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Photooxidation and reproduction of pentacene derivatives substituted by aromatic groups

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Abstract—Pentacene derivatives substituted by aromatic groups at the 6,13-positions were prepared and investigated for their electronic properties and the photoaddition reaction with oxygen. The pentacene derivatives substituted by 2-thienyl and phenyl groups reacted with oxygen in solution under light and afforded their endoperoxides. These first-order kinetic constants were evaluated to be 1.5×10^{-3} s^{-1} and 2.7×10^{-3} s^{-1}. The pentacene derivative with pentafluorophenyl groups was relatively stable in solution. The thermolysis and photolysis of the endoperoxide with 2-thienyl groups in solution afforded the pentacene derivative with yields of 30 and 44%, respectively. In addition, UV irradiation (254 nm) of the thin film of the endoperoxide was studied, which indicated the reproduction of the pentacene derivative.

1. Introduction

Pentacene (**1a**) is one of the highly attractive compounds in organic field-effect transistors (OFETs)[1–3] since its thin films formed by vacuum deposition show a good performance of p-type semiconducting properties with mobilities of 35 and 58 cm^2 V^{-1} s^{-1} at the temperatures of 290 and 225 K, respectively.[2] These values are comparable to those of the hydrogenated amorphous silicon devices.[3] However, the application of pentacene for preparing OFET films is limited to the vacuum-deposition process since pentacene is insoluble in common organic solvents and is unstable in solution. Therefore, synthetic studies on various pentacene derivatives have been conducted.[4] Among these compounds, 6,13-functionalized pentacenes have been synthesized. The introduction of ethynyl groups into the 6,13-positions of pentacene led to the modification of molecular stacking, resulting in high semiconducting properties.[5] Recently, a pentacene derivative with 2-thienyl groups (**1b**) was synthesized and a hole mobility of 0.10 cm^2 V^{-1} s^{-1} was observed in an OFET device using it.[6] The synthesis and crystal structures of bis(alkylthio)pentacenes were also reported.[7] On the other hand, the Diels–Alder adducts of pentacene were synthesized and investigated as pentacene precursors in the study of solution-processed OFETs.[8,9] The adducts of pentacene with *N*-sulfinyl-*tert*-butylcarbamate,[8a] *N*-sulfinylacetamide,[8b] and carbon monoxide[8c] formed the thin films of pentacene after their thermal decomposition processes. Their OFET properties were almost similar to those observed in the devices using pentacene films formed by vacuum deposition. Furthermore, the photolysis of the adduct with a 1,2-diketone unit under argon formed the thin film of pentacene.[8d] In the synthetic studies on pentacene derivatives substituted by aromatic groups at the 6,13-positions, we investigated the photooxidation of pentacenes **1b–d** affording their endoperoxides and the reproduction of the pentacene derivatives (Fig. 1). In this paper, we report the preparation, properties, and photoreaction of pentacene derivatives **1b–d** and the deoxygenation reactions of an endoperoxide.

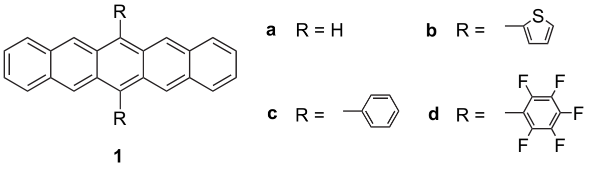

Figure 1. Structure of pentacene derivatives **1a–d**.

Keywords: Pentacene; Photooxidation; Endoperoxide; Deoxygenation.

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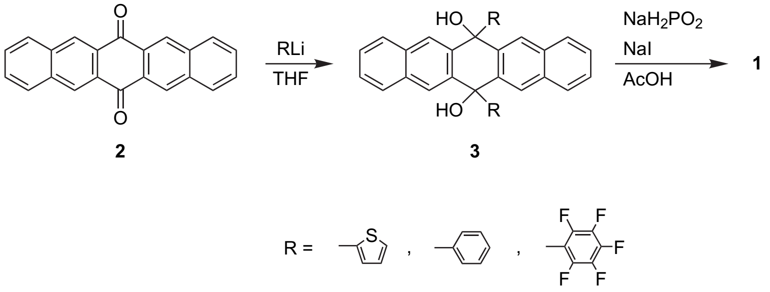
2. Results and discussion

Pentacene derivatives **1b–d** were synthesized as shown in Scheme 1.[10] 6,13-Pentacenequinone (**2**)[11] reacted with aryllithium reagents (3 mol equiv) to afford the corresponding diarylpentacenediols (**3b–d**) with yields of 48–80%. Compounds **3c** and **3d** were obtained as single isomers. Compound **3b** was identified as a mixture of two regioisomers (1.7:1) and it was used for the following reaction. Pentacenes **1b–d** with yields of 47–73% were prepared by the reaction of compounds **3b–d** with $NaH_2PO_2 \cdot H_2O$ (7 mol equiv) and NaI (5 mol equiv) in refluxing acetic acid. The resulting solids were purified by sublimation at 300–320 °C under 10^{-3} Torr to provide deep purple or deep blue crystals (**1b** and **1d**: mp >300 °C, **1c**: mp 292–293 °C). These compounds were soluble in dichloromethane and chloroform. The solutions of **1b** and **1c** were very sensitive to light in air and the decolorization of the solutions was observed. However, pentacene **1d** was relatively stable in solution. The structural determination of these compounds was performed using spectral data and elemental analysis.

The absorption bands based on the pentacene moieties were observed in the range between 450 and 650 nm. The absorption maxima are listed in Table 1. The maxima of **1b** are slightly red-shifted as compared to those of **1c** and **1d**, and this result is due to the presence of the thienyl groups. The cyclic voltammetry (CV) of pentacenes **1b–d** in dichloromethane showed reversible oxidation and reduction waves. The half-wave potentials are summarized in Table 1. The oxidation potential of **1d** is higher than those of **1b** and **1c**, and the reduction potential of **1d** is higher than those of **1b** and **1c**. These results indicated that two pentafluorophenyl groups increased the electron affinity of the pentacene moiety of **1d**.

Pentacenes **1b–d** were soluble in common organic solvents in contrast to pentacene **1a**. In order to investigate the behavior of these compounds in solution, decolorization by irradiation was studied. The solution of **1b** with a concentration of 10^{-5} M in dichloromethane gradually became colorless by exposure to room light, and the color of pentacene disappeared after 20 min (Fig. 2). The decolarization of **1c** as well as **1b** was observed.[12] However, the decolarization of **1d** was very slow due to the bulky electron-withdrawing groups substituted at the 6,13-positions of pentacene. The color of the pentacene could still be observed 2 h later (Fig. 2). The absorption spectrum of **1b** was monitored depending on the exposure time as shown in Figure 3. The absorption bands gradually decreased, and this decay obeyed first-order kinetics. The kinetic constant (k) was measured to be $1.5\times10^{-3}\ s^{-1}$. This value was comparable to that of **1c** ($k=2.7\times10^{-3}\ s^{-1}$), which was reported as $k=2.32\times10^{-3}\ s^{-1}$.[12] The kinetic constant of **1d** was evaluated to be $3\times10^{-5}\ s^{-1}$. According to the ^1H NMR analysis of **1b**, the decolorization cleanly proceeded to yield endoperoxide **4** (Scheme 2). Therefore, the reaction was a photoaddition reaction of pentacene with oxygen.[13] Thus, 100 mg of pentacene **1b** was dissolved in dichloromethane (100 mL), and the solution filtered through a Pyrex filter was exposed



Scheme 1. Synthesis of pentacene derivatives **1b–d**.

Table 1. Absorption maxima[a] and half-wave potentials[b] of **1**

Compound	λ_{max}/nm	$E^{ox}_{1/2}$/V	$E^{red}_{1/2}$/V
1b	605, 560, 521	+0.31	−1.72
1c	600, 555, 517	+0.23	−1.85
1d	595, 550, 512	+0.58	−1.53

[a] In CH_2Cl_2.
[b] nBu$_4$NClO$_4$ (0.1 M) in CH_2Cl_2, Pt electrode, V versus Fc/Fc$^+$.

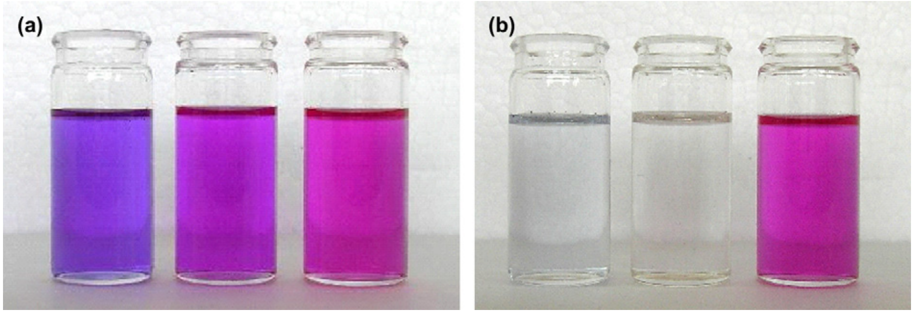


Figure 2. Color of the solutions of **1b** (left), **1c** (center), and **1d** (right); (a) before irradiation and (b) after irradiation for 2 h.

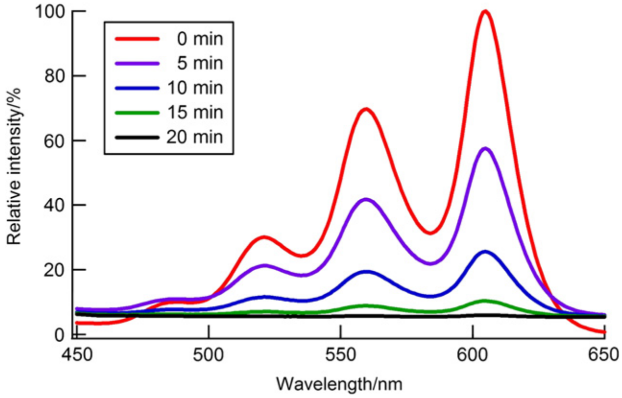


Figure 3. UV–vis absorption spectra of **1b** under light.

to sunlight in air for 2 h. After removal of the solvent, the residue was filtered and washed with hexane to yield 88 mg of the product (81% yield). The molecular structure of endoperoxide **4** was investigated by X-ray crystallographic analysis. A single crystal of **4** was obtained by recrystallization from benzene. The molecule has a bridge structure with an oxygen molecule, which bonds to pentacene at the 6,13-positions (Fig. 4). The oxygen moiety is located between the S atoms of the thienyl groups. The intramolecular distances between the O atoms and the S atoms are 2.71 and 2.78 Å. These values are shorter than the sum of their van der Waals radii (3.32 Å). The molecular structure is analogous to those of the photopatternable pentacene precursors used in OFETs.[8]

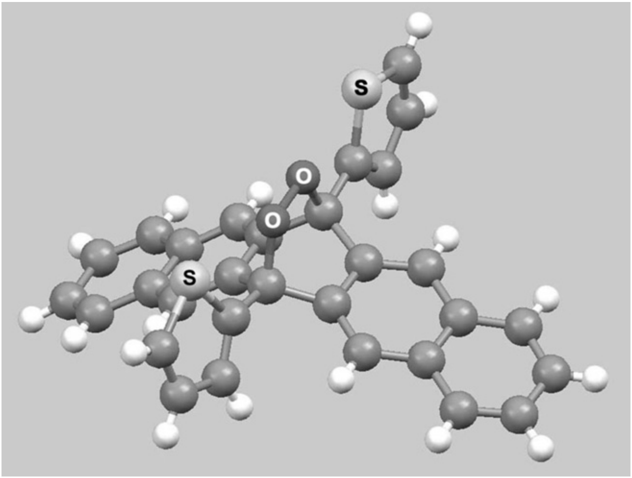


Figure 4. Molecular structure of endoperoxide **4**.

The colorless solution of endoperoxide **4** in decahydronaphthalene (decalin) turned purple upon heating, indicating the reproduction of pentacene **1b** (Scheme 2). The absorption bands based on the pentacene moiety were observed in the UV–vis spectrum after the thermal decomposition. According to the ^{1}H NMR analysis upon heating at 170 °C for 10 min in decalin-d_{18}, the thermal decomposition of **4** gave pentacene **1b** with a yield of 30%. This value is higher than those observed for the thermal decomposition of the endoperoxide of **1c** (7–14% yields).[14] During the melting point measurement of endoperoxide **4**, the white solid was tinged with blue at around 130 °C, and then this solid turned black at 180 °C. The thermogravimetric analysis (TGA) of endoperoxide **4** demonstrated a weight loss of 2.7% at 188 °C. This is corresponding to the change from a white solid to a black one in the melting point measurement. The weight loss is smaller than the theoretical O_2 loss (6.8%) by thermal decomposition [FW 474 (**4**)→FW 442 (**1b**)]. This result may be attributed to the molecular packing in the solid and other types of decomposition reactions take place upon heating. UV irradiation (254 nm) of the solution of endoperoxide **4** in decalin-d_{18} under argon for 10 min produced pentacene **1b** with a yield of 44%. After UV irradiation (254 nm) of the thin film of endoperoxide **4** was carried out in air for 8 min, the absorption bands on the pentacene moiety of **1b** were observed in the UV–vis spectrum (Fig. 5). This result indicated that the deoxygenation reaction in the solid state proceeded by the UV irradiation. Therefore, endoperoxide **4** is also a candidate for the photopatternable pentacene precursors used in OFETs. Further investigation on the UV irradiation of the thin film of **4** is under progress. If the thin films of pentacene **1b** prepared by the photolysis of endoperoxide **4** successfully show semiconducting properties, the conversion between **1b**

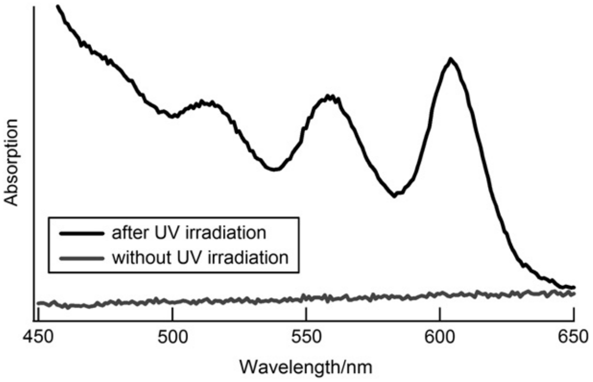
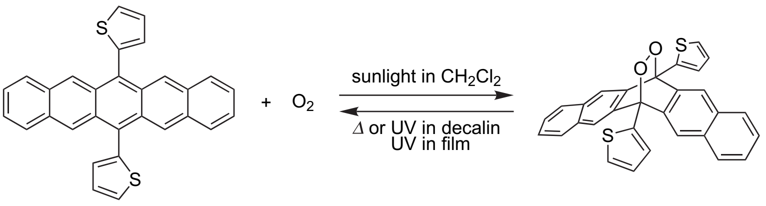


Figure 5. UV–vis absorption spectrum after UV irradiation (254 nm) of the film of endoperoxide **4**.



1b **4**

Scheme 2. Photooxidation of **1b** and deoxygenation of **4**.

and **4** is of interest as an ecological technology for the fabrication of solution-processed OFETs.

3. Conclusions

We synthesized pentacene derivatives substituted by aromatic groups at the 6,13-positions (**1b–d**). The absorption bands based on the pentacene moieties were observed in a similar wavelength region. The electron-donating ability and the electron affinity depended on the aromatic groups. Although these compounds were more stable in solution than pentacene **1a**, compounds **1b** and **1c** were highly reactive with oxygen under irradiation and afforded their endoperoxides. Pentacene **1d** was relatively stable in solution. The thermolysis and photolysis of endoperoxide **4** in solution afforded pentacene **1b** with yields of 30 and 44%, respectively. UV irradiation of the thin film of endoperoxide **4** indicated the reproduction of pentacene **1b**. These deoxygenation reactions are of interest for the film formation technology, which is of use in OFETs because pentacene **1b** was reported as a good semiconductor in the thin films formed by vacuum deposition. Further investigation on the photolysis of endoperoxide **4** in film is under progress.

4. Experimental

4.1. General

Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. IR and UV–vis absorption spectra were obtained with JASCO FT/IR-5300 and Hitachi U-3500 spectrometers, respectively. Mass spectra (EI) were determined with a Hitachi M-2000S mass spectrometer operating at 70 eV by a direct inlet system. Elemental analyses were performed with a Perkin–Elmer 2400II analyzer. ^{1}H and ^{13}C NMR spectra were recorded with Varian GEMINI (300 and 50 MHz) and Bruker AVANCE600 (600 and 150 MHz) spectrometers with tetramethylsilane as an internal standard.

4.1.1. Preparation of 6,13-dihydroxy-6,13-diarylpentacene (3b–d).[10] *n*BuLi in hexane (1.60 M, 2.43 mL, 3.89 mmol) was added dropwise to a solution of 2-bromothiophene (0.38 mL, 3.89 mmol) in dry THF (15 mL) at −78 °C under nitrogen. The solution was stirred for 30 min. After addition of 6,13-pentacenedione (0.40 g, 1.30 mmol), the reaction mixture was stirred at −78 °C for 1 h and at room temperature for 2 h. The mixture was poured into water (20 mL) and ethyl acetate (40 mL) was added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (40 mL×2). The combined organic solutions were washed with water and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (hexane/CH_2Cl_2=4:6→2:8) to afford compound **3b**[6,10] (0.49 g, 80%) as a mixture of two isomers (1.7:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.93 (s, 0.74H), 3.11 (s, 1.26H), 5.85 (dd, J=3.7, 1.0 Hz, 1.26H), 6.26 (dd, J=5.1, 3.7 Hz, 1.26H), 6.78 (dd, J=3.6, 1.2 Hz, 0.74H), 6.89 (dd, J=5.1, 1.0 Hz, 1.26H), 6.97 (dd, J=5.1, 3.6 Hz, 0.74H), 7.34 (dd, J=5.1, 1.2 Hz, 0.74H), 7.51 (dd, J=6.2, 3.3 Hz, 1.48H), 7.59 (dd, J=6.2, 3.2 Hz, 2.52H), 7.87 (dd, J=6.2, 3.3 Hz, 1.48H), 7.97 (dd, J=6.2, 3.2 Hz, 2.52H), 8.20 (s, 1.48H), 8.54 (s, 2.52H). Data for the major product are as follows: Orange crystals. Decomp. >190 °C. IR (KBr): 3513, 3436, 3057, 1231, 1092, 988, 955, 828, 748, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.10 (s, 2H), 5.76 (dd, J=3.7, 0.9 Hz, 2H), 6.21 (dd, J=5.0, 3.7 Hz, 2H), 6.84 (dd, J=5.0, 0.9 Hz, 2H), 7.59 (dd, J=6.2, 3.3 Hz, 4H), 7.90 (dd, J=6.2, 3.3 Hz, 4H), 8.40 (s, 4H). ^{13}C NMR (acetone-d_6, 50 MHz): δ 73.2, 125.5, 126.1, 126.5, 127.1, 127.4, 128.9, 133.8, 140.8, 151.8. MS m/z (%): 458 (100) [M^+-H_2O]. Anal. Calcd for $C_{30}H_{20}O_2S_2$: C, 75.60; H, 4.23. Found: C, 75.45; H, 4.22.

Similar reaction conditions were applied to the synthesis of compounds **3c**[6,15] and **3d**. These compounds were obtained as a single isomer.

Compound **3c**: Yield 50%. Decomp. >244 °C. IR (KBr): 3526, 3434, 3056, 1493, 1096, 868, 694 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.04 (s, 2H), 6.72–6.89 (m, 10H), 7.56 (dd, J=6.3, 3.2 Hz, 4H), 7.94 (dd, J=6.3, 3.2 Hz, 4H), 8.40 (s, 4H). MS m/z (%): 464 (6) [M^+], 446 (42), 430 (45), 341 (100). Anal. Calcd for $C_{34}H_{24}O_2$: C, 87.90; H, 5.21. Found: C, 87.89; H, 5.21.

Compound **3d**: Yield 48%. Decomp. >200 °C. IR (KBr): 3301, 1526, 1487, 993, 951 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.55 (s, 2H), 7.52 (dd, J=6.2, 3.3 Hz, 4H), 7.73 (s, 4H), 7.78 (dd, J=6.2, 3.3 Hz, 4H). MS m/z (%): 644 (31) [M^+], 627 (30), 610 (100), 460 (37), 309 (31). Anal. Calcd for $C_{34}H_{14}F_{10}O_2$: C, 63.37; H, 2.19. Found: C, 63.60; H, 2.23.

4.1.2. Preparation of 6,13-diarylpentacene (1b–d).[10] A solution of compound **3b** (a mixture of two isomers) (0.60 g, 1.26 mmol), $NaH_2PO_2\cdot H_2O$ (1.00 g, 9.43 mmol), and NaI (1.00 g, 6.67 mmol) in acetic acid (7 mL) was refluxed for 30 min. A deep blue solid was precipitated. After cooling, the precipitate was filtered and washed with water to give a deep blue solid (0.56 g), which was sublimed at 320 °C under 10^{-3} Torr to afford pentacene **1b**[6,10] (0.26 g, 47%) as deep blue crystals. Mp >300 °C. IR (KBr): 3048, 1364, 1321, 1221, 874, 828, 735, 696 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.28 (dd, J=6.7, 3.1 Hz, 4H), 7.40 (dd, J=3.3, 1.1 Hz, 2H), 7.46 (dd, J=5.3, 3.3 Hz, 2H), 7.77 (dd, J=5.3, 1.1 Hz, 2H), 7.80 (dd, J=6.7, 3.1 Hz, 4H), 8.50 (s, 4H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 125.4, 125.5, 127.2, 127.4, 128.6, 130.0, 130.0, 130.1, 131.4, 139.5. MS m/z (%): 442 (100) [M^+]. Anal. Calcd for $C_{30}H_{18}S_2$: C, 81.41; H, 4.10. Found: C, 81.41; H, 3.93.

Similar reaction conditions were applied to the synthesis of pentacenes **1c**[6,15] and **1d**.

Compound **1c**: Yield 73%. Deep violet crystals. Mp 292–293 °C. IR (KBr): 3056, 1441, 1383, 1101, 1026, 878, 750 cm^{-1}. MS m/z (%): 430 (100) [M^+]. Anal. Calcd for $C_{34}H_{22}$: C, 94.85; H, 5.15. Found: C, 94.79; H, 5.00.

Compound **1d**: Yield 69%. Deep violet crystals. Mp >300 °C. IR (KBr): 1495, 1364, 1098, 990, 781, 735 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.37 (dd, J=6.7, 3.0 Hz, 4H), 7.85 (dd, J=6.7, 3.0 Hz, 4H), 8.22 (s, 4H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 112.7 (t, J=20.2 Hz), 122.6, 123.9, 126.5, 128.3, 128.6, 132.3, 138.2 (d, J=252.6 Hz), 141.8 (d, J=252.8 Hz), 145.3 (d, J=243.9 Hz). MS m/z (%): 610 (100) [M^+]. Anal. Calcd for $C_{34}H_{12}F_{10}$: C, 66.90; H, 1.98. Found: C, 66.70; H, 1.95.

4.2. Electrochemical measurements

CV was performed with a Toho Technical Research polarization unit PS-07 potentiostat/galvanostat. The CV studies of compounds **1b–d** were carried out in dichloromethane with 0.1 M $n\mathrm{Bu}_4\mathrm{NClO}_4$ using Pt and SCE electrodes. The values are expressed in potentials versus Fc/Fc^+.

4.3. Photooxidation reaction of pentacene 1b

A solution of pentacene **1b** (100 mg, 0.23 mmol) in dichloromethane (100 mL) was exposed to sunlight through a Pyrex filter in air for 2 h. After removal of the solvent, the residue was washed with hexane to give endoperoxide **4** (88 mg, 81%). Decomp. >188 °C. IR (KBr): 3430, 1609, 1233, 1171, 951, 878, 841, 750, 704 cm^{-1}. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.46 (dd, J=6.2, 3.2 Hz, 4H), 7.50 (dd, J=5.1, 3.6 Hz, 2H), 7.66 (dd, J=3.6, 1.2 Hz, 2H), 7.68 (dd, J=5.1, 1.2 Hz, 2H), 7.77 (dd, J=6.2, 3.2 Hz, 4H), 7.84 (s, 4H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 84.7, 122.3, 126.3, 126.8, 126.9, 127.7, 128.3, 132.6, 134.0, 136.2. MS (EI) m/z (%): 475 (100) [M^++1], 459 (74), 443 (57). UV (CH_2Cl_2): λ_{max} (log ε) 280 sh (4.29), 250 (4.93) nm. HRMS(EI) calcd for $C_{30}H_{18}O_2S_2$ 474.0748, found 474.0755.

4.4. X-ray crystallographic analysis of 4

A single crystal was prepared by recrystallization from benzene. Crystal data are as follows: 0.25×0.12×0.12 mm, $C_{30}H_{18}O_2S_2\cdot6(H_2O)$, M=570.59 ($C_{30}H_{18}O_8S_2$), colorless prism, tetragonal, space group $I4_1/a$, a=29.20(2), b=29.20(2), c=13.918(9) Å, V=11,866(14) Å^3, Z=16, D_c=1.242 g cm^{-3}, μ=0.222 mm^{-1}, F(000)=4704. Reflection data were collected with a Rigaku MSC Mercury CCD diffractometer using graphite-monochromated Mo Kα radiation (λ=0.71070 Å) at 173 K. No absorption correction was applied. The structure was solved using the direct method (SHELXS-97).[16] All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares (SHELXL-97)[17] and all hydrogen atoms were placed in geometrically calculated positions and refined by using a rigid model. The final values of R_1=0.1168, GOF=1.012, and max./min. residual electron density=0.474/−0.403 eÅ^{-3} were obtained for 6756 unique reflections [$I>2\sigma(I)$]. CCDC 613494.

4.5. Thermal decomposition of endoperoxide 4 in solution

A solution of **4** in decalin was heated at 170 °C for 10 min. In the UV–vis spectrum of the solution, the absorption bands on the pentacene moiety of **1b** were observed. The conversion yield of pentacene **1b** was evaluated to be 30% by the ^{1}H NMR spectra in decalin-d_{18}.

4.6. TGA of endoperoxide 4

TGA was performed with a Shimadzu TGA-50 microthermobalance. The TGA study of **4** was carried out at an increasing temperature rate of 10 °C min^{-1}. The profile revealed a weight loss of 2.7% at 188 °C. The weight loss was smaller than the theoretical O_2 loss (6.8%) by thermal decomposition [FW 474 (**4**) → FW 442 (**1b**)].

4.7. Photolysis of endoperoxide 4

UV irradiation of the solution of **4** in decalin-d_{18} was examined for 10 min under bubbling argon using UV lamps (254 nm, 15 W×6). The conversion yield of pentacene **1b** was evaluated to be 44% by the ^{1}H NMR spectra. UV irradiation of the thin film of **4** was carried out in air for 8 min using a UV lamp (254 nm, 610 μW cm^{-2}). The film was dissolved in dichloromethane and the UV–vis spectrum of the solution was measured. The spectrum of **4** without UV irradiation was also measured as a reference.

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References and notes

1. (a) Reese, C.; Roberts, M.; Ling, M.; Bao, Z. *Mater. Today* **2004**, *7*, 20; (b) Klauk, H.; Halik, M.; Zschieschang, U.; Schmid, G.; Radlik, W.; Weber, W. *J. Appl. Phys.* **2002**, *92*, 5259; (c) Reichmanis, E.; Katz, H.; Kloc, C.; Maliakal, A. *Bell Labs Tech. J.* **2005**, *10*, 87.
2. Jurchescu, O. D.; Baas, J.; Palstra, T. T. M. *Appl. Phys. Lett.* **2004**, *84*, 3061.
3. Lin, Y.-Y.; Gundlach, D. J.; Nelson, S. F.; Jackson, T. N. *IEEE Trans. Electron Devices* **1997**, *44*, 1325.
4. Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891.
5. (a) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986; (b) Sheraw, C. D.; Jackson, T. N.; Eaton, D. L.; Anthony, J. E. *Adv. Mater.* **2003**, *15*, 2009; (c) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15; (d) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482.
6. Miao, Q.; Chi, X.; Xiao, S.; Zeis, R.; Lefenfeld, M.; Siegrist, T.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 1340.
7. Kobayashi, K.; Shimaoka, R.; Kawahara, M.; Yamanaka, M.; Yamaguchi, K. *Org. Lett.* **2006**, *8*, 2385.
8. (a) Weidkamp, K. P.; Afzali, A.; Tromp, R. M.; Hamers, R. J. *J. Am. Chem. Soc.* **2004**, *126*, 12740; (b) Afzali, A.; Dimitrakopoulos, C. D.; Breen, T. L. *J. Am. Chem. Soc.* **2002**, *124*, 8812; (c) Chen, K.-Y.; Hsieh, H.-H.; Wu, C.-C.; Hwang, J.-J.; Chow, T. J. *Chem. Commun.* **2007**, 1065; (d) Yamada, H.; Yamashita, Y.; Kikuchi, M.; Watanabe, H.; Okujima, T.; Uno, H.; Ogawa, T.; Ohara, K.; Ono, N. *Chem.—Eur. J.* **2005**, *11*, 6212; (e) Afzali, A.; Dimitrakopoulos, C. D.; Graham, T. O. *Adv. Mater.* **2003**, *15*,

2066; (f) Herwig, P. T.; Müllen, K. *Adv. Mater.* **1999**, *11*, 480; (g) Brown, A. R.; Pomp, A.; de Leeuw, D. M.; Klaassen, D. B. M.; Havinga, E. E.; Herwig, P.; Müllen, K. *J. Appl. Phys.* **1996**, *79*, 2136; (h) Joung, M. J.; Ahn, J. H.; Kang, S. Y.; Baek, K. H.; Ahn, S. D.; Do, L. M.; Kim, C. A.; Kim, G. H.; You, I. K.; Yoon, S. M.; Suh, K. S. *Bull. Korean Chem. Soc.* **2003**, *24*, 1862.

9. Bao, Z.; Rogers, J. A.; Katz, H. E. *J. Mater. Chem.* **1999**, *9*, 1895.
10. Vets, N.; Smet, M.; Dehaen, W. *Synlett* **2005**, 217.
11. Ried, W.; Anthöfer, F. *Angew. Chem.* **1953**, *65*, 601.
12. Wolak, M. A.; Jang, B.-B.; Palilis, L. C.; Kafafi, Z. H. *J. Phys. Chem. B* **2004**, *108*, 5492.
13. (a) Zhou, X.; Kitamura, M.; Shen, B.; Nakajima, K.; Takahashi, T. *Chem. Lett.* **2004**, *33*, 410; (b) 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; (c) Reddy, A. R.; Bendikov, M. *Chem. Commun.* **2006**, 1179.
14. Sparfel, D.; Gobert, F.; Rigaudy, J. *Tetrahedron* **1980**, *36*, 2225.
15. Allen, C. F. H.; Bell, A. *J. Am. Chem. Soc.* **1942**, *64*, 1253.
16. Sheldrick, G. M. *SHELXS-97: Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.
17. Sheldrick, G. M. *SHELXL-97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.