Tetrahedron 66 (2010) 6889–6894

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Pentacene precursors for solution-processed OFETs

Hiroki Uoyama, Hiroko Yamada, Tetsuo Okujima, Hidemitsu Uno *

Department of Chemistry and Biology, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan

ARTICLE INFO

Article history:
Received 10 May 2010
Received in revised form 17 June 2010
Accepted 18 June 2010
Available online 25 June 2010

Keywords:
Pentacene
Retro-Diels–Alder reaction
Photochemical cycloreversion
Organic field-effect Transistor
Thermolysis

ABSTRACT

15-Acetoxy- and 15-hydroxy-6,13-dihydro-6,13-ethanopentacenes sublimed over 300 °C and no pentacene was formed below the temperature. The precursors bearing chlorinated epithiomethano bridges suffered complicated decomposition to give oligomeric pentacene derivatives. The precursor bearing an epithio–oxomethano bridge underwent smooth and clean conversion to pentacene by heat or light. An organic field-effect transistor fabricated by the spin-coating method of the precursor followed by light irradiation at 120 °C showed a good FET performance of $\mu = 2.5 \times 10^{-2}$ cm^2 V^{-1} s^{-1} and on/off ratio$= 3.8 \times 10^4$.

1. Introduction

Organic field-effect transistors (OFETs) have attracted much attention as a flexible and low-cost device.[1] Pentacene-OFETs fabricated by a vacuum deposition method showed high mobility and a large on/off ratio.[2] However, the vacuum deposition method has some disadvantages. For an example, the preparation of large-area devices requires very high cost. A solution process such as a spin- or dip-coating method is relatively unexpensive and thought to be alternative. However, this method hardly used for the preparation of pentacene devices due to its low solubility in common solvents.[3] Müllen and coworkers overcame this problem by use of a soluble precursor of pentacene, which was converted to pentacene directly on a substrate by the retro-Diels–Alder reaction.[4] The fabricated pentacene OFET was reported to have a high mobility of 0.1 cm^2 V^{-1} s^{-1}.[4b] Since then, several pentacene OFETs using its Diels–Alder adducts as precursors have been reported: (*N*-sulfinylacetamide adduct: 0.89;[5] *N*-sulfinyl-*n*-butylcarbamate adduct: 0.068;[6] *N*-sulfinylbenzamide adduct: 0.05,[7] *N*-sulfinylmethacryl-amide adduct: 0.021;[8] *N*-sulfinyl-*tert*-butylcarbamate adduct: 0.25;[9] and bis(ethylenedioxo)methano adduct: 7.9×10^{-6} cm^2 V^{-1} s^{-1}).[10] Pentacene OFETs based on the solution process using photo precursors were reported. Chow and co-workers prepared the OFET devices based on thermal and photo pentacene formation from 6,13-dihydro-6,13-methanopentacen-15-one (thermal: 8.8×10^{-3}; photo: 2.4×10^{-3} cm^2 V^{-1} s^{-1}).[11] 6,13-Dihydro-6,13-ethanopentacene-15,16-dione was shown to give pentacene by light (460 nm). Its solution-processed OFET showed high performance (mobility: 0.34 cm^2 V^{-1} s^{-1}; on/off ratio: 2.0×10^6).[12] In order to make high performance OFETs of pentacene by the solution process, we started to explore new precursors of pentacene. In this paper, we discuss our results on behavior of such pentacene precursors.

2. Results and discussion

2.1. Synthesis of pentacene precursors

Preparation of pentacene precursors was shown in Scheme 1. Acetoxyethylene-bridged pentacene **1** was prepared by the Diels–Alder reaction of pentacene and vinyl acetate in 66% yield according to the literature.[13] Hydrolysis of **1** with sodium methoxide gave hydoxyethylene-bridged derivative **2** in 87% yield.[14] Oxidation of **2** with the Dess–Martin reagent afforded **3** in 72% yield. Thiophosgene adduct **4** and its hydrolized derivative **5** were prepared according to the literatures.[15] Contrary to the literature,[15a] adduct **4** was easily isolated by recrystallization in 57% yield. Hydrolysis of **4** with silica gel afforded hydrolized derivative **5** in 79% yield. Oxidation of adduct **4** was carried out by one equivalent of *m*-CPBA to give sulfoxide **6** in 78% yield.

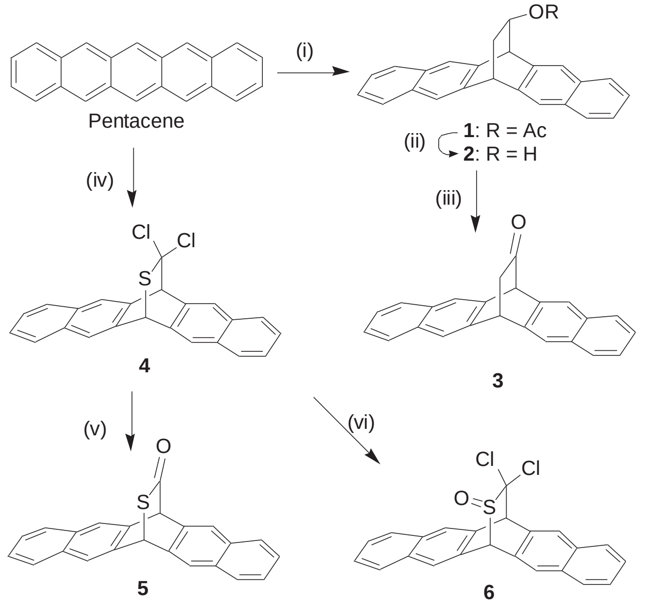
2.2. Thermal conversion of the precursors

We examined thermal behaviors of the pentacene derivatives by thermogravimetric (TG) analyses. In order to know the molecular composition of the obtained pentacene precursors, elemental analyses were carried out by using samples recrystallized from an

---

* Corresponding author. E-mail address: uno@dpc.ehime-u.ac.jp (H. Uno).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.06.051



Scheme 1. Preparation of pentacene adducts. Reagents, conditions, and yields: (i) vinyl acetate, chlorobenzene, autoclave, 220 °C, 66%; (ii) MeONa, MeOH, THF, reflux, 87%; (iii) Dess–Martin reagent, CH_2Cl_2, rt, 72%; (iv) thiophosgene, 65 °C, 57%; (v) silica gel, CH_2Cl_2, 79%; (vi) *m*-CPBA, CH_2Cl_2, 78%.

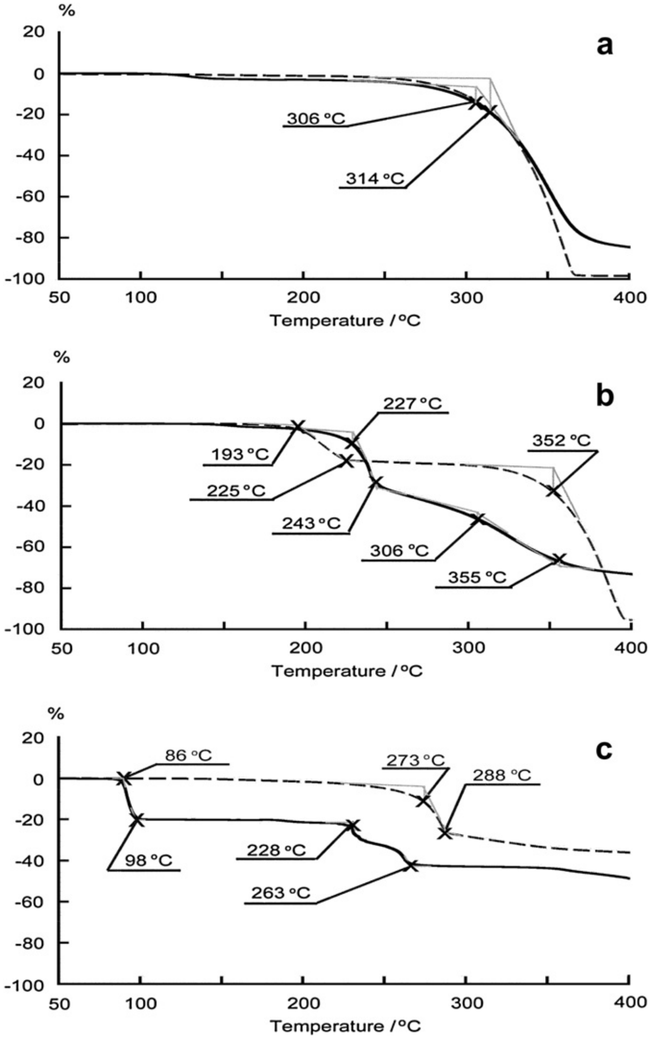


Figure 1. TG curves (a) **1** (solid line) and **2** (broken line); (b) **3** (solid line) and **5** (broken line); (c) **4** (solid line) and **6** (broken line).

appropriate solvent system (dichloromethane or dichloromethane/isopropanol) followed by evacuation (ca. 0.05 mm Hg) overnight at room temperature. Elemental analysis of the sample of **4** gave variable results by sampling. The sample of **4** consisted of powdery white solid and fine colorless block crystals. X-ray analysis of the block crystal revealed the absence of co-crystallized solvent. We concluded that the recrystallization of **4** from dichloromethane gave two or more kinds of crystals. In order to obtain a uniform composition of the sample of **4**, several recrystallization solvents were examined. Among them, the crystals of **4** from $C_2H_4Cl_2$ were stable and contained uniformly one molecule of dichloroethane, which was unambiguously proved by the elemental and X-ray analyses. In other samples, some solvent molecules were involved and the sample compositions were as follows: **2** with a quarter molecule of water, **3** with a quarter molecule of isopropanol, **5** with one eighths of water, and **6** with a quarter molecule of dichloromethane. The TG experiments were performed by a heating rate of 10 °C/min under N_2. The TG curves are shown in Figure 1.

In the cases of vinyl alcohol adducts **1** and **2**, the extensive weight loss started around 300 °C (Fig. 1a). As pentacene started to sublime around 300 °C under the same conditions (see Fig. S1 in the ESI), we concluded that adducts **1** and **2** did not undergo the retro-Diels–Alder reaction below the sublimation temperature of pentacene. TG curves of **3** and **5** are shown in Figure 1b. There were two obvious steep slopes and a flat step in the TG curve of **5**. The first weight loss observed between 193 and 225 °C (17.1%) was corresponding to the calculated value of thiocarbonyl and a quarter molecule of water (18.3%), and the entire weight loss corresponding to the pentacene sublimation started around 300 °C. Therefore, we concluded that precursor **5** underwent the clean retro-Diels–Alder conversion to pentacene. On the other hand, one steep slope and another moderate slope were observed in the TG curve of **3** at the temperature ranges of 227–243 and 306–355 °C, respectively. No step was observed and the weight was gently lost between these ranges. Moreover, a considerable amount of a residue remained even over 400 °C (26.9%). The first weight loss was 28.8%, which was far more than the calculated value of ketene and a quarter molecule of isopropanol (17.8%). In the cases of chlorinated precursors **4** and **6**, a steep slope was observed around 250 °C and a lot of residues remained even at 400 °C (41.4% for **4** and 64.0% for **6**). In the case of **4**, additional steep weight loss (19.3%) corresponding to one $C_2H_4Cl_2$ molecule (20.1%) was observed around 90 °C. The amounts in the steep weight losses of **4** and **6** were 39.6% and 25.9%, respectively. These values were roughly close to the sums of two chlorine atoms and solvents (34.5% for **4** and 23.7% for **6**). If the retro-Diels–Alder reaction would occur in **4** and **6**, 44.5% (dichloroethane and thiophosgene) and 35.4% (thiophosgene *S*-oxide and a quarter molecule of dichloromethane) of the initial weights would be lost. In the case of **6**, gentle weight loss was observed in the temperature range of 290–350 °C, which would be corresponding to the sublimation of pentacene. In the case of **4**, no obvious weight was lost in the temperature range of pentacene sublimation, but additional weight loss started at 350 °C.

In order to clarify the thermal degradation pathways, bulk decomposition experiments were carried out at each beginning temperature of the first steep slop. As volatile materials were removed under the gentle flow of nitrogen in the TG experiments, we performed the experiments under a reduced pressure in order to remove the volatile materials generated. Precursors **3**, **4**, **5**, and **6** were heated at 230, 250, 190, and 270 °C for 1 h under a reduced pressure (ca. 30 mm Hg) by a glass tube oven, respectively. Black residues and sublimed materials at the rim part of the glass tube were obtained except for **3**. In the case of **3**, the color of residue was brown. From the CHN elemental analysis of the residues from **3**, **4**,

5, and **6**, the compositions were C, 92.12, H, 4.63; C, 84.93, H, 4.00; C; 95.17, H; 5.19; and C, 83.65, H, 3.96%, respectively. In the cases of **4**, **5**, and **6**, pentacene was identified in the sublimed materials. The composition of the thermal degradation residue from **5** was well in accord with that of pentacene (Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07%). On the other hand, other compositions were between pentacene and the precursors.

Next, we examined the MALDI-TOF Mass spectra of the residual materials from **3**, **4**, and **6**. The results are shown in Figure 2. From the spectrum of degradation residue from **3**, the peaks of m/z=278 and 291 were found in addition to many higher-mass peaks up to 800 (Fig. 2a). As the pentacene chromophore did not exist in this residue due to no characteristic absorption in the UV spectrum, the peaks were derived from degradation of the polymeric material. In the case of the residue from thiophosgene adduct **4**, strong peaks of m/z=321, 597, 640, and 959 was observed in addition to a small peak of pentacene (Fig. 2b). Judging from the isotopic pattern, there was no chlorine atom in these peaks, and the compositions of m/z=321, 597, 640, and 959 were assigned as pentacene-6-thiocarbonyl cation ($C_{22}H_{13}CS^+$), dipentacenyl thioketone derivative, dimeric pentacenethiocarbonyl derivative, and trimeric pentacenethio-carbonyl species, respectively. On the other hand, new peaks of m/z=278 (pentacene), 323, 325, and 567 as well as many higher-mass peaks were observed in the spectrum of the residue from **6** in addition to the same four strong peaks of m/z=321, 597, 640, and 959 as **4** (Fig. 2c). The new peaks were thought to be derived from pentacenyl chlorocarbene. Pausible decomposition pathways of the precursors containing the epithiomethano moieties are illustrated in Scheme 2, where the possible species and intermediates are shown with the observed mass numbers.

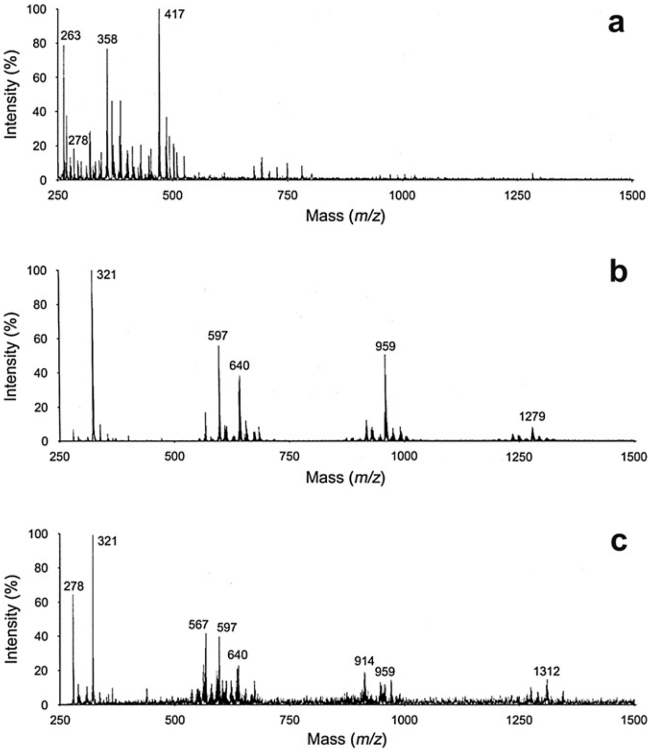
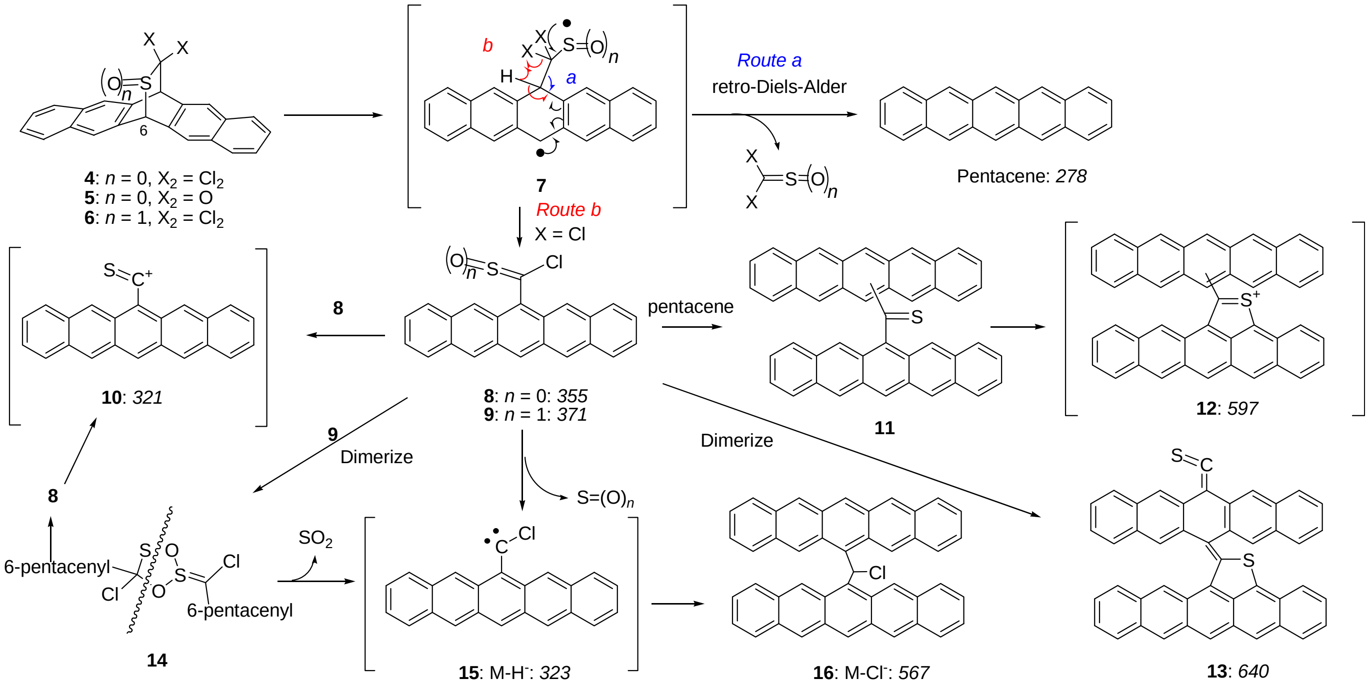


Figure 2. MALDI-TOF MS spectra of residues from **3** (a), **4** (b), and **6** (c).

In the thermal decomposition of **4**, **5**, and **6**, the weakest bond of C^6–S would be first broken to give diradical **7**. There would be two possible fates in the decomposition of the radical. In the case of **5**, retro-Diels–Alder-like decomposition pathway *a* would only occur to give pentacene, because no weak β bond to the thiyl radical exists. In the cases of **4** and **6**, the weak β bond of C–Cl would be cleaved in addition to the pathway *a*, and the resulted chloro radical would abstract the adjacent hydrogen atom to form thiocarbonyl and thiocarbonyl *S*-oxide derivatives **8** and **9**. The thiocarbonyl chloride **8** would undergo some bond-forming reactions such as the Friedel–Crafts reaction giving dimeric compounds **11**, **12**, **13**, and so on. In the case of thiocarbonyl *S*-oxide **9**,[16] 1,3-dipolar cyclodimerization would occur to give dioxadithiol **14**, which would then decompose to give thiocarbonyl chloride **8**, sulfur dioxide, and pentacenyl chlorocarbene **15**. The last intermediate species would undergo the insertion reaction with pentacene to give dipentacenylmethyl chloride (**16**).



Scheme 2. Pausible decomposition pathways of the precursors containing epithiomethano moieties.

2.3. Photo conversion of pentacene derivative to pentacene

Pentacene derivatives **1**–**6** in acetonitrile were irradiated with 254-nm light roughly corresponding to the π–π* transition of naphthalene under a nitrogen atmosphere. Only epithio–oxomethano-bridged derivative **5** underwent the photo conversion to pentacene. The progress was monitored by UV/vis measurement (Fig. 3). As the strong absorption peak at 238 nm decreased, the absorption peaks at 296, 495, 527, and 571 nm due to pentacene increased until 30 s. After 30 s, the absorptions due to pentacene decreased quickly due to precipitation of pentacene from the super-saturated solution.

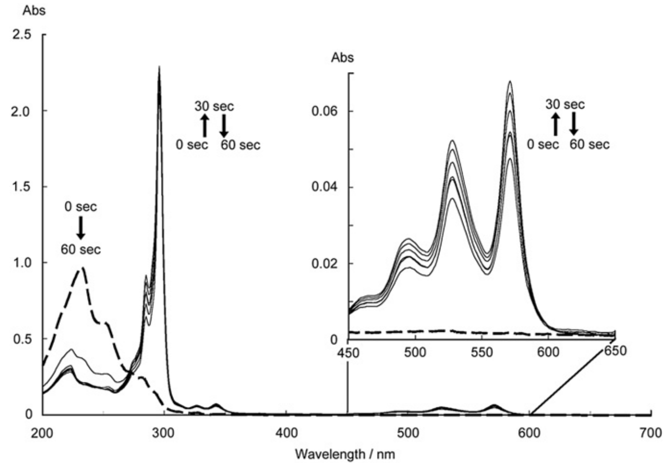


Figure 3. UV/vis spectra during photo conversion of **5** (broken bold line) to pentacene.

We next examined the photo conversion of **5** in acetonitrile by IR spectroscopy (Fig. 4). The carbonyl stretching of **5** was observed at 1693 cm^{-1}. When epithiooxomethano-bridged precursor **5** was irradiated for 2 min, a new absorption at 2040 cm^{-1} due to the cumulenic C=O stretching[17] appeared and increased at the expense of the carbonyl absorption at 1693 cm^{-1}. After five min, the absorption at 1693 cm^{-1} completely disappeared and the absorption at 2040 cm^{-1} became very strong. It is worthy to note that no obvious carbonyl stretching except for the mentioned stretching of carbonyl sulfide was observed in the IR spectra. This fact also suggested the complete conversion of **5** to pentacene by light irradiation.

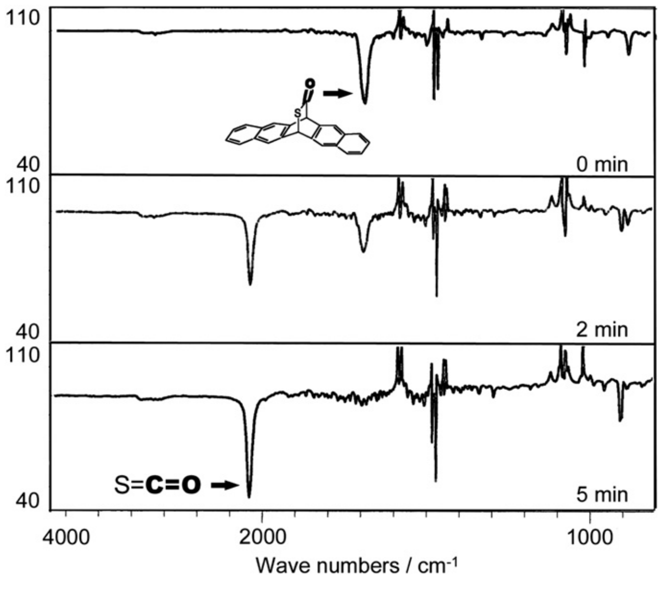


Figure 4. IR spectra in CH_3CN during light irradiation of **5**.

2.4. Device preparation

Only epithio–oxomethano-bridged precursor **5** is a candidate for the solution-processed OFET. When the pentacene devices were annealed at higher temperatures than 150 °C, holes due to sublimation of pentacene were generated and their device performance was reduced.[12c] As the conversion temperature of **5** by heat (>180 °C) was higher than the temperature limitation, we decided to use the light conversion method. The epithio–oxomethano precursor **5** was fairly soluble in halogenated and carbonyl solvents such as chloroform, dichloromethane, dichloroethane, chlorobenzene, acetone, and ethyl acetate, slightly soluble in alcoholic and aromatic hydrocarbon solvents, and hardly soluble in non-aromatic hydrocarbon and ethereal solvents. We made field-effect transistors (FETs) in the top-contact fashion by deposition of pentacene with the visible-light irradiation to the thin-layered precursor as follows. Heavily *n*-doped SiO_2 (500-nm thickness)/Si substrates were spin-coated with a 0.25% MSQ EtOH/BuOH (v/v=1/1) solution (5000 rpm, 50 s) and then dried at 220 °C for 30 min. The precursor **5** in a 1.0% solution of chloroform containing 7.8-molar equivalents of ethanol was spin-coated (1000 rpm, 30 s) on the SiO_2/Si substrate, and the film was dried at 60 °C on a hot plate for 5 min. In order to avoid the undesirable side reactions of deposited pentacene caused by irradiation of high-energy light and existence of oxygen,[12a,12b,18] the thin-layered precursor was converted on a hot plate (30–140 °C) by irradiation (1 min) with a lamp (HOYA-SCHOTT EX250) in a glove box under an inert atmosphere. The thickness of the precursor film was ca. 100 nm. Then gold electrodes were installed (channel length: 0.05 mm, channel width: 0.3 cm) at room temperature by vapor deposition (1.3×10^{-3} Pa).

First, we tested the deposition temperature during the light irradiation, since the temperature was the most significant factor for the OFET performance of the device from 6,13-ethano-6,13-dihydropentacene-15,16-dione.[12c] The mobility increased from $\mu=6.2\times10^{-5}$ to 1.0×10^{-1} $cm^2\,V^{-1}\,s^{-1}$, as the temperature increased from 30 to 140 °C (Table 1). The on/off ratio, however, reached a maximum of 1.9×10^3 at 120 °C and then decreased. We decided that the best conversion temperature was 120 °C, which was the same as the case of 6,13-ethano-6,13-dihydropentacene-15,16-dione.[12c] As a polar solvent additive in the spin-coating process of the precursor was also important in the fabrication of the solution-processed pentacene OFET,[12c] we next tested the solvent system. Complete removal of ethanol improved the on/off ratio to 9.6×10^3, although the mobility μ slightly decreased to 2.3×10^{-3} $cm^2\,V^{-1}\,s^{-1}$. The best performance of $\mu=2.5\times10^{-2}$ $cm^2\,V^{-1}\,s^{-1}$ and on/off ratio=3.8×10^4 was obtained by substitution of ethanol with acetone (Table 1, entry 5).

Table 1
FET performance of the device using **5**

Entry	Solvent	Annealing temperature/°C	Mobility/$cm^2\,V^{-1}\,s^{-1}$	On/off ratio
1	EtOH/$CHCl_3$	30	6.2×10^{-5}	29
2	EtOH/$CHCl_3$	120	5.0×10^{-2}	1.9×10^3
3	EtOH/$CHCl_3$	130	9.0×10^{-2}	1.3×10^2
4	EtOH/$CHCl_3$	140	1.0×10^{-1}	1.4×10^2
5	Acetone/$CHCl_3$[a]	120	2.5×10^{-2}	3.8×10^4
6	$CHCl_3$[b]	120	2.3×10^{-2}	9.6×10^3

[a] Acetone was used instead of ethanol.
[b] Without an additive.

In conclusion, we prepared 6,13-bridged pentacenes based on the Diels–Alder reaction of pentacene with vinyl acetate or thiophosgene and studied thermal and photo reactions of the pentacene derivatives. 15-Acethoxy-6,13-dihydro-6,13-ethanopentacene (**1**) and 6,13-dihydro-15-hydroxy-6,13-ethanopentacene (**2**) were not converted to pentacene below the sublimation temperature of pentacene. Thermal reaction of 16,16-dichloro-6,13-dihydro-6,13-epithiomethanopentacene (**4**) and 16,16-dichloro-6,13-dihydro-15-oxo-6,13-epithiomethano-pentacene (**6**) gave mainly polymeric materials derived from pentacene-6-thocarbonyl species in addition to a small amount of pentacene. 6,13-Dihydro-6,13-epithiomethanopentacen-16-one (**5**) was quantitatively converted to pentacene by heat (220 °C) and light (254 nm). The pentacene OFET fabricated by spin-coating of **5** followed by light irradiation at 120 °C showed good performance of μ=2.5× 10^{-2} cm^2 V^{-1} s^{-1} and on/off ratio=3.8×10^4.

3. Experimental

3.1. General

Melting points were measured on a Yanagimoto micromelting point apparatus and are uncorrected. NMR spectra were obtained with a JEOL AL-400 or EX-400 spectrometer at the ambient temperature by using $CDCl_3$ as a solvent, and tetramethylsilane as an internal standard for ^{1}H and ^{13}C. IR spectra were measured with a Horiba FT-720 infrared spectrophotometer. Mass spectra (EI, 70 eV) were measured with a JEOL JMS-700. The MALDI-TOF MS spectra were measured with a Voyager DE Pro instrument. Elemental analyses were performed with a Yanaco MT-5 elemental analyzer. UV/vis spectra were measured in acetonitrile with a HITACHI U-2810 spectrophotometer. TG measurements were performed with Seiko Instruments EXSTAR 6000. The photo conversion experiments were performed by using a UV lamp (AS ONE SLUV-4: 614 μW/cm^2). All solvents and chemicals were reagent grade quality, obtained commercially and used without further purification except as noted. Acetonitrile for spectroscopy was purchased from Nacalai Tesque Co. Solvents for chromatography were purified by distillation. Thin-layer and column chromatography was performed on Art. 5554 (Merck KGaA) and Silica Gel 60N (Kanto Chemical Co.), respectively. Other commercially available materials were used without further purification.

*3.1.1. 15-Acetoxy-6,13-dihydro-6,13-ethanopentacene (**1**).* Pentacene (278 mg, 1.00 mmol), vinyl acetate (0.37 mL, 4.0 mmol), hydroquinone (5 mg, 0.05 mmol), and chlorobenzene (20 mL) were placed in a stainless steel cylinder equipped with a magnetic stirring bar. The cylinder was screw-capped and heated at 220 °C for 24 h with stirring. The cylinder was cooled to room temperature and the cap was carefully unscrewed. The mixture was filtered to remove pentacene and the filtrate was concentrated. The residue was chromatographed (silica gel, 60% $CHCl_3$/hexane) and recrystallized ($CHCl_3$/MeOH) to give **1** (241 mg, 66%) as colorless crystals: mp 186–189 °C, R_f=0.3 (60% $CHCl_3$/hexane); ^{1}H NMR δ 7.70–7.81 (8H, m), 7.41 (4H, m), 5.23 (1H, m), 4.78 (1H, m), 4.52 (1H, m), 2.53 (1H, m), 1.91 (3H, s), 1.75 (1H, m); ^{13}C NMR δ 170.90, 140.86, 140.81, 137.12, 136.82, 132.70, 132.65, 132.49, 132.33, 127.64, 127.57, 127.55, 127.48, 125.81, 125.55, 125.52, 125.38, 124.18, 123.75, 121.62, 121.43, 72.29, 48.45, 43.49, 36.14, 21.20; IR (KBr): ν_{max} 1738, 1371, 1242, 1028, 891, 752 cm^{-1}; EIMS: *m*/*z* (rel int.) 364 (M$^+$, 6), 278 (100). Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.39; H, 5.71%.

*3.1.2. 6,13-Dihydro-15-hydroxy-6,13-ethanopentacene (**2**).* To a solution of **1** (190 mg, 0.521 mmol) in THF (20 mL) and MeOH (5 mL) was added a 28% solution of MeONa in MeOH (1.0 mL, 5.7 mmol) at room temperature. The mixture was refluxed for 18 h. The mixture was cooled to room temperature and quenched with 1.0 M aqueous HCl. The mixture was extracted with EtOAc. The organic extract was washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel ($CHCl_3$) to give **2** (149 mg, 87%) as colorless powder: mp 223–226 °C, R_f=0.25 ($CHCl_3$); ^{1}H NMR δ 7.95 (1H, s), 7.81 (2H, s), 7.75–7.85 (4H, m), 7.71 (1H, s), 7.42 (4H, m), 4.62 (1H, m), 4.51 (1H, m), 4.36 (1H, m), 2.52 (1H, m), 1.59 (1H, m),1.31 (1H, br s); ^{13}C NMR δ 141.01, 140.65, 138.05, 136.04, 132.83, 132.64, 132.39, 132.32, 127.58, 127.48, 125.66, 125.47, 125.33, 125.23, 123.35, 123.25, 121.75, 121.65, 121.61, 121.51, 69.80, 52.33, 43.78, 39.77; IR (KBr): ν_{max} 3554, 1444, 1389, 1022, 885, 756 cm^{-1}; EIMS: *m*/*z* (rel int.) 322 (M$^+$, 23), 278 (100). Anal. Calcd for $C_{24}H_{18}O$+1/4H_2O: C, 88.18; H, 5.70. Found: C, 88.15; H, 5.85%.

*3.1.3. 6,13-Dihydro-6,13-ethanopentacen-15-one (**3**).* To a stirred solution of **2** (129 mg, 0.400 mmol) in CH_2Cl_2 (8.0 mL) was added the Dess–Martin reagent (254 mg, 0.600 mmol) at room temperature. The mixture was stirred for 6 h. The reaction was quenched with a saturated aqueous $NaHCO_3$ solution and the mixture was extracted with EtOAc. The organic extract was washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by recrystallization with $CHCl_3$/isopropanol to give **3** (109 mg, 72%) as white powder: mp 216 °C (decomp.), R_f=0.7 ($CHCl_3$); ^{1}H NMR δ 7.85 (4H, m), 7.80 (4H, m), 7.45 (4H, m), 5.08 (1H, s), 4.81 (1H, m), 2.58 (2H, m); ^{13}C NMR δ 205.75, 139.79, 134.63, 133.23, 132.77, 128.03, 127.92, 126.59, 126.35, 124.64, 122.71, 63.10, 44.93, 40.84; IR (KBr) ν_{max} 1722, 1608, 1560, 1439, 1340, 742 cm^{-1}; EIMS: *m*/*z* (rel int.) 320 (M$^+$, 2), 292 (7), 278 (100), 139 (24). Anal. Calcd for $C_{24}H_{16}O$+1/4 isopropanol: C, 88.63; H, 5.41. Found: C, 88.38; H, 5.74%.

*3.1.4. 16,16-Dichloro-6,13-dihydro-6,13-epithiomethanopentacene (**4**).* A suspension of pentacene (1.11 g, 4.00 mmol) and thiophosgene (6.0 mL) was heated at 65 °C for 6 h. After cooling to room temperature, CH_2Cl_2 was added to the reaction mixture and unreacted pentacene was removed by filtration. Toluene (40 mL×2) was added and the mixture was evaporated to remove excess thiophosgene completely. The product was recrystallized with 1,2-dichloroethane to give the title compound (1.13 g, 57%) as colorless crystals: mp 252 °C (decomp.); ^{1}H NMR δ 8.00 (2H, s), 7.84 (4H, m), 7.79 (2H, s), 7.47 (4H, m), 5.52 (1H, s), 5.39 (1H, s); ^{13}C NMR δ 137.07, 135.11, 132.85, 132.37, 128.95, 127.92, 127.10, 126.73, 126.41, 120.77, 64.19, 51.03, 43.42; IR (KBr) ν_{max} 3057, 1498, 1446, 1398, 1338, 1230 cm^{-1}; EIMS: *m*/*z* (rel int.) 392 (M$^+$, 10), 357 (7), 321 (6), 278 (100), 139 (12). Anal. Calcd for $C_{23}H_{14}Cl_2S$+$C_2H_4Cl_2$: C 60.99; H, 3.69. Found: C, 61.29; H, 3.67%.

*3.1.5. 6,13-Dihydro-6,13-epithiomethanopentacen-16-one (**5**)*[15a]. To a solution of **4** (789 mg, 2.00 mmol) in CH_2Cl_2 (20 mL) was added silica gel. After the solvent was removed, the silica gel was washed with CH_2Cl_2. The organic extract was concentrated and dried under a reduced pressure to give **5** (546 mg, 79%) as colorless powder: mp 193 °C (decomp.), R_f=0.75 ($CHCl_3$); ^{1}H NMR δ 7.91 (2H, s), 7.89 (2H, s), 7.82 (4H, m), 7.49 (4H, m), 5.82 (1H, s), 5.46 (1H, s); ^{13}C NMR δ 201.89, 137.73, 134.34, 132.55, 132.28, 127.88, 127.81, 126.83, 126.69, 125.23, 121.75, 64.66, 52.19; IR (KBr): ν_{max} 3003, 1668, 1604, 1500, 1336, 1205 cm^{-1}; MS (EI): *m*/*z* (rel int.) 338 (M$^+$, 10), 278 (100), 139 (17); λ_{max} (log ε) 232 (4.90), 250 (4.66) nm. Anal. Calcd for $C_{23}H_{14}OS$+1/8H_2O: C, 81.09; H, 4.22. Found: C, 81.14; H, 4.35%.

*3.1.6. 16,16-Dichloro-6,13-dihydro-15-oxo-6,13-epithio-methanopentacene (**6**).* To a stirred solution of **5** (108 mg, 0.275 mmol) in CH_2Cl_2 (10 mL) was added *m*-CPBA (64.8 mg, 0.274 mmol) at 0 °C. After the mixture had been stirred for 1 h at room temperature, a saturated aqueous $NaHCO_3$ solution was added. The mixture was extracted three times with CH_2Cl_2. The organic extract was washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was washed with ether to give **6** (92.2 mg, 78%) as white powder: mp 273 °C (decomp.), R_f=0.3 ($CHCl_3$); ^1H NMR δ 7.85–8.03 (8H, m), 7.50–7.55 (4H, m), 5.76 (1H, s), 5.29 (1H, s); ^{13}C NMR δ 134.06, 133.38, 133.29, 133.04, 132.16, 128.46, 128.44, 128.14, 128.03, 127.99, 127.90, 127.53, 127.35, 127.24, 127.10, 127.07, 126.97, 126.94, 126.93, 126.92, 101.88, 69.12, 61.48; IR (KBr): ν_{max} 1500, 1331, 1188, 1095, 897, 837, 756 cm^{-1}; EIMS: *m*/*z* (rel int.) 408 (M^+, 5) 360 (11), 325 (20), 278 (100). Anal. Calcd for $C_{23}H_{14}Cl_2OS+1/4CH_2Cl_2$: C, 64.86; H, 3.39. Found C, 64.74; H, 3.37%.

3.2. X-ray analysis

Determination of cell parameters and collection of reflection intensities were performed on Rigaku Mercury-8 (3-kW sealed tube) instrument equipped with graphite monochromated Mo Kα radiation. The data were corrected for Lorentz, polarization, and absorption effects. X-ray data were processed by CrystalClear SM Ver. 1.3.6.[19] The processed data were treated with the CrystalStructure 3.8.2[19] or WinGX 1.80.03.[20] Structures were solved by SIR-97[21] and then refined by SHELXL-97.[22] The structure was validated by Platon cif check.[23] The X-ray analysis results in cif format were deposited at the Cambridge Crystallographic Data Centre. The CCDC numbers of **1**+$CHCl_3$, **4**, and **4**+$C_2H_4Cl_2$ are 771012, 771013, and 771014, respectively.

Acknowledgements

This work was partially supported by Grant-in-Aid for the Scientific Research (20550047) from the Japanese Ministry of Education, Culture, Sports, Science and Technology and by a grant for the Research for Promoting Technological Seeds B (14-B02) from the Japan Science and Technology Agency. Miss Akane Masumoto (Canon Co.) is greatly appreciated for her measurement of FET performance. X-ray, elemental analysis, IR, NMR, FAB MS, and TG measurements were performed at Integrated Center for Sciences, Ehime University.

Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.06.051. These data include MOL files and InChIKeys of the most important compounds described in this article.

References and notes

1. Recent reviews, see: Cao, Y.; Steigerwald, M. L.; Nuckolls, C.; Guo, X. *Adv. Mater* **2010**, *22*, 20–32; Ortiz, R. P.; Facchetti, A.; Marks, T. J. *Chem. Rev.* **2010**, *110*, 205–239; Di, C.-A.; Liu, Y.; Yu, G.; Zhu, D. *Acc. Chem. Res.* **2009**, *42*, 1573–1583; Liu, S.; Wang, W. M.; Briseno, A. L.; Mannsfeld, S. C. B.; Bao, Z. *Adv. Mater.* **2009**, *21*, 1217–1232; Yamashita, Y. *Sci. Technol. Adv. Mater.* **2009**, *10* 024313/1-9; Hasegawa, T.; Takeya. *J. Sci. Technol. Adv. Mater.* **2009**, *10* 2024314/1-16; Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem., Int. Ed.* **2008**, *47*, 4070–4098; Yamada, H.; Okujima, T.; Ono, N. *Chem. Commun.* **2008**, 2957–2974; Mas-Torrent, M.; Rovira, C. *Chem. Soc. Rev.* **2008**, *37*, 827–838.
2. Zhang, X.-H.; Domercq, B.; Wang, X.; Yoo, S.; Kondo, T.; Wang, Z. L.; Kippelen, B. *Org. Electron* **2007**, *8*, 718–726; Oyama, T.; Ye, R.; Baba, M.; Ohta, K. *Mol. Cryst. Liq. Cryst.* **2007**, *471*, 205–211.
3. Natsume, Y.; Minakata, T.; Aoyagi, T. *Org. Electron* **2009**, *10*, 107–114.
4. (a) Brown, A. R.; Pomp, A.; de Leeuw, D. M.; Klaassen, D. B. M.; Havinga, E. E.; Herwig, P.; Müllen, K. *J. Appl. Physiol.* **1996**, *79*, 2136–2138; (b) Herwig, P. T.; Müllen, K. *Adv. Mater.* **1999**, *11*, 480–483.
5. Aflzali, A.; Dimitrakopoulos, C. D.; Breen, T. L. *J. Am. Chem. Soc.* **2002**, *124*, 8812–8813.
6. Afzali, A.; Kagan, C. R.; Traub, G. P. *Synth. Met.* **2005**, *155*, 490–494.
7. Zander, Z.; Hoffmann, N.; Lmimouni, K.; Lemfan, S.; Peit, C.; Vuillaume, D. *Microelectron. Eng.* **2005**, *80*, 394–397.
8. Afzali, A.; Dimitrakopoulos, C. D.; Graham, T. O. *Adv. Mater.* **2003**, *15*, 2066–2069.
9. Weidkamp, K. P.; Afzali, A.; Tromp, R. M.; Hamers, R. J. *J. Am. Chem. Soc.* **2004**, *126*, 12740–12741.
10. Haung, H.-H.; Hsieh, H.-H.; Wu, C.-C.; Lin, C.-C.; Chou, P.-T.; Chuang, T.-H.; Wen, Y.-S.; Chow, T. J. *Tetrahedron Lett.* **2008**, *49*, 4494–4497.
11. Chen, K.-Y.; Hsieh, H.-H.; Wu, C.-C.; Hwang, J.-J.; Chow, T. J. *Chem. Commun.* **2007**, 1065–1067; Chuang, T.-H.; Hsieh, H.-H.; Chen, C.-K.; Wu, C.-C.; Lin, C.-C.; Chou, P.-T.; Chao, T.-H.; Chow, T. J. *Org. Lett.* **2008**, *10*, 2869–2872.
12. (a) Uno, H.; Yamashita, Y.; Kikuchi, M.; Watanabe, H.; Yamada, H.; Okujima, T.; Ogawa, T.; Ono, N. *Tetrahedron Lett.* **2005**, *46*, 1981–1983; (b) Yamada, H.; Yamashita, Y.; Kikuchi, M.; Watanabe, H.; Okujima, T.; Uno, H.; Ogawa, T.; Ohara, K.; Ono, N. *Chem.—Eur. J.* **2005**, *11*, 6212–6220; (c) Masumoto, A.; Yamashita, Y.; Go, S.; Kikuchi, T.; Yamada, H.; Okujima, T.; Ono, N.; Uno, H. *Jpn. J. Appl. Phys.* **2009**, 48 051505/1-5.
13. Alder, K.; Rickert, H. F. *Ann.* **1939**, *543*, 1–27.
14. Wawzonek, S.; Hallum, J. V. *J. Org. Chem.* **1953**, *18*, 288–291.
15. (a) Vets, N.; Smet, M.; Dehaen, W. *Tetrahedron Lett.* **2004**, *45*, 7287–7289; (b) Allgeier, H.; Winkler, T. *Tetrahedron Lett.* **1976**, *17*, 215–218.
16. Block, E.; Penn, E. R.; Olsen, R. J.; Sherwin, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 1264–1265; Block, E.; Penn, E. R.; Revelle, L. K. *J. Am. Chem. Soc.* **1979**, *101*, 2200–2201.
17. Maki, A. G.; Plyler, E. K.; Tidwell, E. D. *J. Res. Nat. Bur. Stand.* **1962**, 163–167 (U.S.), 66A, (Phys. and Chem.) No. 2.
18. Sparfel, D.; Gobert, F.; Rigaudy, J. *Tetrahedron* **1980**, *36*, 2225–2235; Chan, S. H.; Lee, H. K.; Wang, Y. M.; Fu, N. Y.; Chen, X. M.; Cai, Z. W.; Wong, H. N. C. *Chem. Commun.* **2005**, 66–68; Coppo, P.; Yeates, S. G. *Adv. Mater.* **2005**, *17*, 3001–3005.
19. *Diffraction Data Reduction And Crystal Structure Analysis Packages*; Rigaku (3-9-12 Akishima, Tokyo, Japan) and Rigaku/MSC (9009 New Trails Dr.: The Woodlands, TX 77381 USA), 2000–2004.
20. Wingx 1.80.03 suite for small-molecule single-crystal crystallography, University of Glasgow, Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
21. SIR-97: A package for crystal structure solution and refinement, Istituto di Gristallografia, Italy. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
22. SHELXL-97: Program for the refinement of crystal structures from diffraction data, University of Göttingen, Göttingen, Germany; 'A short history of SHELX' Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.
23. PLATON: A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherland Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.