

Ship-in-a-Bottle Synthesis of Copper Phthalocyanine Molecules within Mesoporous Channels of MCM-41 by a Chemical Vapor Deposition Method

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ABSTRACT

We report a "ship-in-a-bottle" synthesis where encapsulation of copper phthalocyanines (CuPc) into mesoporous channels of silicate MCM-41 was achieved by chemical vapor deposition (CVD) using 1,2-dicyanobenzene (DCNB). Silanol protons of MCM-41 were ion-exchanged with copper ions before CVD, and when the initial amount of DCNB was much larger than that of copper ions, CuPc molecules in the channels were found to form a cofacial structure that was confirmed by diffuse reflectance spectra.

In recent years, development of a new family of silicate mesoporous molecular sieves MCM-41 has received much attention.^{1–11} This material has hexagonally packed arrays of one-dimensional channels with much larger surface areas and narrower pore size distributions than ordinary amorphous silica. The pore size of MCM-41 can be tuned in the range from 1.5 to 10 nm or more and is larger than the pore size of typical microporous zeolites (<2 nm).^{1–5} Accordingly, the mesoporous MCM-41 has a potential to encapsulate macromolecules more easily than microporous zeolites,⁷ and it offers novel concepts for molecular syntheses and molecular arrangement using the highly ordered one-dimensional channels.^{8–11} We report herein a simple method for encapsulation of copper phthalocyanines (CuPc) into the MCM-41 channels, that is, a "ship-in-a-bottle" synthesis by chemical vapor deposition (CVD). Phthalocyanines (Pc) have been used extensively as dyes, organic electronic elements, sensing materials, photoactive materials, and catalysts.¹² If Pc molecules can be encapsulated densely within the one-dimensional channels, their linearly arranged structure would be formed in each channel. In this highly ordered linear structure, novel functionality such as conductivity should be

realized, and the functionality can be tuned by controlling the amount and aggregation conditions of Pc. To encapsulate Pc into the one-dimensional channels, the following methods have been proposed: direct adsorption of Pc in an appropriate solvent¹³ or by vacuum evaporation, and "ship-in-a-bottle" synthesis from molten 1,2-dicyanobenzene (DCNB).¹⁴ For encapsulating Pc densely into the channels, CVD using DCNB is a promising method, because DCNB is a smaller sized molecule than CuPc, which has a molecular size of about 1.5 nm square, and DCNB is expected to enter deep into the one-dimensional channels easily. The CVD method^{15–19} is advantageous since the sublimation point of DCNB is much lower than that of CuPc, that is, CVD from DCNB is preferable to the vacuum evaporation of CuPc. In addition, production of CuPc is expected to be highly efficient, because diffusion of gaseous molecules is fast and a capillary condensation effect can accelerate packing molecules deep into the channels.^{3,4,20}

Pure silicate MCM-41 was prepared by using dodecyltrimethylammonium chloride as a templating agent according to the literature.⁶ The prepared MCM-41 was characterized by transmission electron microscopy (TEM), powder X-ray diffraction (XRD) with Cu K α radiation, and N₂ adsorption–desorption measurement at 77 K. The surface area and pore diameter distribution were evaluated from the adsorption–

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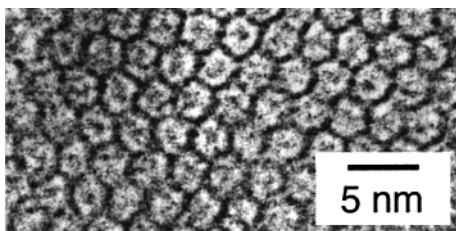


Figure 1. TEM image of the hexagonal pore structure of calcined MCM-41.

desorption isotherm using BET²¹ and BJH²² analyses, respectively. For comparison, BET surface area (S_a), total pore volume (V_p), and adsorbed amount of N_2 were calculated per weight of MCM-41. The XRD pattern of calcined MCM-41 could be indexed as a hexagonal phase and it matched well with published results (d_{100} spacing: 3.4 nm).⁶ The N_2 adsorption–desorption isotherm showed type IV mesopore sorption behavior,²⁰ and the pore diameter distribution showed a narrow single peak. The average pore diameter, S_a , and V_p were 2.5 nm, 1430 m² g^{−1}, and 0.98 cm³ g^{−1}, respectively. A TEM image of the calcined MCM-41 (Figure 1) shows the regular hexagonal array of uniform channels as confirmed by XRD and N_2 adsorption–desorption measurements.

Calcined silicate MCM-41 has silanol groups whose silanol protons can be replaced by metal ions. As a metal source, Cu(II) ions were introduced into MCM-41 by an ion-exchange method, and thus copper-modified MCM-41 (Cu-MCM) was obtained. The white MCM-41 (1.0 g) was suspended in 100 mL of the ethanol solution of Cu(II) acetate monohydrate (5.1×10^{-3} or 3.0×10^{-5} mol dm^{−3}), and the suspension was stirred at 298 K for 1 h to reach adsorption equilibrium. After the adsorption equilibrium was confirmed by measuring the absorption spectra of the supernatant containing residual copper ions, the Cu-MCM was removed by filtration, washed with ethanol, and dried at 353 K for 2 h. The light blue Cu-MCM was evacuated at 473 K and 1×10^{-6} Torr for 2 h, and finally pale-greenish gray Cu-MCM was obtained. The XRD pattern of Cu-MCM was essentially the same as that of parent MCM-41. The amount of Cu(II) loaded into the MCM-41 was adjusted by changing the concentration of Cu(II) solution, and it was determined to be 1.5×10^{-4} or 3.0×10^{-6} mol g^{−1} for 5.1×10^{-3} or 3.0×10^{-5} mol dm^{−3} of Cu(II) solution, respectively. Determination of Cu(II) loaded into MCM-41 was carried out by measuring UV–vis absorption spectra of Cu(II) acetate solution before and after the ion-exchange treatment. DCNB was purified by sublimation in vacuo, and white cotton-like crystals were obtained. DCNB was put in a small glass tube (30 mm × 6 mm o.d.), and this small glass tube was placed in another glass tube (90 mm × 15 mm o.d.) that contained Cu-MCM. The latter tube was sealed in vacuo at 1×10^{-6} Torr and heated at 453 K for 12 h. During heating under vacuum, DCNB was sublimed and transferred into Cu-MCM. Cu-MCM became deep blue during the above procedure. The products are designated as [X,Y]-MCM, where X and Y mean initial amounts of Cu(II) and DCNB in molarity, respectively, and X is normalized to 1.5×10^{-4} mol g^{−1}. Three [Cu,-

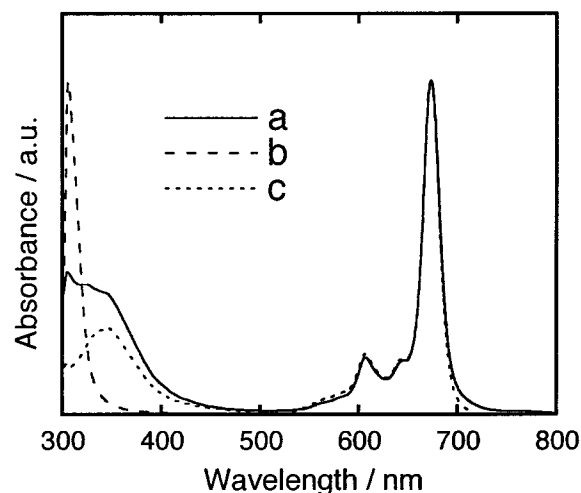


Figure 2. UV–vis absorption spectra of extracts from (a) [1,4]-MCM, (b) DCNB-MCM, and (c) pure CuPc, in pyridine.

DCNB]-MCM samples were prepared; they are [0.02,4]-, [1,4]- and [1,12]-MCMs. As a reference, MCM-41 without Cu(II) was also treated with DCNB (DCNB-MCM) by the same procedure used for [Cu,DCNB]-MCMs.

To identify the products in the MCM-41 channels, [Cu,-DCNB]- and DCNB-MCMs were treated with pyridine by Soxhlet extraction, and UV–vis absorption spectra of extracts were measured (Figure 2, spectra a and b). Figure 2 includes a spectrum of pure CuPc dissolved in pyridine (spectrum c) for comparison. For [Cu,DCNB]-MCMs (Figure 2, spectrum a; only [1,4]-MCM is shown for simplicity), the spectral shape and peak positions are consistent with those of the CuPc in pyridine (Figure 2, spectrum c) in the Q-band region (600–700 nm). This agreement indicates that CuPc was surely formed in [Cu,DCNB]-MCMs. A slight spectral difference is recognized in the Soret-band region (300–400 nm) between spectra a and c (Figure 2). This difference can be ascribed to unreacted DCNB ($\lambda_{\max} = 306$ nm) and intermediates. A mechanism for the reactions of the DCNB with Cu(II) has been proposed; CuPc is formed via oligo-isoidolenine intermediates activated by Cu(II) ions.²³ Thus, a small amount of intermediates are inevitably included in [Cu,DCNB]-MCMs. For DCNB-MCM (Figure 2, spectrum b), only an intense absorption band is observed at 306 nm, and the band can be ascribed to DCNB, which did not react at all without Cu(II) ions. This is also confirmed by the fact that absorption bands corresponding to the Q-band and the Soret-band of Pc cannot be recognized in the spectrum.

Figure 3 shows N_2 adsorption–desorption isotherms for Cu-, [1,4]-, and [1,12]-MCMs. All of these isotherms can be classified as type IV.²⁰ It is easily seen that the adsorbed amount of N_2 reduces with increasing DCNB/Cu ratio. S_a and V_p of these samples were estimated to be 1250 m² g^{−1}, 0.82 cm³ g^{−1} (Cu-MCM); 1190 m² g^{−1}, 0.74 cm³ g^{−1} ([1,4]-MCM); and 1020 m² g^{−1}, 0.64 cm³ g^{−1} ([1,12]-MCM). The reduction of S_a and V_p indicates that materials, including CuPc, were certainly encapsulated within the one-dimensional channels of MCM-41. Since there was not much difference in the XRD patterns among these samples, there

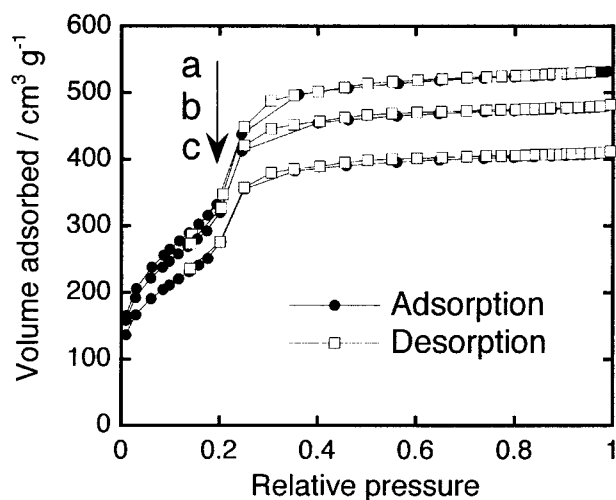


Figure 3. N_2 adsorption–desorption isotherms at 77 K for (a) Cu-MCM, (b) [1,4]-MCM, and (c) [1,12]-MCM. Volume is normalized to standard temperature and pressure.

seems to be no significant collapse of the hexagonally packed array structure during the CVD process.

For comparison with the CVD method, vacuum evaporation was carried out to encapsulate CuPc itself into the channels of MCM-41. MCM-41 was put in a glass tube with pure CuPc and treated in the same way as DCNB-MCM. However, no CuPc was transferred to the MCM-41 channels at all, when the tube was heated at 453 K under the same conditions as used for preparing [Cu,DCNB]-MCMs. When the temperature was raised to 673 K, pale blue product was obtained, indicating deposition of small amount of CuPc. Judging from the color change of MCM-41, the CVD method based on DCNB is effective to produce of CuPc compared with the direct incorporation of CuPc by vacuum evaporation.

It is interesting to consider whether CuPc molecules take a certain arrangement within the MCM-41 channels. To discuss the structural arrangements, diffuse reflectance (DR) spectra were measured using MgO as a dilution medium in an ambient condition. Figure 4 shows the DR spectra of the [0.02,4]-, [1,4]-, and [1,12]-MCM samples; their intensities were calculated by the Kubelka–Munk equation $F(R_\infty)$.²⁴ For each [Cu,DCNB]-MCM, two absorption bands are observed at 690 and 620 nm corresponding to Q-bands of CuPc. Spectral analysis of the Q-band is useful for discussing the Pc–Pc interaction. Although the spectral shape of [0.02,4]-MCM in the Q-band region (Figure 4, spectrum a) is similar to that of pure CuPc in pyridine (Figure 2, spectrum c), the intensity ratio of the band at 620 nm to that at 690 nm increases, and the bandwidth becomes slightly broadened. Generally, when CuPc monomers exist in a good solvent, the most and second-most intense bands in the Q-band region are assigned to the (0–0) and (0–1) transition of monomer, respectively (e.g., Figure 2, spectrum c). The spectral differences in the intensity ratio and the bandwidth are considered to reflect the existence of aggregated species of CuPc, since such spectral characteristics were observed for a small amount of Pc dimers in a poor solvent with Pc monomers.²⁵ The dimer gives a blue-shifted band, which can be ascribed to cofacially stacked species based on the

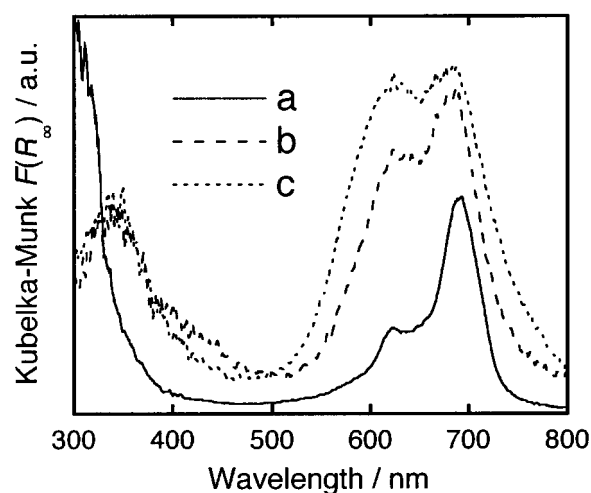


Figure 4. Diffuse reflectance spectra of (a) [0.02,4]-MCM, (b) [1,4]-MCM, and (c) [1,12]-MCM.

molecular exciton theory.²⁶ For the case of [0.02,4]-MCM (Figure 4, spectrum a), the most intense band at 690 nm is assigned to the (0–0) band of monomeric species. On the other hand, the second-most intense band at 620 nm is considered to be composed of both the (0–1) band of monomers and some dimeric species. Although existence of CuPc dimers is recognized in [0.02,4]-MCM, monomer is regarded as the predominant species judging from the low-intensity ratio of the band at 620 nm to the one at 690 nm. Thus, it can be said that the density of CuPc is low and that CuPc molecules are monodispersed in the MCM-41 channels. On increasing the DCNB/Cu ratio such as in [1,4]- and [1,12]-MCMs, the intensity ratio of the band at 620 nm to the one at 690 nm increases remarkably, and no further spectral blue shift is observed (Figure 4, spectra b and c). These results suggest that the amount of cofacial dimeric species increases when more CuPc is produced. From these results, it can be concluded that the amount of CuPc product and molecular aggregation in the MCM-41 channels can be successfully controlled by adjusting the initial amounts of DCNB and Cu(II).

In summary, a “ship-in-a-bottle” synthesis of CuPc within the MCM-41 mesoporous channels was achieved by a CVD method. The DR spectra of [Cu,DCNB]-MCM samples suggested that changing the DCNB/Cu mole ratio could control the intermolecular interaction of CuPc. That is, molecular arrangement can be controlled by the method proposed in this paper, and the proposed method can be extended not only to develop new Pc-based devices, but also to fabricate other functional material systems.

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Supporting Information Available: XRD patterns and N_2 adsorption–desorption isotherms of calcined MCM and modified MCMs, and spectral data of DCNB and extracts

from modified MCMs (9 figures). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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