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Facile one-pot preparation of thermally and photochemically convertible soluble precursors of copper phthalocyanine and naphthalocyanine†

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Soluble copper phthalocyanine (CuPc) and naphthalocyanine (CuNc) precursors which can be converted thermally and photochemically into insoluble CuPc and CuNc, respectively, have been synthesized by a one-step reaction using commercially available chemicals.

Since the first manufacture of the copper complex of phthalocyanine (Pc) as a light and heat resistant robust blue pigment by Imperial Chemical Industries (ICI) in 1935, Pcs have been employed mainly as colorants for paints and plastics, leading to a large amount of industrial production of Pcs worldwide.¹ In the past two or three decades, Pcs have also been developed as advanced materials for optical disks, photosensitizers for photodynamic cancer therapy, photovoltaic cells, organic semiconductors, and so forth, due to their unique photophysical, electrochemical, and catalytic properties.² Unsubstituted Pcs are practically insoluble in water, alcohols, and hydrocarbons because of their highly planar, rigid structures,³ so that many of the Pc derivatives appearing in the applications have substituents in order to increase the solubilities to desired solvents. However, the presence of these substituents can degrade the performance of the Pcs in certain cases. For example, the mobilities of Langmuir–Blodgett (LB) film-based organic field effect transistors (OFETs) fabricated from substituted Pcs are far below those of vacuum-deposited films prepared from unsubstituted Pcs.⁴ Of the unmodified Pcs, copper phthalocyanine (CuPc) has attracted particular attention because of its excellent transfer mobility of OFETs and exciton diffusion lengths for thin-film organic photovoltaics (OPVs), making CuPc the most widely investigated Pc semiconductor material.^{4,5} Although most of the studies have employed the

vacuum deposition technique to fabricate thin-films of CuPc in order to overcome the low solubility problem, this method is unfavorable with respect to facile, large-scale production of the organic electronic devices. Furthermore, vaporization of copper naphthalocyanine (CuNc), a larger CuPc congener having four naphthalene moieties instead of the peripheral four benzene units in CuPc, is generally problematic due to its larger molecular weight, although the higher HOMO energy level and the narrower HOMO–LUMO band gap of CuNc compared to those of CuPc possibly contribute to an improvement of the energy-conversion efficiency of OPVs.⁶ As a solution to the low solubility problem, Ono and coworkers have developed soluble bicyclo[2.2.2]octadiene (BCOD)-fused porphyrin derivatives which can be quantitatively converted into the corresponding insoluble tetrabenzoporphyrins by heating the precursors at 180–220 °C.⁷ Later, this strategy has been extended to Pcs and Ncs by the same group,⁸ although synthetic difficulties and low solubilities of these precursors prompted the researchers to prepare more soluble acetone-protected precursors.⁹

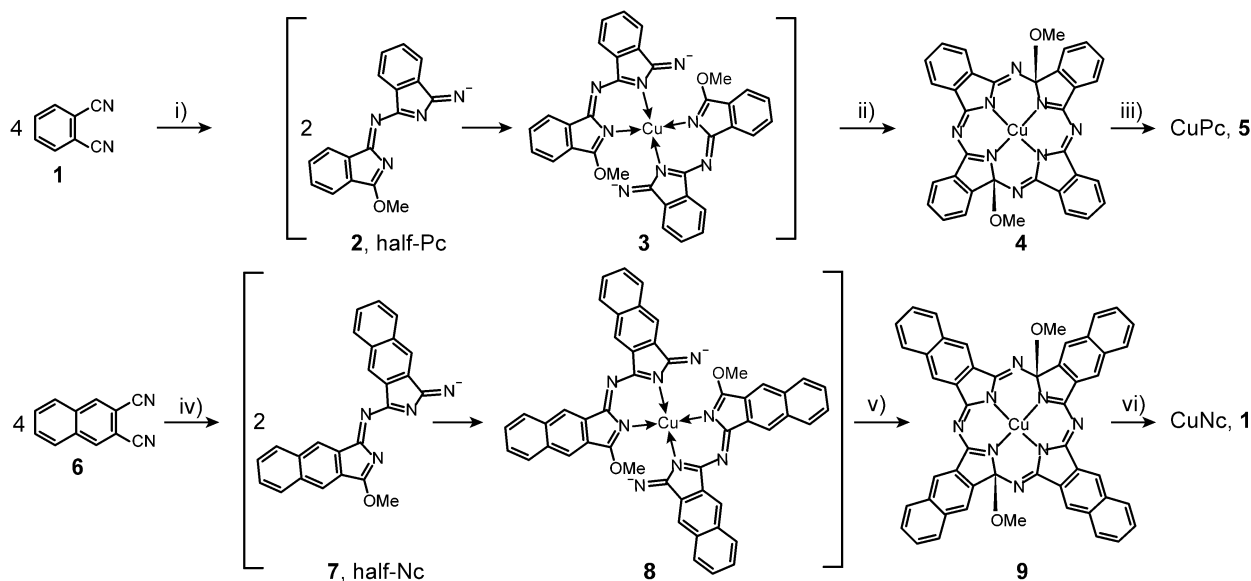
Herein, we report an easy, one-pot preparation of thermally and photochemically convertible soluble CuPc and CuNc precursors by employing the lithium alkoxide-mediated reaction, starting from commercially available chemicals under mild conditions. The reaction of phthalonitrile with lithium alkoxides such as LiOC₃H₁₁ and LiOC₆H₁₃ is often employed for Pc synthesis.¹⁰ This reaction is thought to be initiated by nucleophilic attack of the alkoxide on the cyano groups of phthalonitriles, to give a so-called half-Pc intermediate (**2**, Scheme 1), followed by the coupling of two half-Pc units and elimination of the alkoxy groups, to generate the Pc skeleton.¹¹ Although the intermediate **3** generated during the reaction has not been isolated to date, the structure shown in Scheme 1 is the most likely species.^{11a,12} As a consequence, we considered that non-planar soluble Pc or Nc precursors which can be converted into insoluble Pc or Nc, respectively, could be anticipated when the lithium method is conducted under moderate reaction conditions. In this communication, synthetic procedures for dialkoxy-substituted CuPc and CuNc, **4** and **9** (Scheme 1), have been developed, and their thermal and photochemical conversion processes to CuPc and CuNc in both solution and the solid state have been investigated.

Scheme 1 depicts the synthetic protocols employed in this study. For the synthesis of **4** and **9**, phthalonitrile or

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Scheme 1 Synthesis of Pc and Nc precursors **4** and **9**. Conditions: (i and ii) lithium, CuCl₂, MeOH, 70 °C, 0.5 h, 33%; (iii) 250 °C, (iv and v) lithium, CuCl₂, MeOH, 70 °C, 0.5 h, 6.2%, (vi) 250 °C.

2,3-naphthalenedicarbonitrile was first treated with lithium methoxide in methanol at 70 °C for 10 min. The reaction was continued for an additional 30 min in the presence of copper(II) chloride. After chromatography, the pure forms of **4** and **9** were obtained in 33 and 6.2% yields, based on the dinitriles, respectively. X-Ray quality single crystals of **4** and **9** were grown by slow concentration of methanol solutions.† The ORTEP views of **4** and **9** shown in Fig. 1 clarify that both complexes are isostructural and have two methoxy groups at

the diagonal pyrrole α -carbons in the *syn*-conformation fashion. The presence of sp³-hybridized carbons at C1 and C17, and C1 and C25 for **4** and **9**, respectively, is responsible for the distortion of the molecular skeleton, while each isoindole unit maintains a flat conformation. As a result, the conjugation orders are halved compared to Pc or Nc. The dihedral angles of 119.89° (N8–C1–N1–C8) and 130.70° (N4–C17–N5–C24) for **4**, and 122.90° (N8–C1–N1–C12) and 131.43° (N4–C25–N5–C36) for **9** render the observed bent structure of the macrocycles. The bond distances of 1.479 (C1–N1) and 1.494 Å (C17–N5) for **4** are markedly longer than those of C8–N1 and C24–N5 (1.316 and 1.321 Å, respectively), suggesting a single-bond nature of the former two bonds. McGaff and co-workers obtained similar *syn*-alkoxy-substituted NiPc derivatives by conducting solvent-thermal reactions of nickel acetate tetrahydrate with phthalonitrile in either methanol or ethanol at 70–90 °C for 4–6.5 days.¹³ We have also reported the analogous system, in which a highly deformed Pc analogue dissolved in toluene containing methanol is spontaneously converted into the corresponding dimethoxy-substituted derivative.¹⁴ The copper complexes **4** and **9** are moderately soluble in methanol and soluble in acetone, toluene, THF, CH₂Cl₂ and CHCl₃.

The thermal conversion processes of **4** and **9** were investigated by thermogravimetric analysis (TGA). Micro-crystalline samples were prepared from CH₂Cl₂/hexane, and placed under vacuum at room temperature prior to the measurements, in order to remove the solvated molecules as much as possible. Fig. 2 (dashed line) demonstrates that the weight loss of **4** in the course of the rise in temperature starts beyond ca. 180 °C, and finally reaches 10% at ca. 250 °C. The color of the sample changed from dark red to dark blue. The theoretical weight loss between **4** and CuPc of 9.7% suggests that **4** was quantitatively converted into CuPc as a result of the thermal treatment. In the case of **9**, the total weight loss of ca. 7.0% is also consistent with the theoretical value (7.4%). Although we are unsure whether the elimination of the methoxy groups

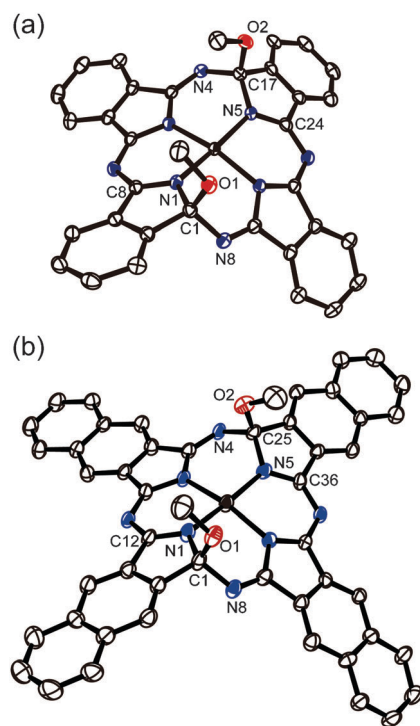


Fig. 1 ORTEP representations of (a) **4** and (b) **9** (50% ellipsoids). Hydrogen atoms and solvent molecules are omitted for clarity. The selected numbering system used in the analysis is depicted.

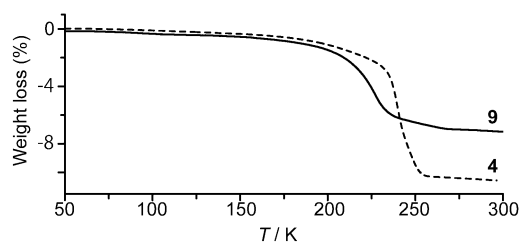


Fig. 2 Weight loss of **4** (dashed line) and **9** (solid line) during the course of thermal elevation under nitrogen. Scan rate = 5.0 K min⁻¹.

occurs in the radical or anion form, it is conceivable that the generated CuPc or CuNc skeleton received missing electrons from the air. Results of the elemental analyses of the products (found C, 66.51; H, 2.83; N, 19.22%, calcd for C₃₂H₁₆N₈Cu (CuPc): 66.72; H, 2.80; N, 19.45%; found C, 72.79; H, 3.02; N, 14.10%, calcd for C₄₈H₂₄N₈Cu (CuNc): C, 74.26; H, 3.12; N, 14.43%) are also consistent with the thermal formation of CuPc and CuNc. Comparison of the X-ray powder diffraction pattern of the generated CuPc with that provided in the literature suggests that the generated crystalline powder can be characterized as the so-called α -phase CuPc (Fig. S1, ESI[†]).^{15,16}

In order to observe spectral changes associated with the transformations, the thermal conversions were attempted in solution. As shown in Fig. S2a and b (ESI[†]), compounds **4** and **9** have practically no absorption bands above 500 nm in 1,2,4-trichlorobenzene (TCB). Upon heating at 180 °C, prominent Q absorption bands appeared at 676 and 775 nm for **4** and **9**, respectively. The spectral shapes and energies are strongly indicative of the formation of CuPc and CuNc in TCB.^{17–19} Fig. 3 shows the color appearance observed before and after the thermal conversion processes. In the solution phase, an almost colorless dilute solution of **4** in TCB turned into the sky-blue of CuPc as a result of heating the solution at 180 °C for 20 min (Fig. 3a). A colorless coating on an ITO glass electrode by using **4** dissolved in acetone can be converted thermally into an insoluble, blue CuPc thin-film by heating at as low as 85 °C for *ca.* 1 min (Fig. 3b), indicating that the conversion temperature depends on the morphologies of **4**. Conversion of **4** into CuPc can also be achieved photochemically. Fig. S2c (ESI[†]) displays the spectral changes in the course of photo-irradiation of **4** dissolved in TCB. Upon photo-irradiation by a deuterium lamp at room temperature, the Q band at 676 nm gained intensity, clearly indicating the formation of CuPc. A similar experiment was also performed for **9**, which, however, resulted in the severe decomposition of the compound.

In summary, we have succeeded in developing facile synthetic procedures for *syn*-dimethoxy substituted CuPc or CuNc

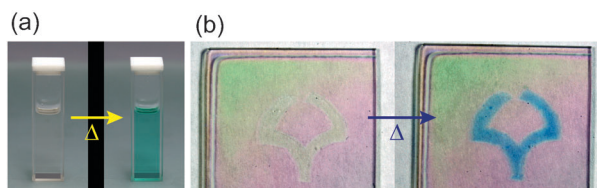


Fig. 3 Thermal transformation of **4** into CuPc (a) in TCB (180 °C for 20 min) and (b) on an ITO glass electrode (85 °C for *ca.* 1 min).

precursors, **4** and **9**, through the reaction of commercially available phthalonitrile or 2,3-naphthalene-dicarbonitrile with lithium methoxide. Bent conformations of **4** and **9** due to the presence of the internal sp³ carbons are responsible for the increased solubilities of these complexes in common organic solvents. Thermal and photochemical conversions of the precursors into CuPc or CuNc were examined by thermogravimetric and photometric analyses, as well as by visual demonstration of the color changes. In addition, we could even perform calligraphic painting using ‘insoluble’ CuPc, which implies that our compounds can also be applied to novel functional colorants (see Fig. S3, ESI[†]). Our method is superior in terms of cost and ease of preparation, compared to the previous Pc precursors.

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