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A novel method for the direct synthesis of crystals of copper phthalocyanine

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Abstract

A novel, solvothermal method for directly growing crystals of the β-form of copper phthalocyanine that involved using quinoline as solvent and cooling the reaction mixture to room temperature is proposed. Needle-like, single crystals of CuPc up to 10 mm in length were prepared using 1,3-diiminoisoindoline and $Cu(AcO)_2 \cdot 2H_2O$ in the quinoline solvent. The influence of the temperatures, growth time and solvent volumes on crystal yield were determined.

Keywords: Solvothermal synthesis; Single crystal; CuPc; Quinoline

1. Introduction

Recently, there has been much interest in electronically functional organic molecules in relation to various applications such as organic photoreceptors, electroluminescent devices [1–3], and transistors [4–6]. Physical studies of not only thin films but also single crystals of the materials are required for understanding and refining organic electronic devices. However, few conventional methods can grow large single crystals of functional organic materials, because most of the materials have low vapor pressure, do not have suitable solvent, and often decompose at temperatures near their melting point.

Phthalocyanines are examples of the electronically functional organic molecules. Laudise et al. had grown CuPc crystals of 5 mm in length by physical vapor growth method [7]. This method, however, requires cautious selection and precise flow control of an inert gas. Therefore, there exists a need for convenient method of growing large single crystals of the functional organic molecules.

In our work, we have proposed a new method for the synthesis of single crystals of CuPc by using quinoline as a solvent. In other words, we have succeeded in preparing crystals of CuPc by using a more convenient method than previous ones [7,8]. We call this method the solvothermal synthesis method.

2. Experimental procedure

2.1. Instruments and materials

2.1.1. Instruments

Mass spectrometer measurements were obtained on a LDI-1700-TOF (Shimadzu) mass spectrometer. Elemental analyses were carried out on a Flash EA1112 Elemental Analyzer. X-ray diffraction pattern was collected by using a Regaku R-AXIS RAPID IP 4-circle X-ray diffraction meter.

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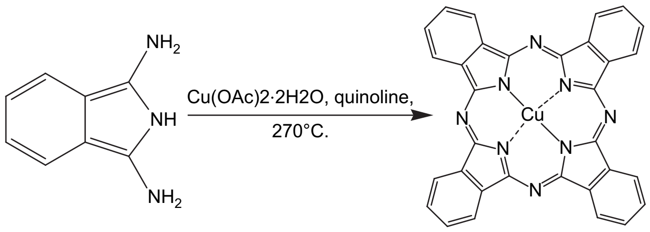

Fig. 1. Synthesis method of CuPc.

2.1.2. Materials

All compounds used in the experiment were commercially available and used directly without further purification.

2.2. Experimental procedure

2.2.1. Single crystal of CuPc

The mixtures of 1,3-diiminoisoindoline (0.058 g, 0.4 mmol) and $Cu(AcO)_2 \cdot 2H_2O$ (0.0217 g, 0.1 mmol), using quinoline (10 ml) as solvent were heated in autoclave (50 ml) under 270 °C for 8 h. Then the mixture was cooled to room temperature. Purple crystals of CuPc were obtained after removal of the solvent (Yield: 0.02954 g, 51.3%). The total reaction is shown in Fig. 1. MS: $m/z = 574.7$ (calcd. 575.05) is shown in Fig. 2. Elemental analysis: ($C_{32}H_{16}CuN_8$, FW: 575.08), found: C 66.68, H 2.89, Cu 11.11, N 19.39, theoretical calculation: C 66.72, H 2.80, Cu 11.03, N 19.45.

3. Results and discussion

3.1. Single crystal X-ray structure

Fig. 3(a) shows a plot of the molecular conformation of CuPc got from Regaku R-AXIS RAPID IP 4-circle X-ray diffraction. Fig. 3(b) shows the crystal-packing diagram of CuPc. The molecular formula of CuPc is $CuN_8C_{32}H_{16}$, belonging to monoclinic system. The space group is $P2_1/n$, Unit cell parameters: $a = 14.668(3)$, $b = 4.8109(10)$, $c = 19.515(7)$, $\alpha = 90$, $\beta = 121.04(2)$, $\gamma = 90$, cell volume is 1179.91 Å^3. Fig. 4 is the X-ray polycrystalline diffraction (XRD) spectrum. From Fig. 4, we find that the position and the intensity of the diffraction peak are in conformity with the standard card, which proves that the crystals belong to β-form crystalline [8–11].

3.2. Discussion of optimum condition

3.2.1. Temperature and time

The search of optimum reaction condition is important to obtain the highest crystal yield. Different reaction conditions such as temperatures and the length of reaction times were altered under the same reaction solvent volume (10 ml). The temperature was changed at the rate of 30 °C from 180 to 270 °C while the time was changed at the rate of 1 h from 2 to 10 h, as shown in Fig. 5. With the same solvent volume, we found that the highest yield was under the condition of 270 °C and 8 h. The crystal yield decreased when the temperature was higher than 270 °C, because the inner wall of autoclave would be destroyed at such high temperature. The single crystals could not be entirely grown, if the temperature was lower than 270 °C or the reaction time was shorter than 8 h.

3.2.2. Solvent volume

The yield of crystals in different volumes of solvent in the reaction materials is shown at different temperatures for 8 h, in Fig. 6. Three data indicate that the yields of the crystals are different under different reaction solvent, and the largest yield was achieved at 10 ml under 270 °C. When the solvent volume

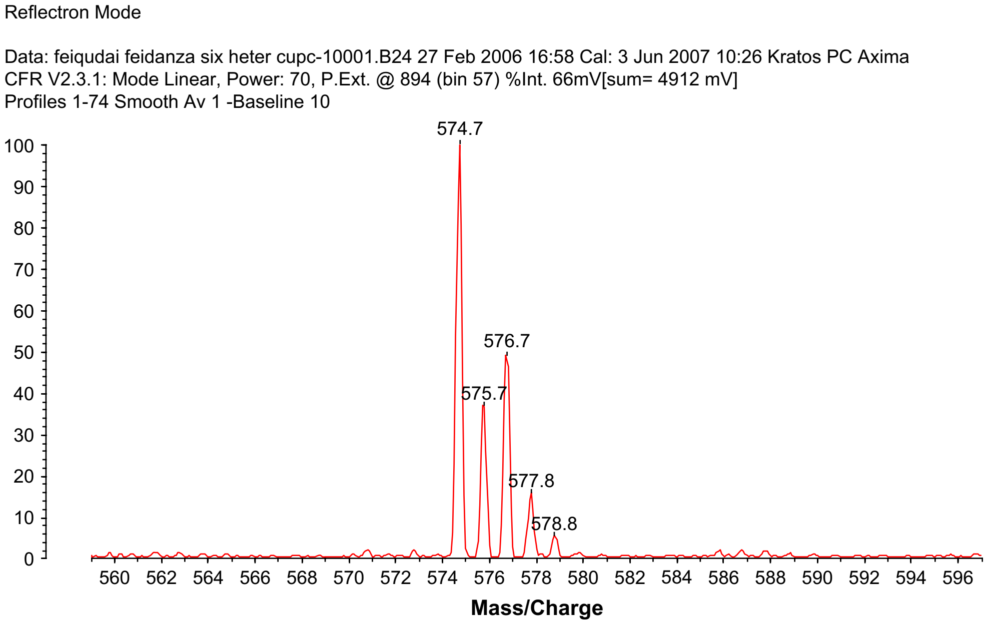

Fig. 2. Mass spectrum of CuPc.

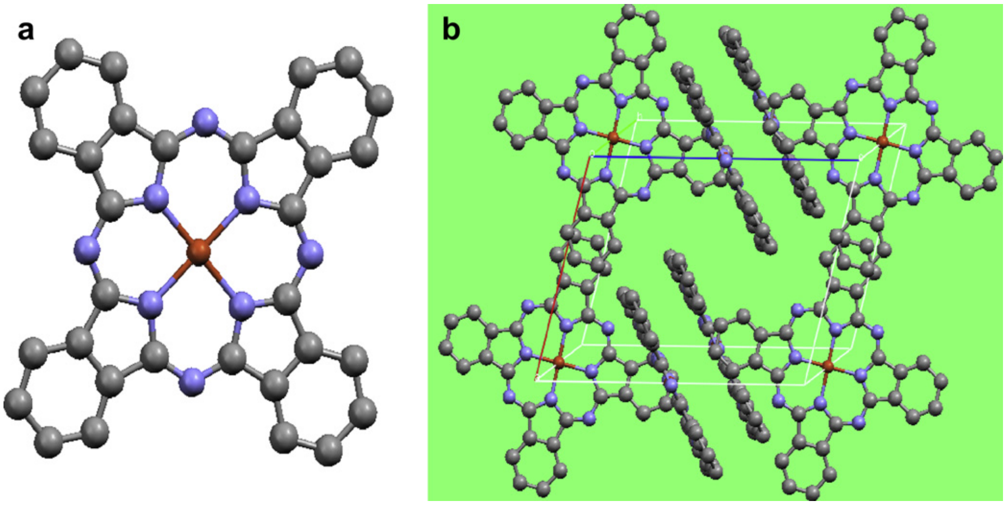

Fig. 3. (a) The structure of CuPc (white: H; grey: C; blue: N; green: Cu). (b) Crystal-packing diagram of CuPc. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

was larger than 10 ml, the solutes were easy to isolate and crystals aligned altogether in the autoclave wall. When the solvent volume was smaller than 10 ml, many solutes were not completely dissolved and the single crystals could not be perfectly grown. All these factors would affect the growth of the crystals. The optimal volume of quinoline was 10 ml under 270 °C in our experience.

3.3. The size of CuPc crystals

The crystals grew away from the solution, so it could not get the supplement of the solute in the width and the thickness. Most crystals were very thin with width of 15–50 μm and thickness of 5–30 μm, as shown in Fig. 7. Size distribution

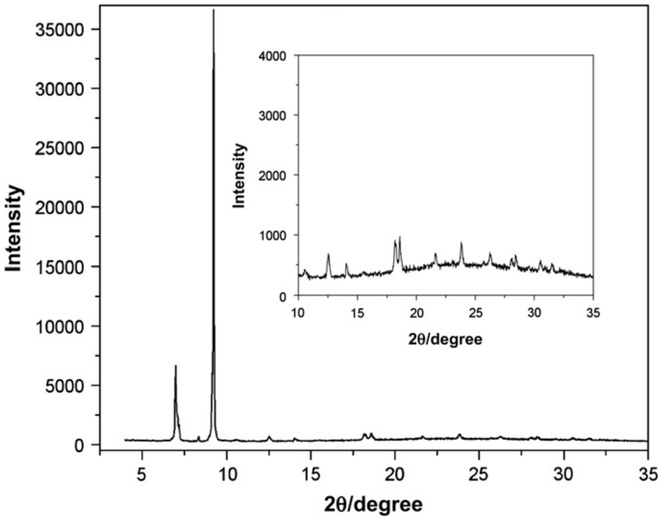

Fig. 4. XRD spectra of CuPc.

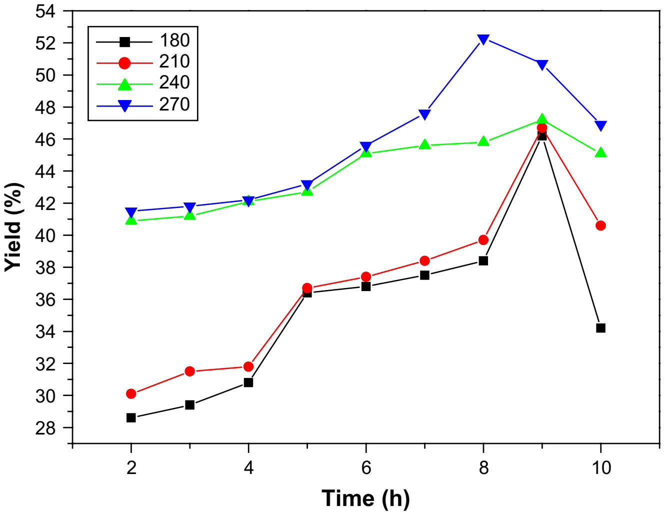

Fig. 5. The crystals synthesized with different reaction times at 180, 210, 240 and 270 °C.

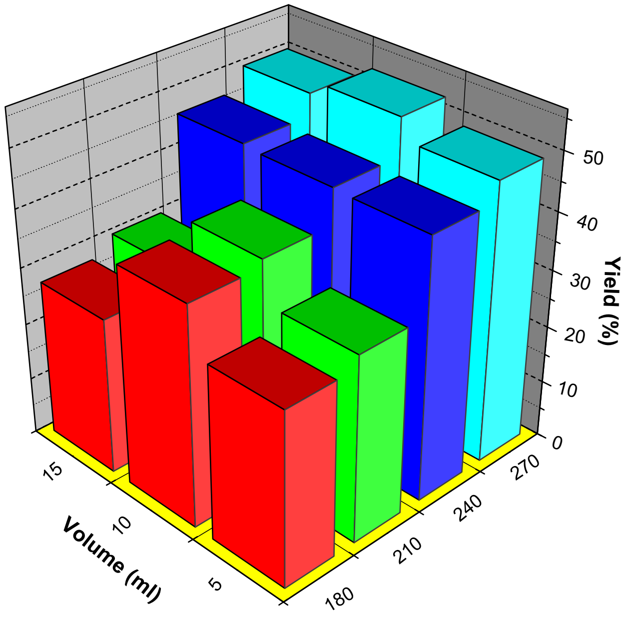

Fig. 6. The crystals synthesized with different solvent volumes at 180, 210, 240 and 270 °C.

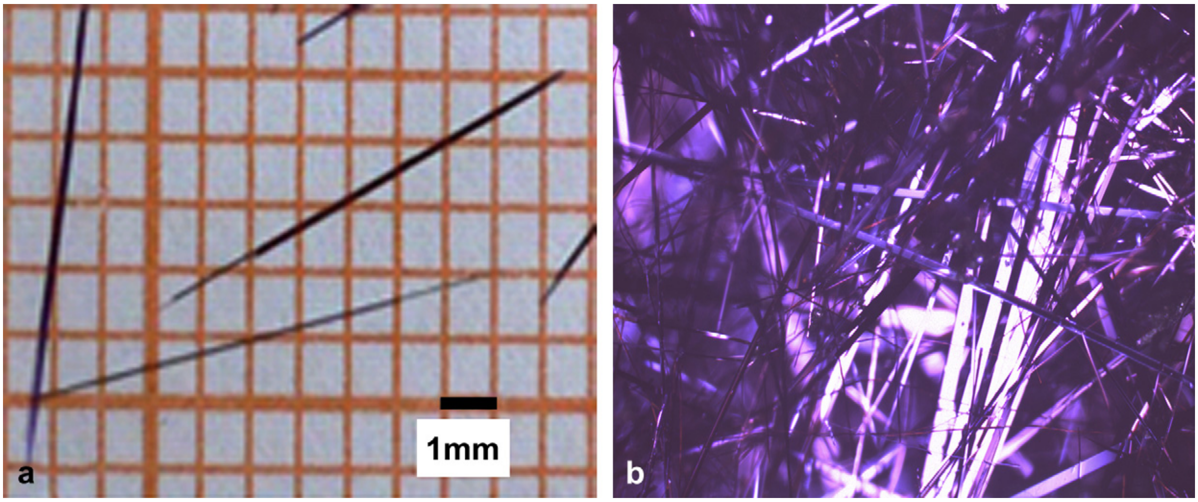

Fig. 7. (a) Optical micrographs of several CuPc single crystals which we picked, (b) Surface of CuPc crystals under 50-time microscope.

of CuPc single crystals synthesized under different reaction times at 270 °C is shown in Fig. 8. It can be seen that crystals with a length of 10 mm were the longest in our experiment when reaction time was 10 h.

Many tiny single crystals of nearly 0.2 mm in length could be observed at the bottom of autoclave. These tiny crystals were formed at the moment when the reaction mixture was cooled to room temperature. This perhaps is due to the fact that the cooling speed was too fast to get high quality crystals.

In the traditional physical vapor deposition method [7], the CuPc crystals were short, and the longest one that had been reported was about 5 mm. Miyahara and coworkers [12–14] used anthracene as solid solvent to grow the phthalocyanines crystals after three growth periods (80 h) [12,13]. In our solvothermal synthesis method, long crystals near 10 mm were generated by directly cooling the solution to room temperature. Longer crystals can be fabricated if a large autoclave is used. More importantly, it was only 8 h needed in our experiment and the yield of CuPc crystal was 52.3%.

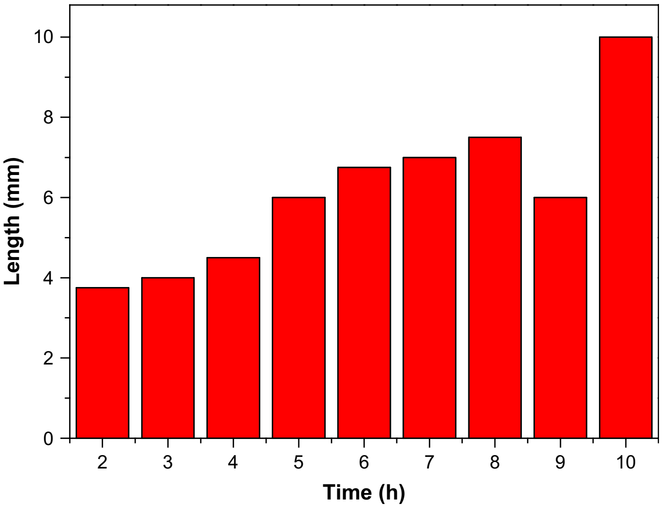

Fig. 8. Size distribution of CuPc single crystals synthesized under different reaction times at 270 °C.

4. Conclusion

We have proposed a convenient novel method for preparing single crystals of functional molecular materials, by using quinoline as a solvent. We named the method as the solvothermal synthesis method. Needle-like single crystals of CuPc up to 10 mm in length were prepared by cooling of autoclave which contained 1,3-diiminoisoindoline and $Cu(AcO)_2 \cdot 2H_2O$ in quinoline solvent. The crystals tend to grow larger in a larger autoclave.

Optimum reaction condition of crystal synthesis was under 270 °C for 8 h in 10 ml quinoline in our experiments. Moreover, this method may be easily applied in the crystal synthesis for other organic materials, and acts as an important part both in scientific experiments and in industrial productions. CuPc crystals are directly obtained using solvothermal synthesis method, which will be widely used and produced in large quantities in industry in the near future.

Acknowledgments

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