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Effective photochemical synthesis of an air-stable anthracene-based organic semiconductor from its diketone precursor

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Abstract—A diketone precursor of air-stable bis-2-thienyl-2,6-anthracene was prepared and quantitatively converted to the target acene by photoirradiation of the n–π* absorption both in solution and as a film, in air.

Organic field-effect transistors (OFETs) are essential for the development of organic electronic devices. Pentacene is one of the best candidates with good mobility and on/off ratio.[1–3] However, its solubility in common organic solvents is exceedingly low and vacuum deposition is required for the fabrication of devices with this material. Realization of the full potential of organic electronics requires the ability to form devices by solution deposition methods for simple processing. To achieve a solution process for pentacene, its solubility has to be improved, and many attempts have been reported: (1) introduction of substituents to improve solubility;[4] (2) finding a suitable solvent to solve a pure pentacene upon heating;[5] (3) preparation of pentacene precursors which can be thermally converted to pentacene via a retro-Diels–Alder reaction after preparation of a film of the soluble precursors;[6] and (4) preparation of photopatternable pentacene films by converting pentacene precursors to pentacene using photochemical polymerization of pentacene precursor-linked monomer or photochemical acid generation.[7] Recently, we have reported a novel α-diketone precursor of pentacene, which could be converted to pentacene quantitatively by direct photoirradiation of the precursor in solution or as a film with elimination of two CO molecules.[8,9] However, the problem yet to be solved is the air-instability of pentacene, which is one of the major obstacles to its practical application as an active organic semiconductor in OFETs.[10] In our previous work,[9] the α-diketone precursor of pentacene was quantitatively converted to pentacene under argon, but only the oxygen adduct was effectively obtained in air.

A wide variety of organic compounds have been reported to improve the environmental stability of OFETs. Bis-2-thienyl-2,6-anthracene (**2**) and its derivative have recently been reported as p-type organic semiconductors to show an improved environmental stability and solubility.[11,12] Although the compound showed field-effect mobility as high as 0.063 $cm^2/V\,s$ and on/off ratio as 8.76×10^5, it still needed vacuum deposition at a relatively low temperature. We report here the solution-processible α-diketone precursor of compound **2**, 9,10-ethano-9,10-dihydro-2,6-bis-2-thienyl-anthracene-11,12-dione (**1**), which is expected to overcome the air-instability of pentacene.

The synthetic route for compound **1** is shown in Scheme 1. Starting material **3** was prepared from 2,6-diaminoanthraquinone in three steps according to the literature.[9] Thiophene-2-boronic acid was coupled with compound **3** by Suzuki coupling to give compound

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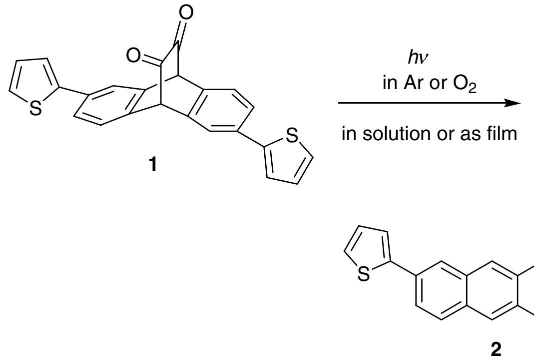


4 in 72% yield. Subsequent hydrolysis followed by Swern oxidation gave diketone **1** in 20% yield.[13]

The photolysis of α-diketone to pentacene was typically performed as follows: α-diketone **1** (7.3 mg) was dissolved in 12 ml of toluene (1.5 mM) in a test tube. After bubbling Ar through the solution for 20 min, the yellow solution was irradiated with a metal-halide lamp (380 W) through a blue filter (>390 nm) and an IR cut-off filter. A yellow precipitate appeared in a few minutes. The irradiation was continued for 15 min, until the solution turned colorless. The yellow precipitate was collected by filtration to give the anthracene derivative **2** in 83% yield. Compound **2** was identified by EI-mass and NMR spectra.

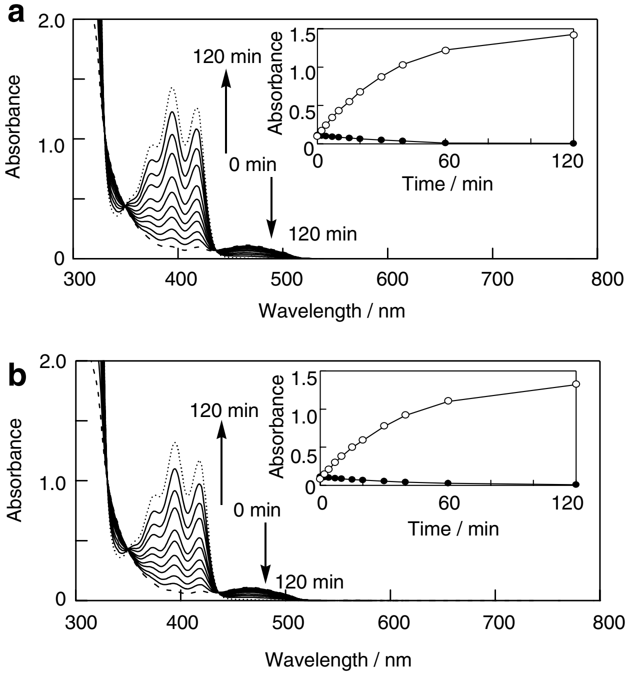
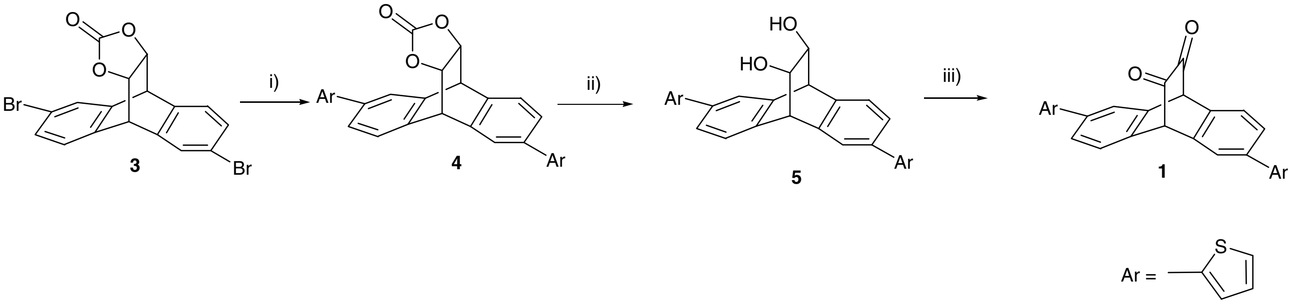


Figure 1. Changes in absorption spectra during the photolysis ($\lambda_{EX} = 467$ nm) of α-diketone **1** in toluene under (a) Ar and (b) O_2 atmospheres. The dashed lines are absorbance of α-diketone **1** (at 0 min) and the dotted lines are those of compound **2** (at 120 min). Insets are the time profiles of the absorbance at 467 (closed circles) and 395 nm (open circles) during the photolysis.

The UV–vis absorption spectra of precursor **1** and anthracene derivative **2** in toluene are shown in Figure 1. The diketone compound **1** (dashed lines) had a peak corresponding to an n–π* transition at 466 nm. Compound **2** (dotted lines) had peaks at 418, 395, and 375 nm, but did not show any absorbance above 450 nm where α-diketone **1** had its n–π* peak. This is very important considering practical applications, because the photoproduct does not inhibit the absorption of light by α-diketone **1**, at least in solution. In order to monitor the photoreaction, changes in the UV–vis absorption spectra were repeatedly measured during photolysis. A 5.25×10^{-1} mM solution of α-diketone **1** in toluene was irradiated with a xenon lamp at 467 nm (1.8 mW) under Ar, with the results shown in Figure 1(a). During irradiation the peak at 467 nm decreased gradually, while new peaks at 418, 395, and 375 nm, belonging to anthracene, appeared. To investigate the environmental stability, the same measurement was performed on an O_2-saturated toluene solution of α-diketone **1**, with the results shown in Figure 1(b). The time profiles of the diketone peak and anthracene peaks were very similar under Ar and O_2, suggesting that the same photoreaction proceeded under both conditions. When the same experiments were performed with the α-diketone precursor of pentacene, pentacene was obtained in 74% yield under Ar atmosphere, but only oxygen adducts to pentacene were obtained under O_2.[9] This phenomenon was explained as follows: pentacene has an absorbance around 460 nm and was excited by the light used to excite the n–π* absorption of the diketone precursors. Once pentacene was excited, an effective intersystem crossing occurred to produce a pentacene triplet excited state, which in turn generated singlet oxygen from triplet oxygen. This singlet oxygen then re-



Scheme 1. The synthesis of diketone precursor **1**. Reagents and conditions: (i) thiophene-2-boronic acid, $PdCl_2(dppf)(CH_2Cl_2)$, KOAc, *dry*-DMSO, reflux, three days, 72%, (ii) NaOH aq, dioxane, reflux, 1 h, 86%, (iii) trifluoroacetic anhydride, dry DMSO, dry CH_2Cl_2, −80 °C, 1.5 h, 23%.

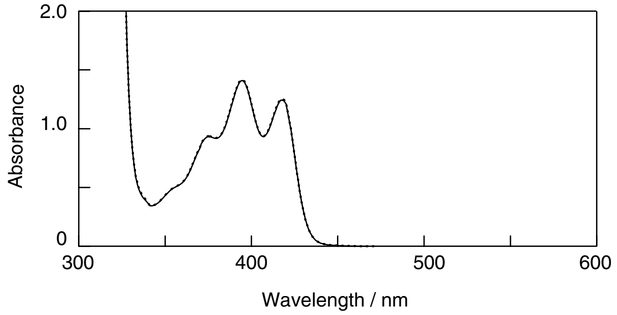


Figure 2. The absorption spectrum of **2** before (broken line) and after (solid line) irradiation in toluene at 418 nm for 60 min.

acted with pentacene to give the oxygen adduct 6,13-pentacene-endoperoxide. By contrast, the absorptions of compound **2** did not overlap with those of α-diketone **1** and therefore anthracene compound **2** was not excited by the light over 450 nm. In order to confirm the environmental stability of compound **2**, it was irradiated by 418 nm light for 1 h under O_2. As shown in Figure 2, its absorption spectrum changed slightly during the irradiation of π–π* absorption of anthracene moiety, confirming the environmental stability of compound **2**.[11,12]

The photoreaction was also performed as a film of α-diketone **1**. A 14 mM solution of α-diketone **1** in $CHCl_3$ was spin-coated (1000 rpm, 30 s) on glass in air. The resulting film was photoirradiated by a metal-halide lamp through a blue filter (>390 nm) and an IR cut-off filter. The film was irradiated for 3 h until the change of UV–visible absorption spectra stopped. The UV–visible absorption spectra of the deposited film before and after photoirradiation are shown in Figure 3. Before irradiation, the deposited film was pale yellow and translucent, and a typical n–π* absorption was observed at 470 nm. After irradiation, the film was colorless and transparent, with the absorption spectrum shown in Figure 3. The anthracene peaks were broadened and red-shifted because of π–π stacking compared to the absorption spectrum in solution, similar to the results of the previously discussed pentacene film.[9] The major difference between the α-diketone precursors of compound **1** and pentacene was the sensitivity to oxygen during the photoreaction in the films; the photoreaction of compound **1** in the film could be performed under air, whereas the diketone precursor of pentacene had to be treated in an oxygen-free environment, to avoid the formation of oxygen adducts.

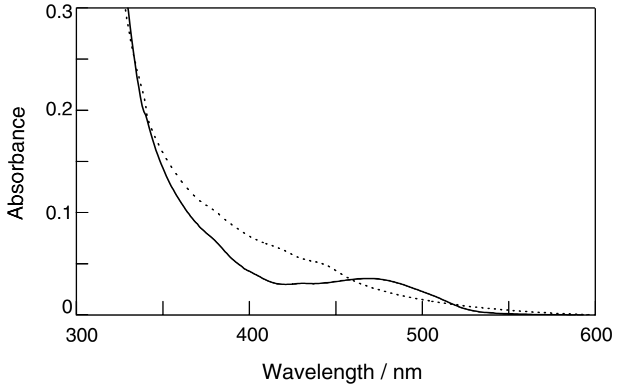


Figure 3. The absorption spectra of a film of α-diketone **1** before (solid line) and after (dotted line) irradiation. $\lambda_{EX} > 390$ nm.

In conclusion, we have succeeded in preparing solution-processible diketone precursor **1**, which could easily be converted to acene compound **2** by photoirradiation in solution and as a film, in air. This air stability will be a great advantage for the application as an organic semiconductor, such as OFETs.

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13. Synthesis of **4**: Compound **3** (2.0 mmol, 0.844 g), 2-thiopheneboronic acid (7.0 mmol, 0.897 g), $PdCl_2$(dppf) CH_2Cl_2) (0.062 mmol, 0.051 g), KOAc (8.2 mmol, 0.801 g) were added to dry DMSO (10 ml) and Ar gas was bubbled for 15 min. The mixture was heated to 80 °C and reflux was continued for three days. The reaction mixture was cooled to rt, ice-water was added and extracted with CH_2Cl_2. The organic layer was washed with water and sat. NaCl aq, then dried over Na_2SO_4. After the solvent was evaporated, the residue was purified on silica gel column chromatography ($CHCl_3$) to yield a yellow solid in 72 % yield (1.7 mmol, 0. 73 g). ^{1}H NMR ($CDCl_3$) $\delta = 7.58$ (s, 1H), 7.54 (s, 1H), 7.43 (m, 2H), 7.31 (m, 2H), 7.20 (m, 2H), 7.17 (m, 2H), 7.02 (m, 2H), 4.83 (2H, m), 4.64 (m, 2H), 2.18 (m, 2H), MS (TOF) $m/z = 430$ [M^++1]. Compound **5**: Compound **4** (1.48 mmol, 0.636 g) was added to 4 M NaOH (26 ml) and 1,4-dioxane (40 ml) under N_2 atmosphere and the mixture was refluxed for 1 h. After cooled to rt, the reaction mixture was poured into water and extracted with $CHCl_3$. The combined organic layers were washed with water and dried over Na_2SO_4. The solvent was evaporated and the residue was purified on silica gel column chromatography. Crystallization from toluene yielded a white solid in 86% yield (1.27 mmol, 0.513 g). Mp 217 °C; ^{1}H NMR ($CDCl_3$) $\delta = 7.62$ (s, 1H), 7.57 (s, 1H), 7.48 (d, $J = 7$ Hz, 1H), 7.41 (m, 2H), 7.34 (1H, $J = 7$ Hz, d), 7.25 (m, 2H), 7.17 (m, 2H), 7.06 (m, 2H), 4.43 (m, 2H), 4.12 (m, 2H), 2.18 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 144.11$, 144.02, 140.33, 139.04, 138.85, 137.63, 133.20, 133.15, 128.96, 128.15, 127.92, 126.88, 125.21, 124.72, 124.66, 124.45, 124.38, 124.15, 123.05, 122.44, 68.08 and 51.15; IR (KBr) $\nu_{max} = 3429$ (br), 2950, 2913, 1477, 1419, 1153, 1065, 1008 and 696 cm^{-1}; MS (TOF) $m/z = 403$ [M^++1]. Elemental analysis calcd (%) C, 72.42; H, 4.89. [$C_{24}H_{18}O_2S_2$+1/4C_7H_8] Found (%) C, 72.67; H, 4.74. Compound **1**. To a mixture of dry-DMSO (33 mmol, 2.4 ml) and freshly distilled CH_2Cl_2 (18 ml), was added trifluoroacetic anhydride (29.8 mmol, 4.1 ml) dropwise at −80 °C under a N_2 atmosphere. After stirring for 10 min, diol **5** (0.95 mmol, 0.384 g) dissolved in a minimum amount of dry-DMSO was added dropwise over 10 min. After stirring for 90 min, Et_3N (68.8 mmol, 9.6 ml) was added dropwise and the stirring was continued for additional 90 min at −80 °C. After the temperature of the reaction mixture was left to rise up to rt, the mixture was poured into 2 M HCl (100 ml) and the organic layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and sat. NaCl aq and dried over Na_2SO_4. The solvent was evaporated and the residue was purified on silica gel column chromatography ($CHCl_3$) followed by rinsing with ether to give compound **1** as a yellow solid in 23% yield (0.21 mmol, 0.085 g). Mp 238 °C; ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.70 (m, 2H), 7.63 (m, 2H), 7.50 (m, 2H), 7.33 (m, 4H), 7.09 (m, 2H) and 5.04 (s, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 183.11$, 142.78, 135.95, 135.44, 133.38, 128.20, 126.97, 126.82, 125.73, 123.94, 123.50, and 59.68; IR (KBr) $\nu_{max} = 1730$, 1475, 1105, 822 and 710 cm^{-1}; MS (FAB) m/z 398 [M^+] and 342 (–2CO). Elemental analysis calcd (%) C, 68.12; H, 3.58. [$C_{24}H_{14}O_2S_2$+1/4$CHCl_3$] Found (%) C, 68.00; H, 3.35.