtered and washed with DCM. The filterate was evaporated and the resulting solid was purified by silica-gel column chromatography (methanol/DCM 0.5:10 v/v) and recrystallized (THF/hexane) to afford pure **1** as a dark purple solid (512 mg, 83.4%). ^{1}H NMR (CDCl$_3$ + pyridine-d_5) δ 8.71 (d, $^3J_{H-H}$ = 4.69 Hz, 4H), 8.53 (d, $^3J_{H-H}$ = 4.69 Hz, 4H), 8.68 (d, $^3J_{H-H}$ = 6.26 Hz, 4H), 7.82 (d, $^3J_{H-H}$ = 6.26 Hz, 4H), 7.57 (t, $^3J_{H-H}$ = 8.60 Hz, 2H), 6.87 (d, $^3J_{H-H}$ = 8.60 Hz, 4H), 3.35 (s, 12H). ^{13}C NMR (CDCl$_3$ + pyridine-d_5) δ 160.54, 152.02, 150.62, 148.12, 144.52, 131.21, 130.66, 130.05, 128.81, 120.86, 115.57, 113.06, 104.39, 56.30. MS (MALDI-TOF): m/z = 800.80 for M$^+$; Calcd 800.21.

Synthesis of Porphyrin Microcrystals: A DCM solution of porphyrin **1** (100 μL of a 2 mL solution) was injected into a vial containing magnetically stirred acetonitrile (2 mL) at 75 °C or 60 °C and the mixture was allowed to stir for 2, 5 or 10 min. After cooling to room temperature, colloidal porphyrin particles were obtained. Isolation of all porphyrin microcrystals after synthesis was easily carried out *via* centrifugation and decantation of the mother liquor (Isolated yields of the reactions in AcCN; 92% for 2 min, 96% for 5 min and 94% for 10 min. Isolated yields of the reactions in toluene; 91% for 2 min, 86% for 5 min and 88% for 10 min).

Results and Discussion

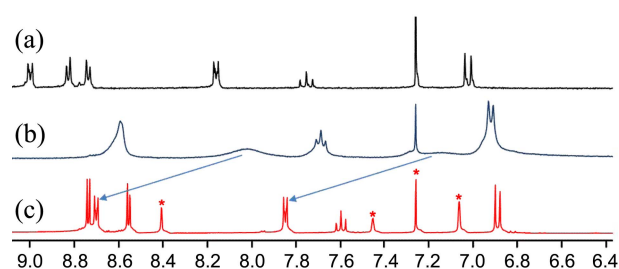The porphyrin building block **1** has been easily prepared

Figure 1. ^{1}H NMR spectra of free-base porphyrin (a), and Zn-porphyrin **1** (b) in CDCl$_3$ and in CDCl$_3$ with d_5-pyridine (c).

via the condensation reaction between [2,6-dimethoxyphenyl]dipyrromethane and 4-pyridinecarboxaldehyde followed by metallation with Zn(OAc)$_2$ in DCM and MeOH. To prove the coordinative interaction between the substituted pyridines and Zn, porphyrin **1** was carefully examined by ^{1}H NMR spectroscopy. Figure 1 compares the spectra for **1** in pure CDCl$_3$ and in 5% of pyridine-d_5 in CDCl$_3$. Salient features are substantial upfield shifts of peaks for the phenyl, β-pyridyl and, particularly, α-pyridyl protons of **1**, evidencing the effects of large porphyrin ring currents compared to the corresponding peaks for free-based porphyrin **L1**.[11] After addition of 5% of pyridine-d_5 to the previous sample prepared in CDCl$_3$, the peaks of **1** showed progressive downfield shifts, consistent with rapid exchange between substituted pyridine on porphyrin framework and pyridine-d_5. Those upfield shifts of peaks are annulled due to the ligation of pyridine-d_5 to the metal center. Thus, we have clearly observed that there are strong coordinative interactions between the substituted pyridines and Zn.

Encouraged by ^{1}H-NMR spectroscopic study, microscopic crystalline particles have been assembled by using a typical reprecipitation method.[10] When a solution of **1** in DCM (2.0 mM) is injected into stirring acetonitrile at 75 °C, a translucent purple suspension was obtained after approximately 2 min. With careful investigation by scanning electron microscopy (SEM), a collection of fairly uniform hexagonal plate with an average of 2 μm long and 300 nm thick is identified from these suspensions (Fig. 2(a)). When the reaction time is increased to 5 min, the growth of additional plates on hexagonal plates was identified (Fig. 2(b)). Furthermore, when the reaction time is increased to 10 min, the growth of multiple plates on hexagonal ones was observed (Fig. 2(c)). The size of platform hexagonal plates remains unchanged in all cases. Surprisingly, when **1** in DCM solution is injected into toluene at 60 °C, rhombus plates identified by SEM are produced after 2 min of stirring (Fig. 2(d)). The size evolution of these rhombus plates from 2 to 10 and 15 μm have been observed as the reaction time was increased to 5 and 10 min, respectively (Fig. 2(e), (f)). Presumably, the coordinative interactions between the substituted pyridines and Zn are main responsible for the formation of microscopic crystalline objects together with the different solubilities of building block in both acetonitrile and toluene.[12]

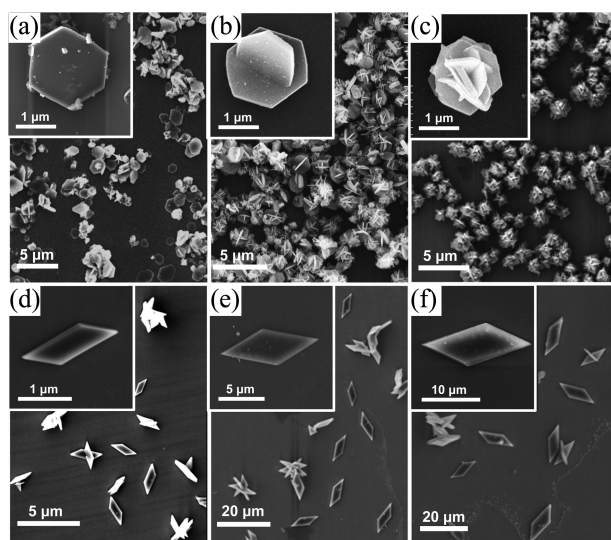Although obtaining suitable single crystals for X-ray

Figure 2. SEM images of the microscopic crystalline porphyrin particles obtained from building block **1** after stirring for 2 min (a), 5 min (b), and 10 min (c) in acetonitrile at 75 °C, and after stirring for 2 min (d), 5 min (e), and 10 min (f) in toluene at 60 °C.
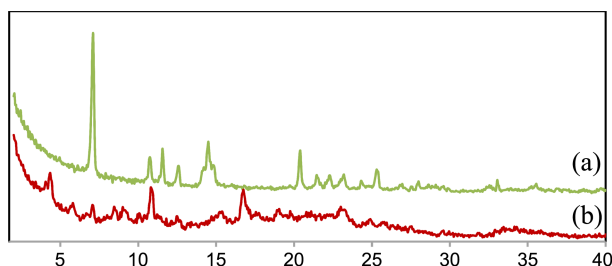

Figure 3. The PXRD patterns for the two microscopic crystalline porphyrin particle samples of **1**. (a) Hexagonal plates grown in acetonitrile at 75 °C. (b) Rhombus plates grown in toluene at 60 °C.

structure analysis has not been successful, powder X-ray diffraction (PXRD) measurements of porphyrin micro crystalline objects deposited on Si wafers indicate unequivocal evidences of the structural orderness of porphyrins in each samples (Fig. 3).

Since all micro crystals are constructed from self-assembly of multiple porphyrins, they exhibit absorption and emission spectra that considerably differ from those of the monomeric porphyrin building block (Fig. 4).[7,13] The UV-Visible absorption spectrum of porphyrin **1** in DCM shows a Sorét band at 419 nm and Q-bands at 544, 567 and 653 nm. This solution sample was prepared in DCM with a concentration of 3.12×10^{-6} M. Interestingly, the UV-Visible absorption spectra of the porphyrin particles dispersed on quartz glass plates are more complicated. In case of hexagonal plates which were grown in acetonitrile, the Sorét band is broadened and appears at 442 nm which is red-shifted slightly while the Q-bands broaden and appear at 565, 617 and 655 nm. On the other hand, the Sorét band is broadened and appears at 436 nm which is also red-shifted slightly while the Q-bands broaden and appear at 563, 611 and 653 nm in case of rhombus crystals grown in toluene.
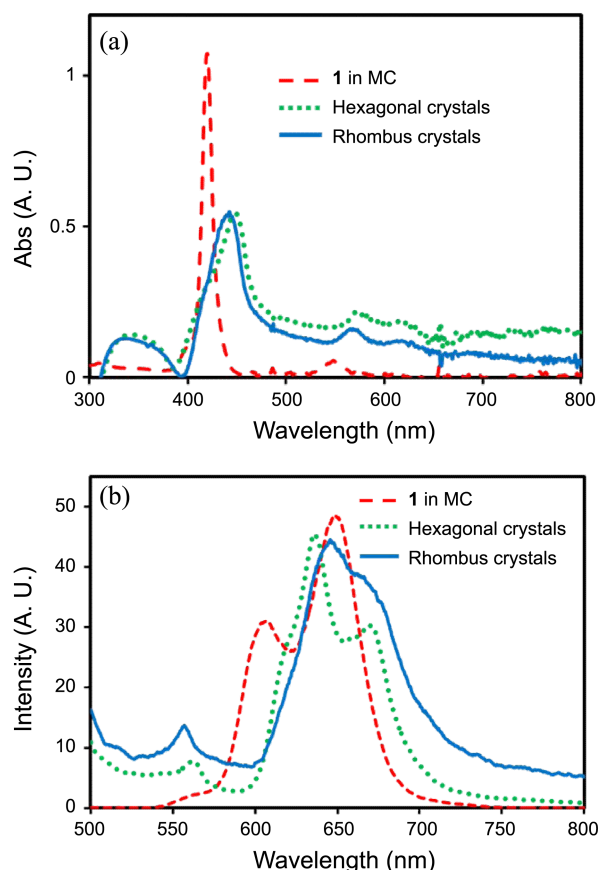

Figure 4. UV-vis (a) and fluorescence (b) spectra of **1** (2.0×10^{-6} M) and microcrystals made from **1**.

The spectra show an agreement of the Sorét band transitions due to J-type of densely packed aggregation in the solid state between porphyrin building blocks.[14] These spectral shifts are unequivocal evidence of effective intermolecular interactions and are mainly due to the exiton delocalization of porphyrins with similar packing.[7,14] The emission spectra of porphyrin particles show multiple bands at 618, 634 and 675 for hexagonal crystals grown in acetonitrile, and multiple bands at 643 and 662 for rhombus hexagonal crystals grown in toluene, while only two bands at 603 and 645 nm are observed for a DCM solution of **1** (Fig. 4(b)).

Presumably, the porphyrin **1** undergoes the nucleation process originated by 2-D coordination interactions with adjacent porphyrins to generate a 2-D assembled layered structure which further comes together to form 3-D structures driven by the crystal lattice packing based on π-π stacking of 2-D assembled layered structures during the crystallization process.

Summary

In summary, porphyrin based microscopic crystalline porphyrin objects have been prepared from porphyrin building block **1**. We have clearly demonstrated that the coordinative interactions between pyridyl substituents and Zn play an important role in order to promote intermolecular interactions

and, therefore, to generate crystalline microscopic materials. Porphyrin building blocks containing just pyridyl or Zn do not interact themselves and the formation of amorphous solids is observed. These crystalline materials assembled from porphyrins may find in use of photonic and electronic applications.

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