A new type of soluble pentacene precursor for organic thin-film transistors†

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A new type of soluble pentacene precursor is synthesized, which extrudes a unit of CO upon heating at 150 °C, to produce pentacene in nearly quantitative yield.

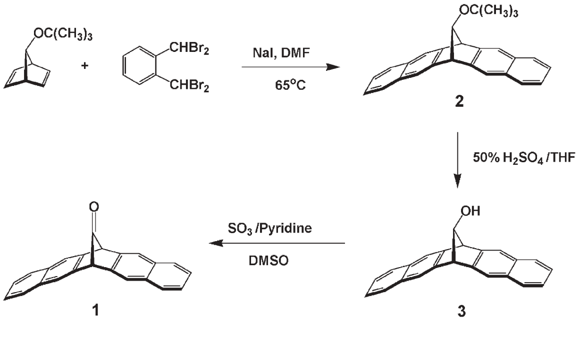
Pentacene has been widely recognized as a promising material for application on organic thin-film transistors (OTFTs) due to its high field effect mobility.[1] It exhibits a strong tendency to form highly ordered films on various substrates under different growth conditions. An optimal mobility in excess of 5 $cm^2\ V^{-1}\ s^{-1}$ has been achieved.[2] The effectiveness of the devices depends critically on the crystal morphology of the pentacene films.[3] The pentacene film in OTFT devices is generally fabricated by vapor-phase deposition under a high vacuum. The low solubility of pentacene in most solvents, however, is a major drawback which limits its utility through solution processes.[4] Many efforts have been attempted in trying to prepare "soluble" pentacene precursors in order to overcome this problem. A few types of precursor have been reported previously, most of them being cyclic adducts of a small volatile dienophile with pentacene.[5,6] Solid films were prepared by spin-coating the solution of the precursor, and then a chemical reaction was triggered afterward either by heat or by light to extrude the volatile component. The purity of pentacene film therefore depends not only on the yield of fragmentation reaction, but also on the thoroughness of expulsion process.

In earlier examples the volatile fragment usually contains heavy atoms, *e.g.* sulfur or halogen atoms, which may cause contaminations in pentacene films.[5] Carbon monoxide, by virtue of its small size and good stability, is considered to be a better leaving group in chelotropic type cyclo-reversion reactions. Indeed in a recent publication by Ono *et al.*, CO was expelled from a precursor upon photolysis to yield pentacene in 74% yield. However, this reaction was accompanied by a major side-product which was caused by the reaction with oxygen.[6,7] Our calculations based on B3LYP/6-31G* estimated that CO extrusion from a designated precursor, *i.e.* 6,13-dihydro-6,13-methanopentacene-15-one (**1**), should proceed at about 400 K with an activation energy of *ca.* 27.8 kcal mol^{-1}.[8] The thermal process is predicted to proceed in a synchronous manner hence reducing the likelihood of oxygen trapping. In this work we describe the synthesis of this compound, as well as its CO extrusion reaction for the production of pentacene in nearly quantitative yield. The improved solubility in organic solvents allows the usage of spin-coating processes to fabricate crystalline films. This compound is stable at ambient conditions, and can be prepared from 7-*tert*-butoxynorbornadiene *via* three steps in a net yield of *ca.* 27%.

The synthesis is depicted in Scheme 1. The first step is a double annulation of two naphthalene moieties onto the C=C bonds of 7-*tert*-butoxynorbornadiene by reacting with α,α,α,′α′-tetrabromo-*o*-xylene and sodium iodide.[9] The presence of two naphthalene moieties can be verified by two ^1H NMR multiplets at δ 7.4 (4H) and 7.7 (8H). The *tert*-butoxy group can then be hydrolyzed by 50% sulfuric acid to the hydroxyl group of **3**. A final oxidation was completed with the sulfur trioxide–pyridine complex at ambient temperature. The final product possesses a C_{2v} symmetry as indicated by the presence of four ^1H NMR signals in a ratio of 2 : 2 : 2 : 1. A strong absorption at 1778 cm^{-1} in IR confirms the presence of a carbonyl group.

Compound **1** is slightly soluble in chloroform, dichloromethane, benzene, toluene, acetone and tetrahydrofuran in a range of ~0.7 mg mL^{-1}, yet insoluble in polar solvents such as methanol, ethanol and acetonitrile. Thermally initiated carbonyl extrusion is manifested by both TGA (thermal gravimetric analysis) and DSC (differential scanning calorimetry) studies. As shown in Fig. 1, compound **1** undergoes a fragmentation at 150 °C, quite close to theoretical prediction,[8] with 9% weight loss corresponding to a molecule of CO in the structure. The pentacene thus produced is stable up to 350 °C, beyond which thermal decomposition occurs.

The thermal transformation was characterized by UV spectra before and after the heating. Two low energy absorption bands of



Scheme 1

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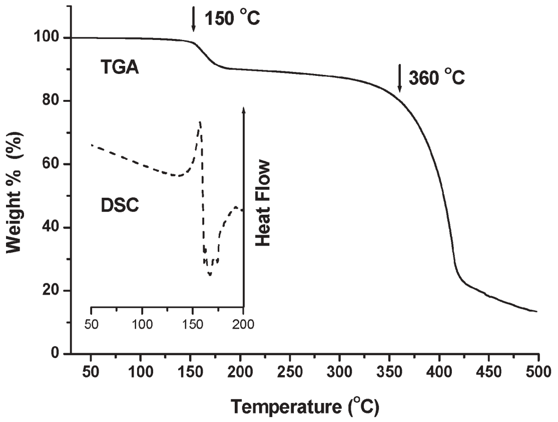

Fig. 1 Thermogravimetric curve for the decarbonylation of **1** at 10 °C min^{-1} heating rate. The inset at the bottom shows a curve of differential scanning calorimetry, also at 10 °C min^{-1}. The decarbonylation appears at 150 °C to yield pentacene, which decomposes at *ca.* 360 °C as measured by a 5% weight loss.

1 appear at 276–326 nm, which exhibit fine vibronic progressions (Fig. 2). These bands are analogous to those of naphthalene, as the structure of **1** consists of two naphthalene units. A much stronger absorption band is also observed at 244 nm. After heating the solid at 160 °C for 1 h, this absorption band disappeared completely, while another strong peak arose at 301 nm. The two low energy bands red-shifted to 346 and 576 nm as a result of the more extended π-conjugation of pentacene. The spectrum of the thermal product was consistent with that of authentic pentacene. A clear transformation of **1** to pure pentacene was also shown in the IR spectra, where the strong absorption peak at 1778 cm^{-1} corresponding to the carbonyl stretching of **1** disappeared completely upon heating.

A solid layer of **1** on a glass plate was prepared from saturated solutions by the spin-coating technique. The size of microcrystals grew gradually upon repeating the spin-coating process several times on the same plate. Heating the resultant layer at 160 °C for 1 h generated a purplish film of pentacene. The transformation can be monitored by the transmission spectra shown in Fig. 3. The plate with the spin-coated precursor film did not exhibit any distinctive absorption bands in the 500–600 nm region before heating yet the characteristic bands of pentacene appeared clearly after heating.

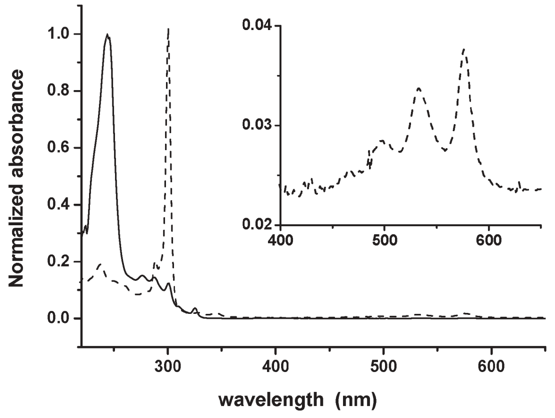

Fig. 2 UV-Vis spectra of **1** (solid line) and the thermal pentacene product (dotted line) in dichloromethane. The inset shows a magnification of the weak bands in the region 500–600 nm, which is characteristic of pentacene.

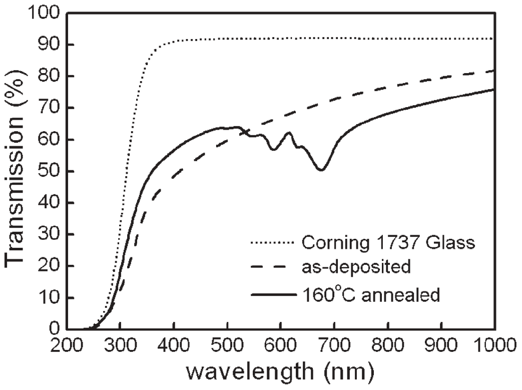

Fig. 3 Transmission spectra of a spin-coated film of compound **1** on a glass plate before and after annealing at 160 °C under a nitrogen atmosphere for 1 h. The absorption band at 500–600 nm arising from pentacene was clearly observed after annealing.

It has been reported that pentacene crystals exhibited polymorphism while coated on surfaces.[10,11] In a common morphology of pentacene, molecules are aligned with their long axis perpendicular to the surface.[11] A spin-coated layer of **1** was examined by powder X-ray diffractometry before and after thermolysis. The crystalline phase of **1** exhibited four lines at 2*θ* angles of 5.50, 16.69, 20.01 and 28.06° as shown in Fig. 4. All these lines disappeared after annealing, while three new signals arose at 5.64, 11.37 and 17.19°. These signals were known to arise from the (00*l*) diffractions (where l = 1, 2 and 3) of pentacene crystals, which correspond to an interplanar *d* spacing of 15.4 Å.[12,13] The single-crystal structure of pentacene is known to be triclinic with a long-axis length of 16.01 Å.[14] It is thus suggested that the long axis of pentacene aligns at an angle of about 17° from the surface normal.[13] The absence of other (*hkl*) reflections indicated that the crystallites are randomly oriented around the surface normal. These phenomena were consistent with the results of previous reports of crystalline pentacene films prepared by vapor deposition.

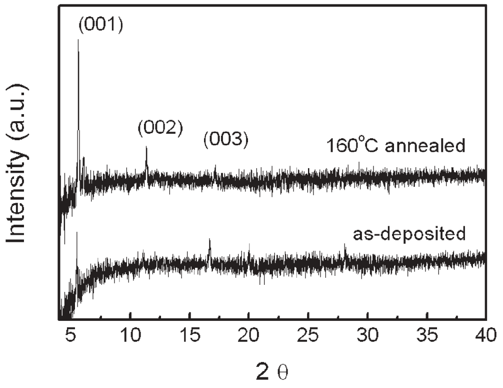

Fig. 4 X-ray diffraction patterns of a spin-coated thin film of **1** before (bottom) and after (top) heating (160 °C, 1 h). The (00*l*) series diffraction lines of pentacene crystals clearly appeared after heating.

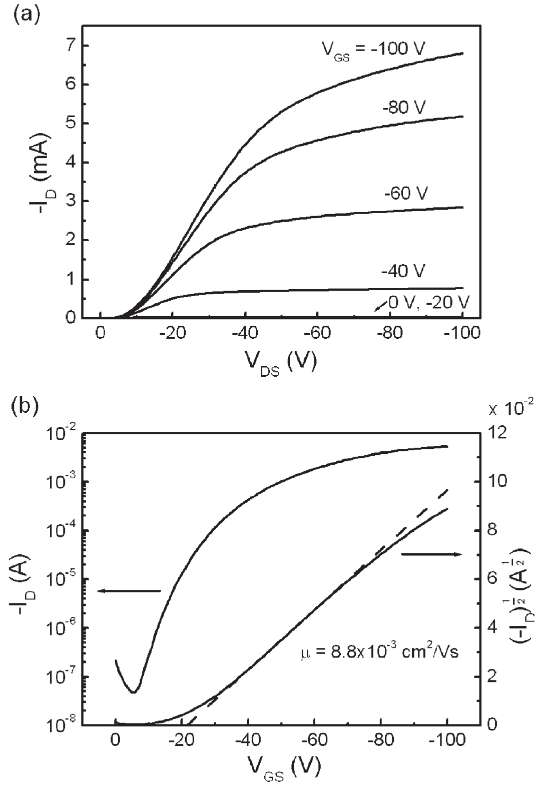

Fig. 5 (a) Plot of drain current I_D *vs.* drain-source voltage V_{DS} at various gate voltages V_{GS} obtained from an OTFT with a channel width of 20 cm and a channel length of 10 μm. (b) log(I_D) *vs.* V_{GS} for $V_{DS} = -60$ V, and $\sqrt{I_D}$ *vs.* V_{GS} in the saturation mode.

Owing to the limited solubility of compound **1**, the thin films prepared by the spin-coating process were not entirely contiguous. Nevertheless, OTFTs prepared using **1** exhibited typical FET characteristics. The OTFT devices were fabricated using a heavily n-doped Si wafer as the substrate and the gate and using a 2000 Å thermally grown SiO_2 film as the gate insulator. Au (30 nm) was deposited and lithographically patterned on top of the SiO_2 as the interdigitated source/drain electrodes. Compound **1** was then spin-coated over the structure and was thermally converted to pentacene. The output characteristics [*i.e.* the plot of drain current (I_D) *vs.* drain-source voltage (V_{DS}) at various gate voltages (V_{GS})] for such an OTFT (with a channel width of 20 cm and a channel length of 10 μm) is shown in Fig. 5(a). The OTFT operates in the p-type enhancement mode and exhibits a hard saturation. Fig. 5(b) shows the corresponding transfer characteristics [log(I_D) *vs.* V_{GS} for $V_{DS} = -60$ V, $\sqrt{I_D}$ *vs.* V_{GS} in the saturation mode]. The OTFT exhibits an on/off current ratio of about 1.2×10^5. From $\sqrt{I_D}$ *vs.* V_{GS} in the saturation mode, the apparent field-effect mobility μ is estimated to be 8.8×10^{-3} cm^2 V^{-1} s^{-1}. Since the pentacene did not cover the whole area between the source and the drain, the actual mobility is actually higher. Efforts to improve the quality of films are currently under way, such as changing the solvent systems, modifying the surface of supporting plates, as well as crystal reorientation by thermal annealing.

In summary, we have prepared a stable and soluble pentacene precursor which extrudes a unit of CO upon heating at 150 °C. Pentacene films can be prepared by the spin-coating technique followed by thermal annealing. The yield of thermal fragmentation was nearly quantitative, and the pentacene film thus produced is stable up to *ca.* 360 °C. Fabrication of OTFT devices using this precursor has been demonstrated. Further improvement of film morphology for devices is actively under way in our laboratory.

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