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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

Takamitsu Fukuda*, Naoto Ishikawa*

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

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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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* Corresponding authors. Tel./fax: +81 6 6850 5410.
E-mail addresses: tfukuda@chem.sci.osaka-u.ac.jp (T. Fukuda), iskw@chem.sci.osaka-u.ac.jp (N. Ishikawa).

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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

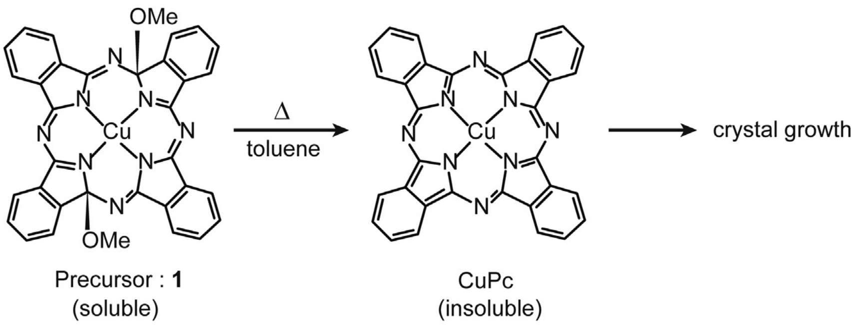
Similarly to the procedure described in (c), CuPc microcrystals were prepared from **1** (5.84 mg) dissolved in toluene (10 mL).

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.

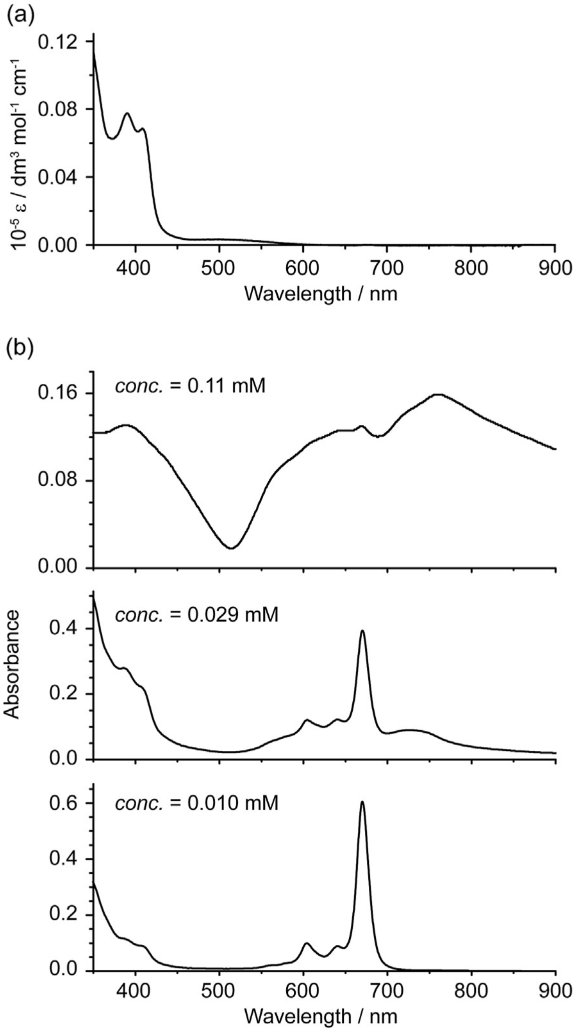


Fig. 1. Absorption spectra of dimethoxy-substituted precursor, **1**, in trichlorobenzene (a), and thermally formed CuPc solution/suspensions in toluene (b). Initial concentrations of **1** before the thermal conversions are 0.11, 0.029, and 0.010 mM from top to bottom, respectively.

3.2. *Electronic absorption spectra*

Fig. 1(b) displays the absorption spectra of the thermally treated toluene solutions of **1**. Note that the spectra were obtained immediately after the thermal treatments so that the crystal growth during the cooling process can be avoided as much as possible. The line shape of the spectra depend significantly on the initial concentrations of **1**. At *conc.* = 0.11 mM, the absorption spectrum exhibits the broad bands beyond 500 nm with the peak maxima at 760, 670, and 389 nm, which is characteristic of the crystalline metallo Pcs (Fig. 1(b), top) [16]. On the contrary, at *conc.* = 0.010 mM, the observed spectrum exhibiting the prominent absorption band (Q-band) at 670 with some accompanying vibronic progression bands in the shorter wavelength side is almost identical with that observed for CuPc dissolved in 1,2,4-trichlorobenzene (Fig. 1(b), bottom) [13]. At the intermediate concentration, *conc.* = 0.029 mM, the observed spectrum contains both characteristics, i.e. both the sharp band at 670 nm and low-lying broad components appear in the spectrum, suggesting that the generated CuPc is partially dissolved in toluene (Fig. 1(b), middle).

3.3. *Field emission scanning electron microscopy*

The FESEM images of the obtained CuPc precipitates collected by using PTFE membrane filters after the follow-up process (a) or right after the thermal process (b-d) are displayed in Fig. 2. For the purpose of comparison, the FESEM image of commercially available CuPc pigment (β-form, TCI P1006, C.I.-74160) is provided in Fig. S2 (Supporting Information). In the case of *conc.* = 0.010 mM, the presence of two distinct crystal morphologies having either fibrous or prismatic appearances can be perceived in the image (Fig. 2(a)). The crystals having the former morphology are obviously larger than 0.2 μm in length, indicating that these are grown during the follow-up process. The latter submicron crystals have comparable sizes to the pore size of the membrane filter. It is difficult to unambiguously determine whether these are generated during the thermal conversion process or in the course of the successive follow-up process based on the absorption spectra only. However, it can be speculated that these are likely formed from the dissolved CuPc rather than the direct formation during the thermal conversion process. The formed submicron crystals are 'combed' by the simultaneously generated fibrous crystals. At *conc.* = 0.029 mM, all

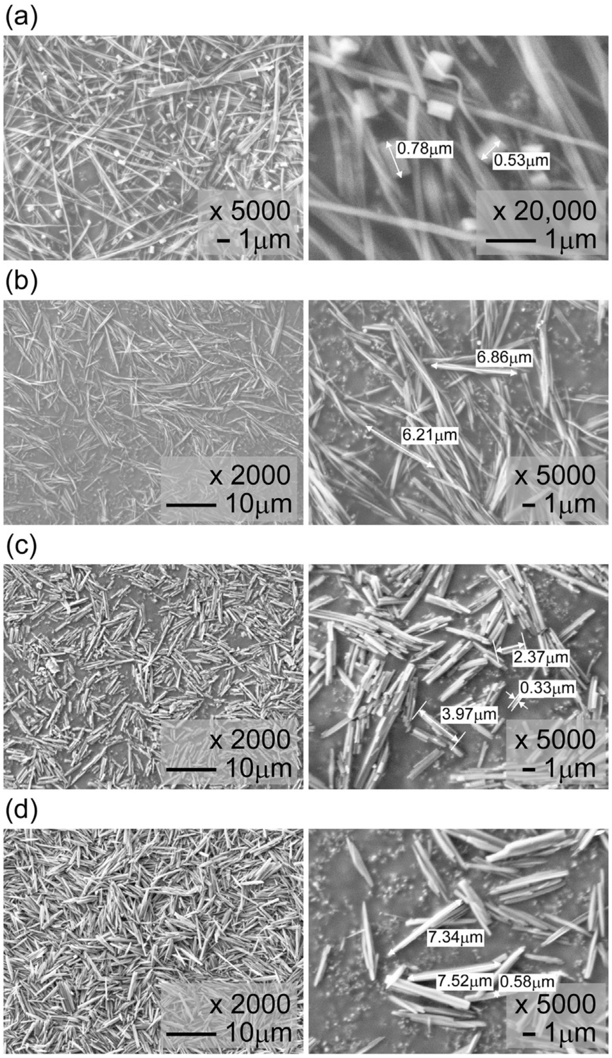


Fig. 2. FESEM images of CuPc microcrystals prepared by the thermal conversions with the initial concentrations of **1** at (a) 0.010, (b) 0.029, (c) 0.11, and (d) 0.92 mM. Note that the crystals in (a) are obtained after the follow-up process of the original reactant, while the others are collected directly from the reactants by suction filtrations by using PTFE membrane filters.

of the observed crystals are fibrous type, and no small block crystals are recognized. The crystals are approximately 6–7 μm in length. It is conceivable that these fibrous crystals are responsible for the broad components of the absorption spectrum. Since no small block crystals were 'combed' by the fibrous crystals in this case, the sharp Q-band appearing in Fig. 1(b) (middle) can be ascribed not to the suspended submicron crystals but to the dissolved CuPc, also supporting our speculations on the formation mechanism of the submicron crystals at *conc.* = 0.010 mM. At the initial concentrations of **1** higher than 0.11 mM, the observed FESEM images exhibit similar appearances to each other (Fig. 2(c) and (d)). While the length of the obtained crystals is comparable to those observed at *conc.* = 0.029 mM, it is likely from the FESEM images that broader crystals in average are generated with increasing the initial concentrations (See Fig. 2(c) and (d) for numerical comparison of the crystal sizes). The thermal conversion of **1** in acetone instead of toluene at 120 °C for 1 h (*conc.* = 0.16 mM) by using a pressure-proof sealed pyrex glass tube gave similar crystal appearances, implying that the interactions between the solvent and formed CuPc are less significant for the crystal growth (see Fig. S3 in Supporting Information for the FESEM image).

4. Conclusions

In summary, we have demonstrated that a simple thermal treatment of a soluble dimethoxy-substituted CuPc precursor, **1**, dissolved in toluene successfully produces microcrystals of insoluble CuPc. Although the size of the crystals in length shows no significant dependence on the initial concentration of **1** higher than 0.029 mM, thicker crystals are observed by employing higher concentrations. While the, so-called, acid pasting method is excellent procedures for converting the phthalocyanine compounds into industrially useful bright pigment materials having relatively large grain sizes (Fig. S2 in Supporting Information) [17], our thermal conversion method performed in the liquid phase is advantageous for the facile preparation of microcrystalline CuPc materials. In addition, the observations of submicron CuPc crystals by employing the sufficiently low initial concentrations of **1** indicate that the thermal conversion process is also potentially useful for preparing nano CuPc crystals.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2014.05.021.

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