Organic−Inorganic Composites Comprised of Ordered Stacks of Amphiphilic Molecular Disks

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Since the discovery of mesoporous MCM-41 having a hexagonally ordered structure,[1] manipulation of inorganic superstructures under a template effect of organic supramolecular aggregates has been a highly active area of research.[2] Sol−gel polymerization of inorganic precursors at the surface of aggregates (templates) allowed the creation of highly ordered organic−inorganic composites by exploiting noncovalent interactions such as electrostatic, hydrogen-bonding, and van der Waals interaction. The deposition of inorganic walls around organic aggregates also preserved the morphologies of flexible organic supramolecular structures.[3]

π-Conjugated disklike molecules such as triphenylene and metallophthalocyanine are attractive building units for the formation of highly ordered columnar stacks.[4] These ordered stacks might enable an efficient electron or energy transport parallel to the columnar axis. To obtain ordered stacks of disklike molecules, a number of chemical and physical techniques involving liquid crystal, vacuum deposition, and Langmuir−Blodgett film transfer have been investigated.[5] Nolte et al. reported the spontaneous formation of ordered stacks of phthalocyanine derivatives through three noncovalent interactions: core−core interaction, van der Waals interaction among aliphatic side chains, and the sandwich-type complex formation between crown ether voids and K^+ ion.[6] Recently, we reported the formation of fibrous assemblies made of amphiphilic metallophthalocyanines stabilized by hydrogen bonding among hydroxy groups.[7] However, the dissolution in solvents and the heating of these ordered stacks leads to dissociation into single building units. Herein we describe the preservation of columnar morphology by the deposition of inorganic walls. Furthermore, wrapping by inorganic wall may result in the isolation of a single column consisting of one-dimensional ordered stacking of numerous molecular disks.

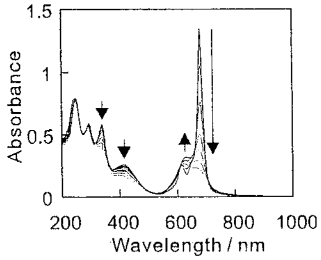
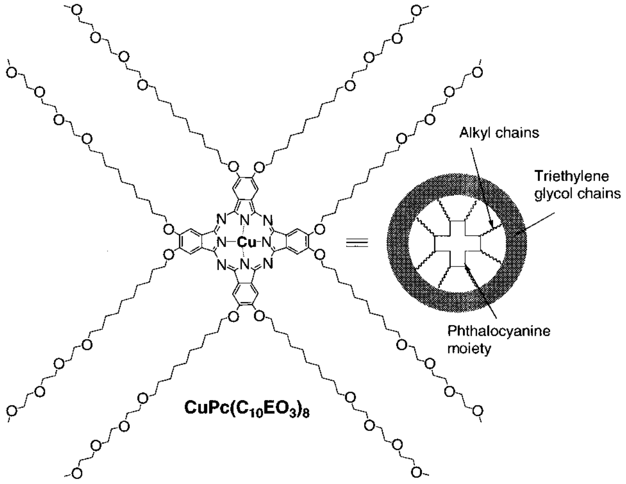


Figure 1. Absorption spectra of $CuPc(C_{10}EO_3)_8$ in CH_2Cl_2 and CH_2Cl_2−ethanol of ratio of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1. [$CuPc(C_{10}EO_3)_8$] = 11.2 μM.



Novel amphiphilic disklike molecule $CuPc(C_{10}EO_3)_8$ was synthesized according to the conventional method developed for octaalkoxyphthalocyanines (see Supporting Information). These compounds contain a central phthalocyanine core, eight decoxy spacers, and peripheral eight triethylene glycol chains. The nonionic surfactants and block polymers containing oligo- and poly(ethylene glycol) headgroups have been widely used as templates for the preparation of mesoporous silica.[8] The introduction of triethylene glycol chains into the disklike molecules can induce the assembly of inorganic sources. The synthesized phthalocyanine derivatives exhibited excellent solubility in polar and nonpolar solvents except for hydrocarbons. Figure 1 shows the UV−vis spectra of $CuPc(C_{10}EO_3)_8$ in CH_2Cl_2 and a mixture of CH_2Cl_2 and ethanol. UV−vis spectrum in CH_2Cl_2 had a strong sharp peak at 677 nm, typical of nonaggregated phthalocyanine.[9] When ethanol was admixed, the Q-band was broadened, and the maximum was blue shifted. These spectral changes can be ascribed to the formation of phthalocyanine stacks having a coafacial arrangement. By increasing polarity of solvent, the

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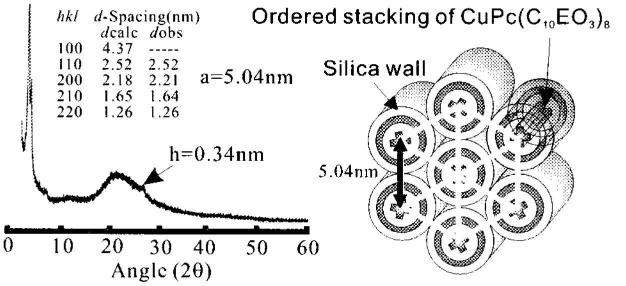

hkl	*d*-Spacing(nm) *d*calc	 *d*obs
100	4.37	-----
110	2.52	2.52
200	2.18	2.21
210	1.65	1.64
220	1.26	1.26

Figure 2. Powder XRD patterns of the organic−inorganic composite containing $CuPc(C_{10}EO_3)_8$ and silica and assigned Miller indices (*hkl*).

hydrophobic phthalocyanine cores come closer and form a coafacial one-dimensional stack in polar solvents.

The mesomorphic behavior of $CuPc(C_{10}EO_3)_8$ was examined by temperature-controlled polarizing microscopy, differential scanning calorimetry (DSC), and powder X-ray diffraction (XRD) measurements. When the isotropic liquid of $CuPc(C_{10}EO_3)_8$ was cooled slowly, a mosaic texture appeared under the polarizing microscope, a texture which is characteristic for the hexagonal columnar mesophase D_h.[10] Upon heating, the two phase transitions were detected by DSC at 136 and 220 °C, corresponding to the transition from crystalline solid (K) to D_h and the clearing point, respectively. XRD studies of $CuPc(C_{10}EO_3)_8$ gave three Bragg reflections in the ratio $1{:}1/\sqrt{3}{:}1/2$, indicating that the mesophase consists of a two-dimensional hexagonal lattice of columnar stacks with a lattice constant $a = 4.25$ nm (see Supporting Information). In addition, $CuPc(C_{10}EO_3)_8$ exhibited a sharp reflection at 0.34 nm due to the stacking distance between the phthalocyanine cores, suggesting the presence of long-range periodicity along the columnar axis.

Sol−gel polymerization of tetraethoxysilane (TEOS) in the presence of $CuPc(C_{10}EO_3)_8$ was carried out according to the method reported by Stucky et al. (see Supporting Information).[11] After stirring of the reaction mixture at 25 °C, green precipitate was corrected, washed with water, and dried at 50 °C. The product yield was above 90% on the basis of the initial amounts of $CuPc(C_{10}EO_3)_8$ and silicon. The sol−gel polymerization process in the presence of $CuPc(C_{10}EO_3)_8$ was monitored by the optical polarized microscopy of a mixed solution prepared by $CuPc(C_{10}EO_3)_8$, TEOS, and 2.0 M HCl aqueous solution ($CuPc(C_{10}EO_3)_8$:TEOS: H_2O = 1:2:1 (by weight)). This mixture appeared birefringent under polarized microscope, indicating a formation of hexagonal phase.[12] When the solidified mixture was heated above the clearing point of $CuPc(C_{10}EO_3)_8$ at 220 °C, the optical texture remained unaltered. The hexagonal mesostructure of the organic−inorganic composite was also confirmed by XRD (Figure 2). In the powder XRD pattern of the precipitate, three peaks observed at 2.52, 2.18, and 1.65 nm can be indexed to a hexagonal structure with $a = 5.04$ nm. Moreover, the reflection at 0.34 nm corresponding to the stacking distance was also detected. The increase of the lattice constant compared to that of only $CuPc(C_{10}EO_3)_8$ suggests the formation of silica wall around ordered stacks of $CuPc(C_{10}EO_3)_8$. Washing with organic solvents ($CHCl_3$ and DMF) scarcely released the incorporated $CuPc(C_{10}EO_3)_8$ from the composite. After hydrolysis of TEOS in acidic media in the presence of $CuPc(C_{10}EO_3)_8$, the stacking of $CuPc(C_{10}EO_3)_8$ was stabilized by the association between peripheral triethylene glycol chains and silica.

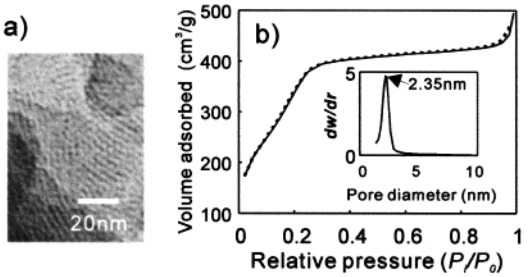

Figure 3. (a) TEM image of calcinated sample synthesized using $CuPc(C_{10}EO_3)_8$. (b) Nitrogen adsorption (solid line)−desorption (dotted line) isotherm and pore size distribution curve for the calcinated sample.

The ordered inorganic structures after removal of $CuPc(C_{10}EO_3)_8$ by calcination were also investigated by TEM, XRD, and nitrogen BET adsorption measurements. Calcination of the composite at 450 °C for 2 h gave a gray powder material. TEM image of calcinated sample showed a hexagonal array of regularly sized holes of ~2.8 nm diameter separated by ca. 1.0 nm-thick silica walls (Figure 3a). XRD pattern can be indexed to the hexagonal structure with $a = 3.46$ nm, consistent with the TEM image. The calcinated sample had a BET surface area of 1300 m^2/g and a narrow pore-size distribution around 2.35 nm (Figure 3b). These results indicate the formation of highly ordered mesoporous silica through the preservation of long-range ordering during the calcination process. The regulated array of holes in silica provided evidence of the isolation of a single column of $CuPc(C_{10}EO_3)_8$ stacks by the deposition of silica walls.

In conclusion, the present paper demonstrates the creation of organic−inorganic composites containing one-dimensional ordered stacking of molecular disks by liquid crystal template sol−gel polymerization. The experimental results support the claim of the creation of highly ordered organic−inorganic composite material. Work is underway in our laboratory to measure the electronic conductivity of the single column having ordered stacking of copper phthalocyanines encapsulated within silica walls.[13]

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Supporting Information Available: Synthetic procedures, optical polarized microscopy pictures, and XRD pattern of $CuPc(C_{10}EO_3)_8$. Synthetic procedure, SEM picture, FT-IR spectra, and TGA curve of silica composite materials (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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