Soluble precursors of 2,3-naphthalocyanine and phthalocyanine for use in thin film transistors†

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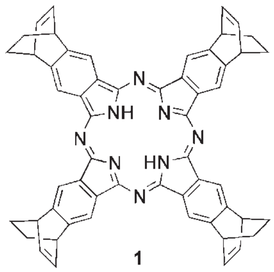
Soluble precursors of 2,3-naphthalocyanine (Nc) and phthalocyanine (Pc) were prepared and were converted into insoluble semiconducting thin films of Pc and Nc by heating after fabrication *via* spin-coating.

Organic semiconductors have emerged as an important class of new materials with applications, for example, in organic light emitting diodes, organic photovoltaics (OPVs), and organic field-effect transistors (OFETs).[1–6] Various organic compounds such as acenes, oligomeric thiophenes, and other π-conjugated molecules have been used as semiconductors in these applications. Among these, phthalocyanines (Pcs) and 2,3-naphthalocyanines (Ncs) are especially attractive, for they absorb strongly in the near IR region, and possess remarkable thermal and photochemical stability. Hence, they have been studied widely as semiconducting materials. The mobilities of vacuum-deposited Pc films were generally found to be in the range 10^{-5}–10^{-3} cm^2 V^{-1} s^{-1},[7–10] while a single-crystal CuPc-based OFET afforded the highest mobility of 1.0 cm^2 V^{-1} s^{-1}.[11] Langmuir–Blodgett (LB) films of Pcs have also been used for OFETs, which showed high performance.[12,13] The red-shifted electronic absorption maxima and photoconductive properties of Nc make it more suitable than Pc for application in OPVs. However, there have been no reports on thin films of Nc due to difficulties in its vaporization. In this paper we report a new method of obtaining thin films of Pc and Nc from soluble precursors with thermally removable groups. We have already developed a new method of making thin films of tetrabenzoporphyrins (TBPs) from their soluble precursors without vacuum deposition.[14] Porphyrins fused with bicyclo[2.2.2]-octadiene (BCOD) were used as precursors for fabricating TBP-based OFETs[15] and solar cells.[16] Thus, BCOD-fused tetraazaporphyrins **1** and **2** were expected to be soluble precursors of Nc and Pc, respectively. Although **1** was readily prepared, synthesis of **2** was extremely difficult[17] because the retro Diels–Alder reaction of **2** or its precursor, BCOD-2,3-dicarbonitrile, took place during ring formation. Furthermore, the solubility of **1** was too poor to obtain good thin films for OFETs. Herein we report the preparation of new soluble precursors **3** and **4**, which have better solubility and can be used to make OFETs by a solution process.



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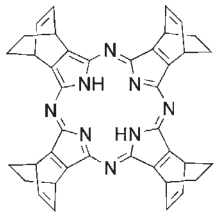

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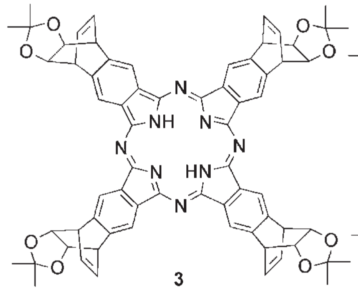

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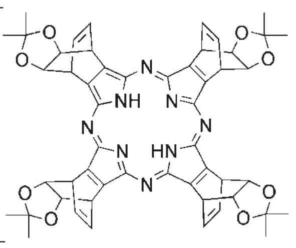

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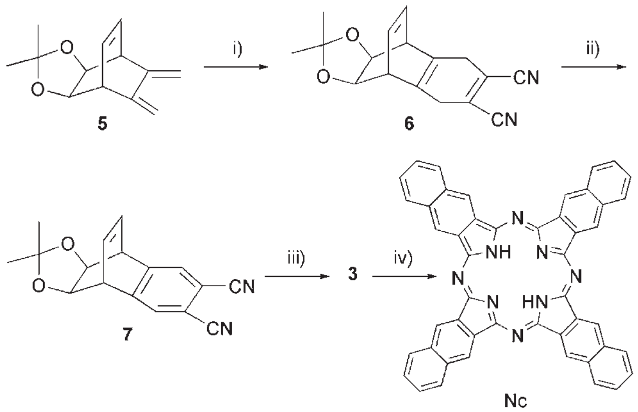

Scheme 1 Synthesis of Nc. *Reagents and conditions*: (i) dicyanoacetylene, $CHCl_3$, rt, 24 h, 46%; (ii) DDQ, 1,4-dioxane, $CHCl_3$, reflux, 6 d, 97%; (iii) LiOBu, BuOH, reflux, 1 d, 47%; (iv) 350 °C.

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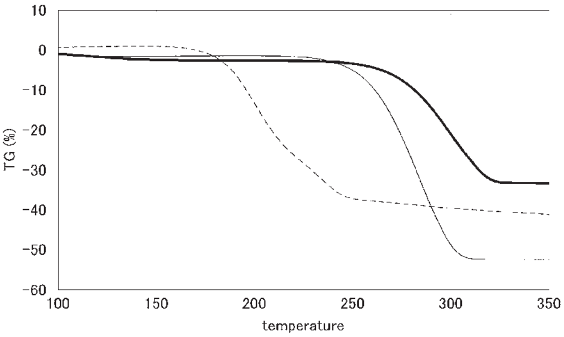
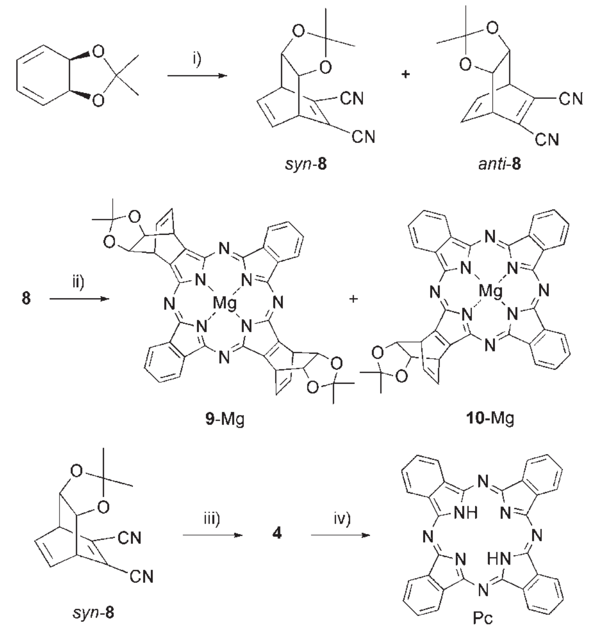


Fig. 1 TGA of **1** (solid line), **3** (bold line) and **4** (broken line).

The synthesis of **3** is shown in Scheme 1. The Diels–Alder reaction of dicyanoacetylene with **5** at room temperature gave **6** in 46% yield.[18] Diels–Alder adduct **6** was oxidized with DDQ for six days to give **7**. Reaction of **7** with LiOBu in BuOH at reflux for a day gave **3**, which was purified by column chromatography to give pure **3** as a mixture of diastereomers in 47% yield. Subsequent heating of **3** at 350 °C gave Nc in nearly quantitative yield. Thermogravimetric analysis (TGA) curves of **1** and **3** are shown in Fig. 1. The weight loss of **3** started at around 280 °C and ceased after 330 °C. The retro Diels–Alder reaction of **1** started at 250 °C and was completed by 300 °C. Thus, the reaction temperature for **3** was higher than that of **1**.

Precursors **4** or **4**-Mg were prepared by cyclization of **8** with LiOBu or $Mg(OBu)_2$ in BuOH as shown in Scheme 2. The Diels–Alder reaction of *cis*-5,6-isopropylidenedioxycyclohexa-1,3-diene[18] with dicyanoacetylene gave a mixture of *syn*- and *anti*-**8**. This mixture was treated with $Mg(OBu)_2$ to give a mixture of dibenzotetraazaporphyrin **9**-Mg, tribenzotetraazaporphyrin **10**-Mg and a trace of **4**-Mg. Column chromatography of the products afforded **9**-Mg and **10**-Mg in 24% and 11% yield, respectively. Compounds *syn*- and *anti*-**8** were separated by column chromatography, and their structures were determined by X-ray crystallographic analysis (CCDC No. 692987 (*anti*-**8**) and 692988 (*syn*-**8**): see the supplementary information†). They were analyzed by TGA (Fig. S-7†). The retro Diels–Alder reaction of *syn*-**8** started at around 190 °C, whereas that of *anti*-**8** started at 150 °C. Thus, *syn*-**8** is more suitable than *anti*-**8** for preparation of pure **4** as a mixture of diastereomers. Compound *syn*-**8** was treated with LiOBu in BuOH at 110 °C to give **4** free of the retro Diels–Alder products. Pure **4** was isolated in 2% yield after column chromatography. The TGA curve of **4** is shown in Fig. 1, in which it is seen that weight loss started at 180 °C and ceased after 250 °C. The loss of weight was *ca.* 40%, consistent with the calculated value of 43%. Heating **4** at 250 °C resulted in clean formation of pure Pc. This is the first preparation of pure Pc without vacuum technology.



Scheme 2 Synthesis of Pc. *Reagents and conditions*: (i) dicyanoacetylene, $CHCl_3$, rt, 57%; (ii) $Mg(OBu)_2$, BuOH, rt, 1 d, 24% (**9**-Mg), 11% (**10**-Mg); (iii) LiOBu, BuOH, 110 °C, 1 d, 2%; (iv) 250 °C.

Nc precursor **3** spin-coated on a glass plate showed a broad Q band at 530–800 nm (Fig. 2(a)). After heating at 350 °C for 5 min, the absorption maxima showed a marked bathochromic shift as **3** was converted to Nc. The broad Q band of the Nc film was observed at 600–900 nm. Similarly, while a glass plate coated with Pc precursor **4** showed four bands at 480–730 nm, the broad Q band of Pc appeared at 520–840 nm after treatment (Fig. 2(b)). Both Nc and Pc films exhibited a broad absorption at around 1000 nm.

Precursors **3** and **4** were soluble in many organic solvents such as $CHCl_3$, CH_2Cl_2, THF and EtOAc. They were used as soluble precursors for the fabrication of Nc- or Pc-based

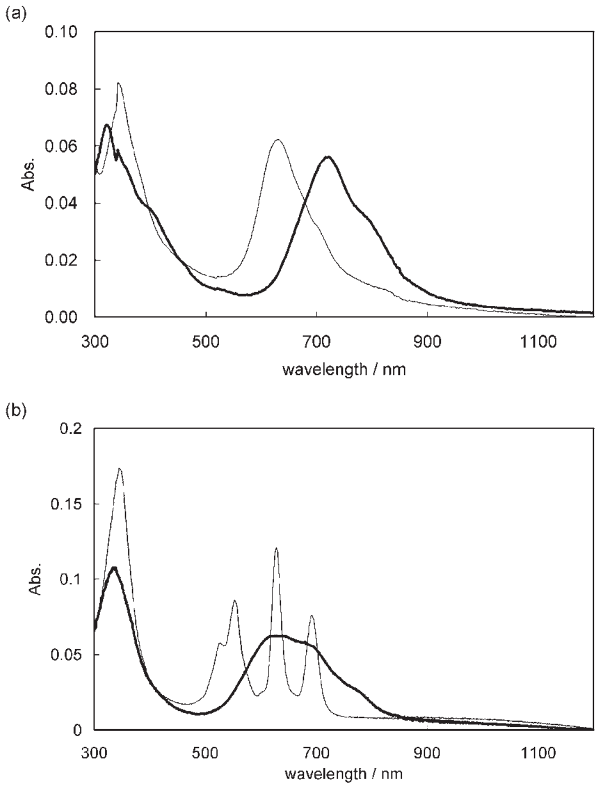


Fig. 2 UV-Vis absorption spectra of thin films of (a) **3** (solid line), Nc (bold line), (b) **4** (solid line) and Pc (bold line).

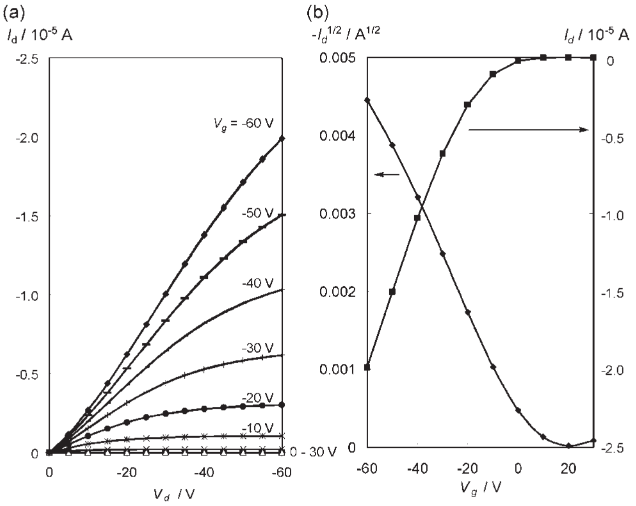


Fig. 3 Electronic properties of an FET with Nc. (a) I_d–V_d plots as a function of V_g. (b) I_d and $I_d^{1/2}$ *versus* V_g plots at V_d −60 V.

OFET devices in the same manner as for TBP.[15] Nc and Pc were readily obtained as good thin films on heavily doped n-type Si substrates coated with 300-nm thermally grown SiO_2, respectively. The source and drain electrodes were formed by photolithography of Au (90 nm)/Cr (10 nm), with a channel length and width of 10 and 500 μm, respectively. Nc precursor **3** in a 0.7 wt% $CHCl_3$ solution was spin-coated onto the channel region, and the obtained films were converted into the Nc form by heating at 350 °C for 5 min. FET properties were measured with an Agilent 4155C semiconductor analyzer. Electronic properties of an FET with Nc are shown in Fig. 3. The field-effect mobility (μ_{FET}) was determined using the saturation regime and an on/off current ratio (I_{on}/I_{off}) of the source-drain current (I_d) between the gate voltages (V_g) = 0 and −60 V. A good μ_{FET} of 1.9×10^{-2} cm^2 V^{-1} s^{-1} and a large I_{on}/I_{off} of 2.9×10^4 were obtained. A Pc-based FET was also fabricated in the same way using **4** instead of **3**.

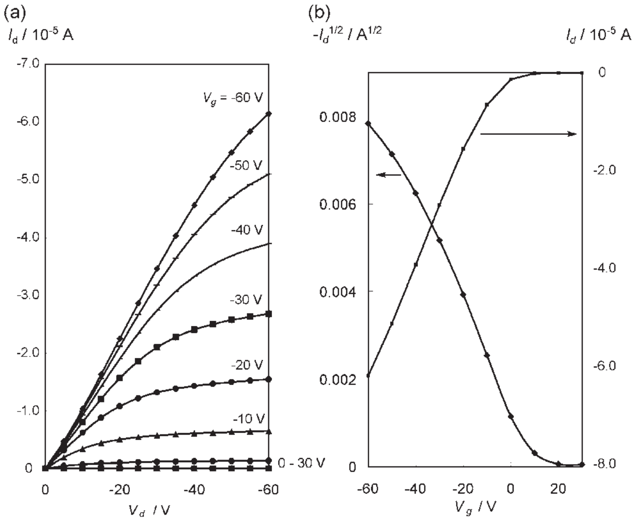


Fig. 4 Electronic properties of an FET with Pc. (a) I_d–V_d plots as a function of V_g. (b) I_d and $I_d^{1/2}$ *versus* V_g plots at V_d −60 V.

Fig. 4 demonstrates the characteristics of the Pc-FET: μ_{FET} = 6.0×10^{-2} cm^2 V^{-1} s^{-1}; I_{on}/I_{off} = 1.8×10^4. Thus, the solution-processed Pc-based FET showed a higher performance than was reported for vacuum deposited or LB films of Pcs.[7–10]

In conclusion, we have prepared stable soluble precursors of Nc and Pc, which were converted into Nc or Pc by heating at 350 or 250 °C, respectively. Nc and Pc films were prepared by spin-coating their corresponding precursors followed by thermal annealing. The yield of the retro Diels–Alder reaction was nearly quantitative and the Nc film was stable up to *ca.* 400 °C. OFET devices were made using these precursors; this was the first successful fabrication of thin film devices of Nc using a solution process. We also succeeded in the first preparation of pure Pc without a vacuum technique and the first application of this compound in an FET by a solution process.

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