Syntheses

6,13-Dihydro-6,13-methano-15-*tert*-butoxypentacene (2). A solution of 7-*t*-butoxynorbornadiene (100 mg, 0.60 mmol) in dry DMF (10 mL) was stirred at 65 ℃, then α,α,α’α’-terarbromo-*o*-xylene (25 mg × 20, 1.2 mmol) and sodium iodide (27 mg × 20, 3.6 mmol) were added in twenty equal portions over 120 hours. The reaction was quenched by pouring into cold water (100 mL) containing sodium bisulfite (5.00 g). Brown precipitates were collected, and were purified by silica-gel column chromatography eluted with hexane: ethyl acetate (v/v = 20/1) to give the product **1** (120 mg) in 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.73(m, 8H), 7.38 (m, 4H), 4.45 (s, 2H), 4.41 (s, 1H), 1.17 (s, 9H).

6,13-Dihydro-6,13-methano-15-hydroxypentacene (3). Compound **2** (1.00 g, 2.7 mmol) was added to a mixed solvent of tetrahydrofuran (20 mL) and 50% aqueous sulfuric acid (10 mL). The mixture was stirred at room temperature for 48 hr. It was quenched by the addition of distilled water, and was extracted by ether. The combined ether layers was washed with brine, and dried over anhydrous magnesium sulfate. The organic solvent was removed *in vacuo*, and the product was purified by silica-gel chromatography eluted with hexane:ethyl acetate (v/v = 4/1) to give **2** (0.70 g) in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.85 (s, 2H), 7.74 (m, 6H), 7.42 (m, 4H), 4.59 (s, 1H), 4.52 (s, 2H), 2.30 (br, 1H).

6,13-Dihydro-6,13-methanopentacene-15-one (1). To a solution of **3** (0.50 g, 1.6 mmol) in dichloromethane (10mL) were added dimethyl sulfoxide (5 mL) and triethylamine (0.60 g, 6.0 mmol). To the resulted solution was added drop-wise a solution of sulfur trioxide/pyridine complex (0.70 g, 4.4 mmol) in dimethyl sulfoxide (9 mL) over a period of 30 min. The mixture was stirred at room temperature for 12 hr. The reaction was quenched by pouring into saturated aqueous NH_4Cl (50 mL). It was extracted several times with CH_2Cl_2. The combined phase was washed with brine, dried over anhydrous magnesium sulfate, and dried *in vacuo*. The product was purified by silica-gel column chromatograph eluted with hexane:ethyl acetate (v/v = 4/1) to give **3** (0.30 g) in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.92(s, 4H), 7.81 (dd, J = 3.3, 6.2 Hz, 4H), 7.46 (dd, J = 3.2, 6.2 Hz, 4H), 4.98 (s, 2H). IR (KBr) 3063, 2922, 1779, 1609, 1500, 893, 757 cm^{-1}.

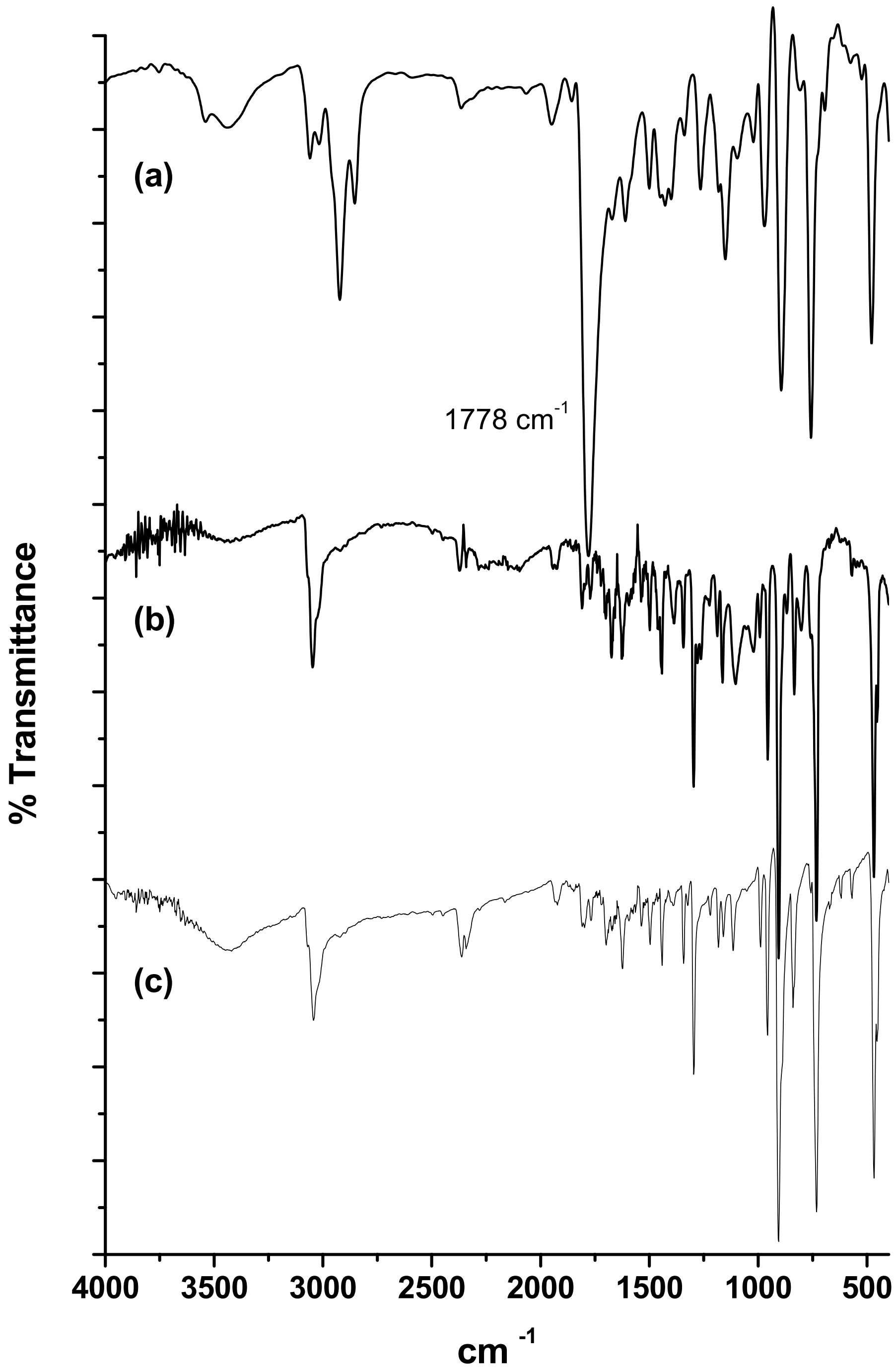

Figure 1. Infrared spectra of compound **1** (a) before and (b) after heating at 160℃ for 1 h. The strong peak at 1778 cm^{-1}, corresponding to the carbonyl stretching, disappeared after heating. A standard infrared spectrum of commercial pentacene (c) is presented at the bottom for comparison.

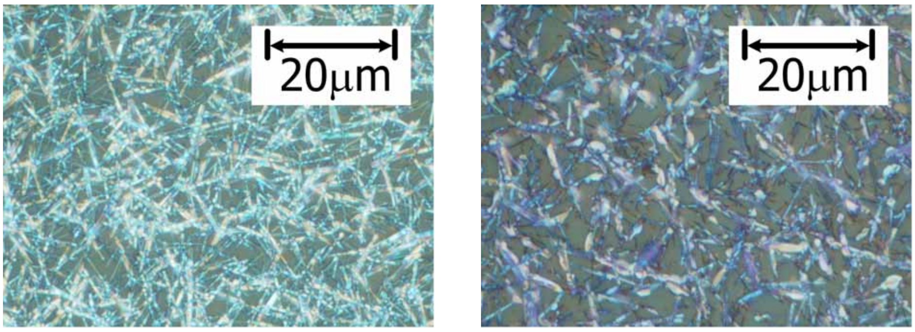

Figure 2. Macroscopic image of a film spin-coated with compound **1** on a glass surface (left). The spin-coating process was repeated 10 times in order to increase the film thickness. After heating (right) pentacene was formed in a similar appearance.