

A Photopatternable Pentacene Precursor for Use in Organic Thin-Film Transistors

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Organic semiconducting molecules are of great interest for fabrication of organic thin-film transistors (OTFTs).¹ The development of simple, solution-phase processing methods to deposit semiconducting organic molecules would facilitate the development of new technologies such as large active matrix displays and inexpensive, mechanically flexible “plastic” electronics. Pentacene has received special attention because single crystals² and thin films^{3,4} exhibit high carrier mobilities. However, the low solubility of pentacene⁵ and many other organic semiconductors has been a significant obstacle to their widespread use. In this work we report the synthesis of a new soluble pentacene derivative that incorporates an acid-labile moiety into the molecular structure; this modification enables its conversion back to pentacene to be initiated by ultraviolet light in the presence of a photoacid-generating compound (PAG). We further demonstrate the use of this precursor to photopattern and fabricate OTFTs having good carrier mobilities.

Previous studies have reported modification of pentacene to improve its solubility and to achieve improved electrical properties via increasing the π -orbital overlap in the solid state.^{6,7} Recent studies have also demonstrated that modification via Diels–Alder chemistry can lead to pentacene precursors that can be converted back to pentacene after deposition by heating^{8–11} and, in some cases, by photopolymerization.⁹ OTFTs incorporating the resulting pentacene films have carrier mobilities in the range of 10^{-2} – 10^{-1} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, which are comparable to those of amorphous silicon, the semiconductor currently used for most large-area electronic applications. However, there remains great interest in developing molecules and processing methods to achieve improved processability and higher mobilities.

We have developed a pentacene adduct that, like previous precursors, is soluble in common organic solvents and can undergo the reverse reaction back to pentacene under moderate conditions. However, by also incorporating an acid-labile group (here the *t*-BOC group) into the molecular structure, we greatly enhance the ability to photopattern the films using UV light. To synthesize the precursor, pentacene **1** was combined with *N*-sulfinyl-*tert*-butylcarbamate¹² **2** in refluxing chloroform and in the presence of the cationic palladium catalyst $[\text{Pd}(\text{dppp})(\text{PhCN})_2](\text{BF}_4)_2$ ¹² to give the pentacene precursor **3** (71% yield) via a Diels–Alder reaction (Scheme 1). After flash chromatography of the crude products, the adduct **3** was isolated as a white microcrystalline solid, the structure of which was determined from its ¹H NMR,¹² ¹³C NMR,¹² FTIR, and UV–visible spectra.

To observe the conversion back to pentacene, precursor **3** was spin-coated from chloroform solution,¹³ heated, and analyzed for changes in the infrared and UV–visible spectra. The substrates for IR and UV–vis measurements were silicon wafers and quartz disks, respectively. Immediately following spin-coating, samples were

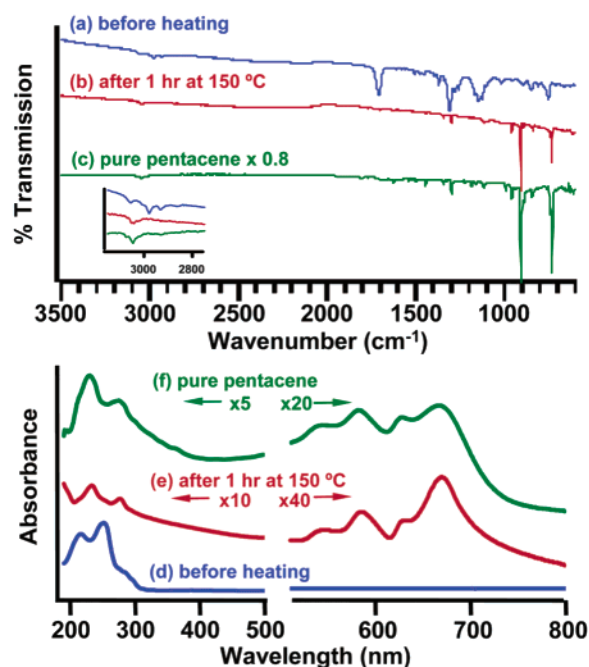
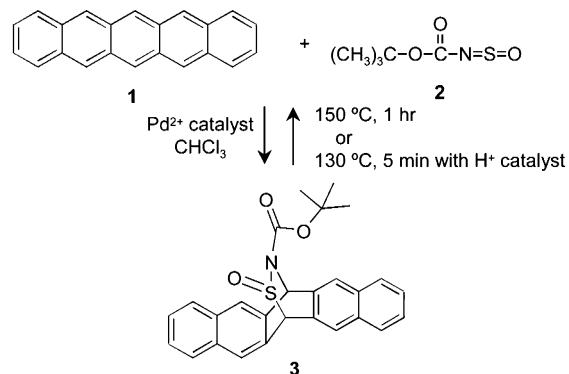


Figure 1. Infrared (a–c) and UV–visible (d–f) spectra of the precursor **3** before heating (a,d) and after 1 h at 150 °C (b,e). The spectra of pure pentacene **1** (c,f) are also shown.

Scheme 1



briefly heated (30 s) to 100 °C to remove the solvent. IR and UV–visible spectra (Figure 1) were obtained before and after heating for 1 h at 150 °C. Before heating, the infrared spectrum of the precursor (Figure 1a) shows a strong carbonyl stretching peak at 1706 cm^{-1} , multiple peaks between 1100 and 1300 cm^{-1} from the *N*-sulfinyl carbamate functionality,¹⁴ and unsaturated C–H peaks near 2931 and 2978 cm^{-1} (inset). Figure 1b shows that, after heating, these peaks are greatly diminished or absent completely, while new peaks arise at 907 and 731 cm^{-1} that are characteristic

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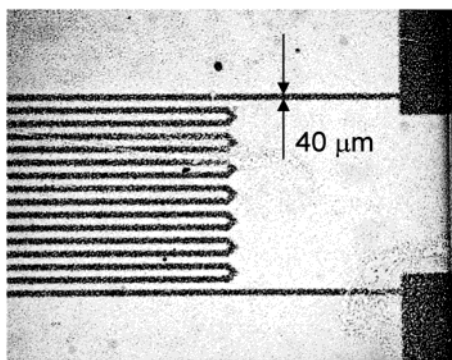


Figure 2. Optical microscope image of pentacene patterned by exposure of precursor **3** to UV light through a chrome/quartz mask and heating in the presence of photogenerated acid.

of pure pentacene (Figure 1c). The conversion back to pentacene is also evident in the UV–visible spectrum. While the precursor has strong peaks at 217 and 252 nm with little or no absorbance above 400 nm (Figure 1d), heating leads to clear peaks at 232 and 276 nm and in the 500–700 nm range (Figure 1e) that signify pentacene (Figure 1f).¹⁵ Thus, the UV–vis and IR spectra demonstrate that the precursor **3** is converted back to pentacene upon heating at moderate temperatures.

To photopattern the films, we used the fact that acids lower the decomposition temperature of t-BOC significantly.¹⁶ By using a PAG to initiate the decomposition, it is possible to selectively convert the precursor **3** back to pentacene in specific regions illuminated by ultraviolet light. We used the PAG di-*tert*-butylphenyliodonium perfluorobutanesulfonate¹² (3 mol %) as part of a chemical amplification reaction. This method of acid-catalyzed decomposition leaves a thin film of pentacene and can thus be used to photopattern structures such as OTFTs.

Figure 2 is an optical microscope image showing a pattern on silicon after UV exposure for 1 min and heating at 130 °C for 5 min. Patterned areas where the film had converted to pentacene were discernible after the post-exposure bake, as they became dark purple in color. Figure 2 demonstrates how patterns with features as small as 40 μm are readily defined by this process. It is evident that the H⁺ catalyzes conversion of the UV-exposed regions at lower temperatures (around 130 °C) and in significantly less time (5 min) than the areas not exposed to UV. Because the unconverted precursor can be removed by washing in MeOH without affecting the converted area, it is possible to pattern pentacene regions within a large-area film and then isolate them by removing the surrounding unconverted precursor.

In addition to the patterning of pentacene thin films, we examined their semiconducting properties in a bottom-contact OTFT geometry (Figure 3, inset). Figure 3 shows the transfer characteristics of a device as drain voltage was varied at different gate voltages. Mobility was calculated in the linear regime from the transconductance¹⁷ to be 0.13 cm² V⁻¹ s⁻¹ for a device with a channel width of 1000 μm and a channel length of 15 μm. The $I_{\text{on}}/I_{\text{off}}$ ratio for this device was 2×10^5 . In the saturation regime, the mobility was also calculated to be 0.13 cm² V⁻¹ s⁻¹ with an $I_{\text{on}}/I_{\text{off}}$ ratio of 3×10^5 . The highest measured mobility in the saturation regime was 0.25 cm² V⁻¹ s⁻¹, with a current modulation in excess of 8×10^4 . These results are comparable to earlier results with *N*-sulfinyl pentacene derivatives^{8,9} and are in the range that makes them a viable option for organic electronics.

The use of Diels–Alder chemistry to link an acid-labile functional group to the pentacene molecule is significant because

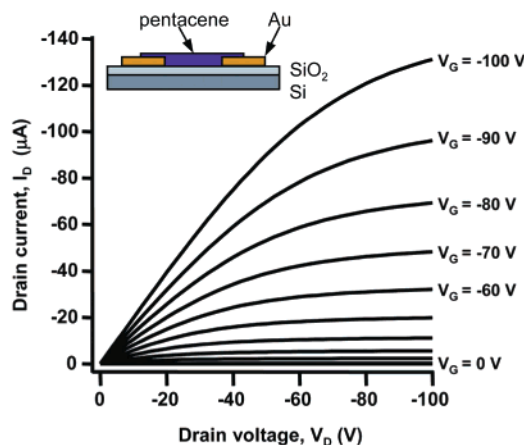


Figure 3. Drain current, I_D , versus drain voltage, V_D , as a function of gate voltage, V_G , for a thin-film transistor with pentacene as the channel material. The channel was converted from the precursor **3** to pentacene **1** by exposing it to UV light through a mask and then heating in the presence of photogenerated acid.

it provides a pathway toward the fabrication of organic electronic devices via entirely wet-chemical methods. In addition to forming a highly soluble compound, integrating an acid-sensitive moiety with catalytic photoacid generators makes it possible to photoinitiate the conversion back to pentacene at low processing temperatures. Our work demonstrates that these ideas enable the fabrication of organic thin-film transistors with good electrical properties at temperatures that are compatible with common polymeric substrates, thereby enhancing the development of fully “plastic electronics”.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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