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Facile, liquid phase preparation of copper phthalocyanine microcrystals by means of thermal conversion of the dimethoxy-substituted solvent soluble phthalocyanine precursors

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ABSTRACT

A simple procedure for the preparation of microcrystals of insoluble copper phthalocyanine (CuPc) by thermolysis of a dimethoxy-substituted precursor has been developed. Although the morphologies of the resultant microcrystals are practically independent from initial solution concentrations higher than ca. 0.03 mM of the dimethoxy-precursor, crystals with increased width are obtained with increasing the initial concentration of the precursor.

1. Introduction

Microcrystals of organic compounds have drawn increasing attention in recent years, because their chemical and physical properties are distinctly different from those of the corresponding bulk crystals or amorphous solids, and therefore, they have been developed as potential candidates for novel materials for electronics and photonics [1,2]. In addition, the material technology based on nano-structural hybrid composites consisting of organic microcrystals and inorganic nanoparticles has been rapidly evolving more recently [3,4]. Although, vapor-phase and liquid-phase methods are established for the preparation of microcrystals of inorganic materials such as metals and ceramics [5,6], preparation techniques for organic microcrystals are still developing. While mechanical crushing or thermal evaporation methods often lead to the decomposition of the compounds or inhomogeneity of the crystal morphologies, the reprecipitation method reported by Nakanishi and co-workers successfully yields microcrystals of a variety of organic materials such as anthracene (AN) and tetrakis(thiohexyl)vanadyl phthalocyanine ($VOPc(C_6S)_4$) [1–3]. In the foregoing methods, the crystal growth is initiated by injecting the solution of an organic material into a vigorously stirred poor solvent. For example, the injection of $VOPc(C_6S)_4$ dissolved in acetone into stirred water or cyclohexane as the poor solvent yields the corresponding highly dispersed microcrystals. It has been reported that the particle size can be controlled by changing the mixing temperature and stirring rate [1]. The reprecipitation method is advantageous in terms of easy operation which enables the preparation of the microcrystals in standard laboratories and is applicable to a wide range of organic materials. However, the applications of this technique to insoluble organic material is problematic because it is difficult to prepare the homogeneous solution of the target compounds.

Copper phthalocyanine (CuPc), has been established as one of the most chemically and physically stable coloring materials, and as a result, a large amount of CuPc has been industrially produced worldwide [7]. In addition, CuPc also shows excellent semiconductor properties and photoconductivity, leading to extensive applications of CuPc to electronic and optoelectronic devices [8]. For these purposes, thin films or nano- and micro-sized particles of pristine CuPc, i.e. CuPc having no substituents, have attracted particular attention. However, CuPc is sparingly soluble in common solvents such as water, alcohols, and hydrocarbons including toluene unless appropriate substituents are introduced to the aromatic skeleton [9], and therefore, solid-phase processes such as vacuum deposition technique are usually employed in order to fabricate thin films or nanoparticles of phthalocyanine complexes

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[10]. As a consequence, reports on the liquid-phase procedures for the preparations of phthalocyanine nano- and microcrystals remain relatively limited [11,12].

Recently, our group has successfully developed a facile synthetic procedure for alkoxy-substituted CuPc precursors by performing the lithium-assisted coupling reaction at lower temperature than that employed for the typical Pc synthesis (see compound **1** in Scheme 1 as an example) [13,14]. Importantly, these precursors exhibit high solubilities in a variety of organic solvents, making the wet coating of **1** onto a substrate possible. Upon heating the substrate, the two methoxy groups substituted at the diagonally opposed positions of the pyrrole α-carbons in **1** are eliminated to yield thermodynamically more stable aromatic CuPc. Recently, solution-processed small molecule organic photovoltaic devices, by taking advantage of compound **1** as one of the key materials, have been fabricated [15].

In the present paper, we report procedure for the preparation of microcrystals of CuPc by employing compound **1** as the starting material. Since **1** is soluble and the resultant CuPc is insoluble in general organic solvents, formation of crystalline CuPc is anticipated by conducting the thermal conversions of **1** in solution. In addition, it is also expected that the rate of the crystal growth depends on the initial concentration of **1**, i.e. the higher concentration results in the increased growth rate and vice versa.

2. Material and method

Compound **1** was prepared according to our method [13,14]. Field emission scanning electron microscopy (FESEM, JEOL JSM-7500F) was used to obtain surface images of the obtained microcrystalline samples.

2.1. Preparation of CuPc microcrystals starting from different initial solution concentrations (conc.)

(a) *conc.* = 0.010 mM

Compound **1** (1.0 mg) dissolved in toluene (150 mL) was added to a 200 mL three-necked round-bottom flask, and the colorless solution was heated at 120 °C with stirring for 1 h. A portion of the resultant blue solution (100 mL) was filtered by using a PTFE membrane filter (ADVANTEC T020A025A, pore size = 0.20 μm), and the filtrate was added to cooled methanol (100 mL). The solution was concentrated to ca. 20 mL in vacuo, and the formed blue precipitate was collected by filtration.

(b) *conc.* = 0.029 mM

Compound **1** (2.76 mg) dissolved in toluene (150 mL) was added to a 200 mL three-necked round-bottom flask, and the colorless solution was heated at 120 °C with stirring for 1 h. The resultant blue suspension was filtered by using a PTFE membrane filter to collect the formed CuPc microcrystals.

(c) *conc.* = 0.11 mM

Compound **1** (0.68 mg) was added to a pressure-proof sealed pyrex glass tube containing 10 mL of toluene, and the solution was heated at 120 °C with stirring for 1 h. The resultant suspension was centrifuged (1000 rpm, 3 min) and the supernatant liquid was removed by decantation. The residue was washed with toluene, and the formed CuPc microcrystals were collected by filtration.

(d) *conc.* = 0.92 mM

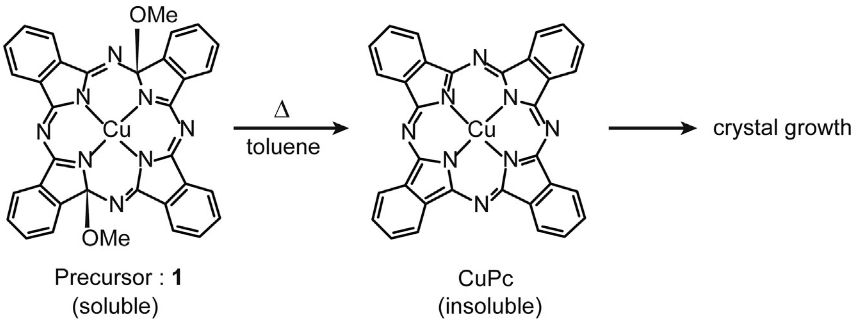
Similarly to the procedure described in (c), CuPc microcrystals were prepared from **1** (5.84 mg) dissolved in toluene (10 mL).

3. Results and discussion

3.1. Thermal conversion in the solution phase

The solution of **1** in toluene is almost colorless at room temperature, and exhibits no characteristic band components for CuPc in the absorption spectrum (Fig. 1(a)). At the initial solution concentration of 0.010 mM, the homogeneous blue solution containing the generated CuPc was obtained after heating the solution at 120 °C for 1 h with a vigorous stirring, (Fig. S1 in Supporting Information). Suction filtration of the resultant toluene solution shortly after the heating by using a PTFE membrane filter (ADVANTEC T020A025A, pore size = 0.20 μm) gave no blue residues on the filter, indicating that the thermally generated CuPc in toluene is either dissolved or suspended as the CuPc particles less than 0.2 μm in size. In order to promote the formation of the precipitates, an equivalent volume of cold methanol was added to the filtrate followed by ten-fold concentration in vacuo as the follow-up process. The obtained blue precipitate, accordingly, was examined by the FESEM experiments (see below). Attempts at centrifugal separation of the crystals without the follow-up process were unsuccessful. Although our previous thermogravimetric analyses of **1** in the crystalline solid phase indicate that **1** is thermally stable at temperatures lower than 200 °C [13,14], we have observed in the present paper that **1** is converted into CuPc at the temperature of as low as 120 °C in the liquid phase.

Upon increasing the initial concentration of **1**, deeper colored solutions predictably resulted but which contained clearly discernible precipitates which were obtained without performing the follow-up process. Centrifugal separation of the solutions gave the blue CuPc precipitates and the pale yellow supernatant liquid, supporting that the formed CuPc is practically insoluble in toluene at higher concentrations than ca. 0.03 mM.



Scheme 1. Preparation of microcrystals of CuPc.