

Photochemical Synthesis of Pentacene and its Derivatives

Hiroko Yamada,^{*,[a]} Yuko Yamashita,^[a] Makoto Kikuchi,^[a] Hikaru Watanabe,^[a]
Tetsuo Okujima,^[a] Hidemitsu Uno,^[b] Takuji Ogawa,^[c] Keishi Ohara,^[a] and
Noboru Ono^{*,[a]}

Abstract: A novel α -diketone precursor of pentacene, 6,13-dihydro-6,13-ethanopentacene-15,16-dione, was prepared and converted successfully to pentacene in 74% yield by photolysis of the precursor in toluene: Irradiation of the diketone solution in toluene with light of 460 nm under an Ar atmosphere caused the solution to change from yellow to fluorescent orange-pink within a few minutes, after which, purple precipitates appeared. After 35 min, the solution changed to colorless and the purple precipitates were filtered to give pentacene in 74% yield. By contrast, in the presence of oxygen, the color of the solution

changed from yellow to pale yellow, and only 6,13-endoperoxide of pentacene was quantitatively obtained. The rate of the reaction upon photolysis was measured by observing the decay of $n-\pi^*$ absorption of the precursor at 460 nm, and was found to be similar in both the presence and absence of oxygen. Therefore, the photoreaction of the α -diketone precursor seemed to occur via the singlet excited state. Because the T-T absorption of pentacene

was observed upon photolysis of the precursor in the nanosecond transient absorption measurement under an Ar atmosphere, the excited triplet state of the pentacene generated singlet oxygen by sensitization, and it reacted with the ground-state pentacene to give the 6,13-endoperoxide. The α -diketone deposited on glass was also converted successfully to pentacene film by photoirradiation. In addition, diketone precursors of a mixture of 2,8- and 2,9-dibromopentacene and 2,6-trianthrylene were also prepared and their photoconversion was performed.

Keywords: diketones • organic semiconductors • pentacene • photolysis • singlet oxygen

Introduction

Organic semiconducting molecules are very attractive for the fabrication of organic thin-film transistors (OTFTs) in various molecular electronics applications, such as electronic papers and flexible displays.^[1–3] Because of its high carrier mobility as both single crystals^[4] and thin films,^[5] pentacene is one of the most promising candidates as a *p*-type semiconductor for offsets. Field-effect mobilities of greater than $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been reported for OTFTs by using vacuum-deposited pentacene. Unfortunately, the low solubility of the pentacene in common organic solvents is a significant obstacle to its widespread use, because the expensive vacuum deposition method is required for the preparation of the pentacene devices. The development of a simple, solution-based fabrication method is vital for the widespread use of pentacene in this field. To achieve solution-processed OTFTs of pentacene, the existence of several soluble pentacene derivatives with simple structures have been reported,^[6,7] and some of them showed conductivity performance as *p*- or *n*-type semiconductors.^[7] Although such derivatiza-

[a] Prof. H. Yamada, Y. Yamashita, M. Kikuchi, H. Watanabe, Dr. T. Okujima, Dr. K. Ohara, Prof. N. Ono
Department of Chemistry, Faculty of Science
Ehime University, Matsuyama 790–8577 (Japan)
Fax: (+81)89-927-9615
E-mail: yamada@chem.sci.ehime-u.ac.jp
ononbr@dpc.ehime-u.ac.jp

[b] Prof. H. Uno
Division of Synthesis and Analysis, Department of Molecular Science
Integrated Center for Sciences (INCS)
Ehime University, Matsuyama 790–8577 (Japan)
and CREST, Japan Science Technology Corporation (JST) (Japan)

[c] Prof. T. Ogawa
Research Center for Molecular-Scale Nanoscience
Institute for Molecular Science
National Institutes of Natural Sciences
Myodaiji, Okazaki 444–8585 (Japan)

Supporting information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author.

tion is important, the use of pentacene itself is also critical. To utilize the pentacene, the soluble precursors, which can be converted easily to pentacene on substrates, have shown promise. Some Diels–Alder adducts of pentacene have been utilized for this purpose.^[8] The adducts were reported to reconvert to pentacene by means of the retro Diels–Alder reaction at 120–250 °C in solvents, or in the form of thin films. The mobilities of the pentacene films, prepared by a solution process using these precursors, tend to become larger as the weight ratio of the leaving groups is reduced; that is, 0.1 cm² V^{−1} s^{−1} for 1,2,3,4-tetrachlorobenzene (losing weight, 43 %);^[8a] 0.25 cm² V^{−1} s^{−1} for *N*-sulfinyl-*tert*-butylcarbamate (37 %);^[9] 0.42 cm² V^{−1} s^{−1} for *N*-sulfinylacetamide (27 %).^[8c] One reason for this trend is thought to be the contamination of the leaving groups in the prepared film, which cannot be removed from films following the retro Diels–Alder reaction.^[4] If this trend is general, then the mobility should be higher when the precursors with smaller leaving groups are used, and ideally the leaving groups are volatile at the reaction conditions to avoid contamination in the film.

Although the thermal conversion of the pentacene precursors on the substrate is very promising for solution-processed OTFT applications, photochemical conversions of precursors to pentacene would have the additional advantage of being useful for photopatternable devices. To the best of our knowledge, only two photopatternable pentacene precursors have been reported.^[9,10] In these reports, two steps were required for the preparation of the photopatterned pentacene films, because the precursors did not change directly to pentacene: firstly, a photochemical polymerization of a pentacene-precursor-linked monomer^[10] or a photochemical acid generation,^[9] and secondly, thermal retro Diels–Alder reaction from the precursors to pentacene. Furthermore, the films obtained were not pure, but included impurities, such as photopolymer or photoinitiator, which might have lowered their mobilities. In view of these points, the direct photoconversion of the precursors to pentacene would be desirable for the preparation of high-performance pentacene films.

Homallylically conjugated bi- or polycyclic α -diketones are known to eliminate two molecules of carbon monoxide upon the formation of cyclic conjugated dienes by photoirradiation.^[11] As the two CO molecules are removed from pen-

tacene precursors to give pentacene, the change in weight is only 17 %, which is the smallest change of the other known pentacene precursors stated above. Considering the trend of mobility and the weight % of the leaving groups, diketone precursors are highly promising as the solution-processed precursors for the OFETs. Furthermore, CO molecules generated during the preparation may escape from the film to the air, which may increase the purity of the pentacene film obtained. Here, we report a novel diketone precursor of pentacene, 6,13-dihydro-6,13-ethanopentacene-15,16-dione, which can be easily and directly converted to pentacene by photoirradiation.^[12] Although the general photochemistry of α -diketones has been well studied,^[13] only a few reports have been issued concerning the mechanism of the photochemical elimination of two CO molecules from homallylically conjugated bi- or polycyclic α -diketones, resulting in the formation of cyclic conjugated dienes.^[11a,d] We have examined carefully the reaction mechanism upon photolysis of the diketone precursors, and conclude that the cleavage reaction proceeds from a singlet excited state of diketone precursors to give pentacene. The spin-coating film of the α -diketone precursor was also prepared and converted successfully to pentacene film by photoirradiation.^[12]

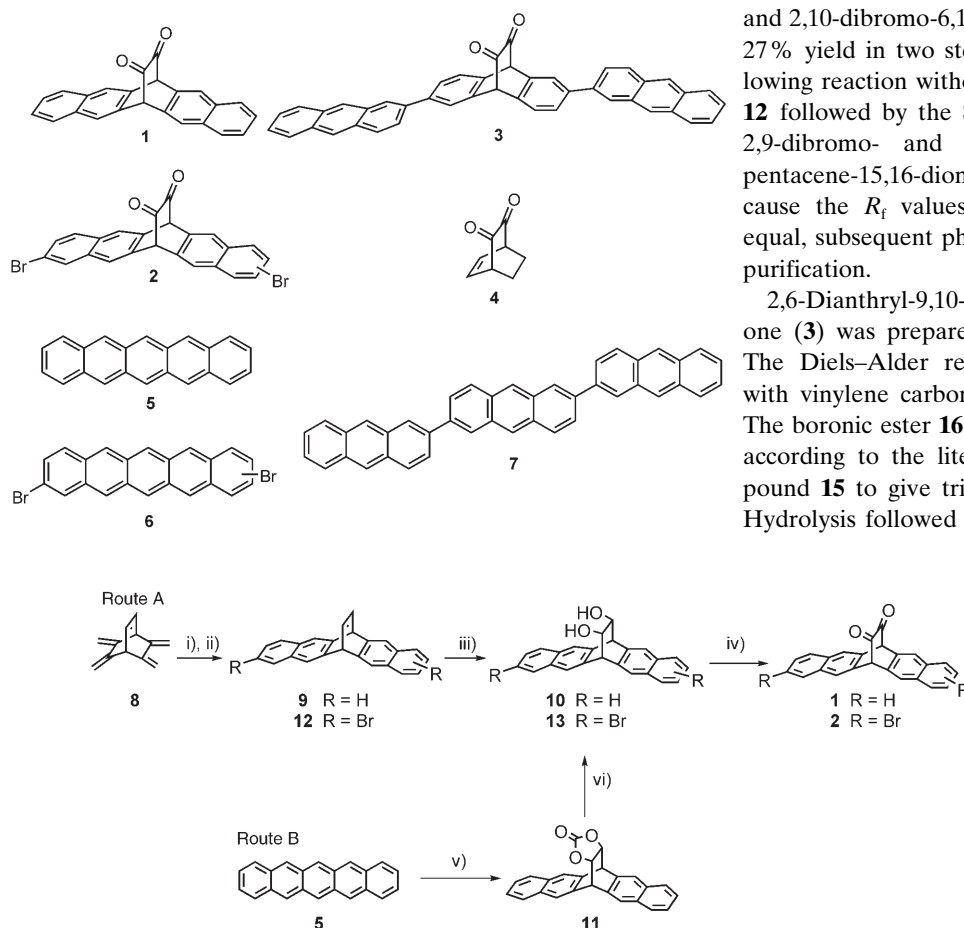
To investigate the utility of the photolysis reaction of α -diketone precursors to acenes, the precursors of dibromopentacene and trianthrylene were also prepared and photolysis reactions were performed. Because the solubility of pentacene in common organic solvents is quite low, the derivatization of pentacene is very difficult. However, the precursors of dibromopentacenes are soluble and show the potential to be developed into a variety of derivatives by using the bromo substituents. Therefore, the preparation of the precursors is promising for the development of high-performance pentacene compounds. Furthermore, we could prepare the diketone precursor of 2,6-trianthrylene, 2,6-dianthryl-9,10-dihydro-9,10-ethanoanthracene-11,12-dione. 2,6-Trianthrylene and its derivatives were reported to show mobilities comparable to that of pentacene,^[14] and are expected to be chemically stable materials, compared to higher acene series, such as pentacene. In conclusion, we report the general synthesis of diketone precursors of acene analogues and their photochemical conversion to corresponding acenes.

Results and Discussion

Preparation of 6,13-dihydro-6,13-ethanopentacene-15,16-dione (1) and its derivatives: The diketone precursors, 1–3, prepared in this study, are shown below with reference compound 4^[11d] and photochemically obtained acenes, 5–7. The synthetic routes for 6,13-dihydro-6,13-ethanopentacene-15,16-dione (1)^[12] and its dibromo derivative 2 are shown in Scheme 1. 6,13-Dihydro-6,13-ethenopentacene (9) was prepared from commercially available bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride via tetraene 8, as previously reported.^[15] Dihydroxylation of the etheno bridge of 6,13-dihydro-6,13-ethanopentacene (9) with OsO₄ gave diol

Abstract in Japanese:

ペンタセンのジケトン前駆体、6,13-ジヒドロ・6,13-エタノペンタセン・15,16-ジオンの合成に成功した。さらに、この前駆体をトルエン中、アルゴン雰囲気下で光照射することにより、2分子のCOを脱離し、ペンタセンへと変換することに成功した。酸素雰囲気下ではペンタセンは得られずペンタセンの一重項酸素付加生成物、6,13-エンドペルオキシドが得られた。さらに、ジケトン前駆体薄膜の光によるペンタセン薄膜への変換にも成功した。ジブロモペンタセンやアントラセントリマーのジケトン前駆体についても同様に光反応を行い対応するアセンの合成に成功した。



Scheme 1. Synthesis of diketones **1** and **2**. Reagents and conditions: Route A: i) for **9**, anthranic acid, isoamyl nitrite, dry THF, reflux, 2 h; for **12**, 2-amino-5-bromobenzoic acid, isoamyl nitrite, dry THF, reflux, 2 h. ii) DDQ, CHCl_3 , RT, 2 h, 71 % for **9** and 27 % for **12** in two steps. iii) OsO_4 , *N*-methylmorpholine (NMO), acetone, RT, 32 h, 98 % for **10** and 7 h, 67 % for **13**. iv) trifluoroacetic anhydride, dry DMSO, dry CH_2Cl_2 , $-60 \rightarrow 70^\circ\text{C}$, 1.5 h, 43 % for **1** and 15 % for **2**. Route B: v) vinylene carbonate, xylene, autoclave, 180°C , 3 d, 88 %. vi) aqueous NaOH, dioxane, reflux, 2 h, 90 %.

10 in good yield (route A).^[16] Otherwise, the diol **10** was prepared from pentacene by a Diels–Alder reaction with commercially available vinylene carbonate, followed by hydrolysis in good yield (route B).^[17] Swern oxidation of diol **10** under the modified conditions gave the targeted α -diketone **1** in moderate yield.^[17] An X-ray crystallographic measurement was performed on **1** (Figure 1). The bond lengths of C(7)–C(8), C(8)–C(9), C(18)–C(19), C(19)–C(20), C(8)–C(24), and C(19)–C(23), were 1.520(4), 1.513(5), 1.518(4), 1.518(4), 1.501(4), and 1.511(4) Å, respectively, and were shorter than the length of C(23)–C(24), 1.558(6) Å. The angle made by two naphthalene planes was calculated to be $121.57(3)^\circ$. The angles made by naphthalene planes and the O(1)–C(23)–C(24)–O(2) plane were $117.97(3)$ and $120.37(0)^\circ$, respectively.^[18]

The dibromo derivative **2** was prepared according to route A (Scheme 1). Tetraene **8** was reacted with 2-amino-5-bromobenzoic acid in the presence of isoamyl nitrite, followed by the oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to give a 1:1 mixture of 2,9-dibromo-

and 2,10-dibromo-6,13-dihydro-6,13-ethenopentacene (**12**) in 27 % yield in two steps. This mixture was used for the following reaction without purification. The OsO_4 oxidation of **12** followed by the Swern oxidation gave a 1:1 mixture of 2,9-dibromo- and 2,10-dibromo-6,13-dihydro-6,13-ethanopentacene-15,16-dione (**2**) in 10 % yield in two steps. Because the R_f values of the two dibromo derivatives are equal, subsequent photolysis was performed without further purification.

2,6-Dianthryl-9,10-dihydro-9,10-ethanopentacene-11,12-dione (**3**) was prepared by the method shown in Scheme 2. The Diels–Alder reaction of 2,6-dibromoanthracene (**14**) with vinylene carbonate gave compound **15** in 72 % yield. The boronic ester **16** was prepared from 2-bromoanthracene according to the literature,^[14] and was coupled with compound **15** to give trianthrylene precursor **17** in 25 % yield. Hydrolysis followed by Swern oxidation gave diketone **3** in 69 % yield in two steps.

Photolysis of the α -diketone **1** and its reaction mechanism:

The UV-visible absorption spectra of α -diketone **1**, pentacene **5**, and reference diketone compound **4**^[11d] in toluene are shown in Figure 2. The peaks of the $n\text{--}\pi^*$ absorption of the α -diketone compounds and the peak of pentacene at 577 nm were normalized to 1.0. The α -diketone **1** shows a typical $n\text{--}\pi^*$ absorption at 465 nm ($\epsilon = 1220 \text{ M}^{-1} \text{ cm}^{-1}$), which is similar to the $n\text{--}\pi^*$ absorption of reference compound **4**.^[11d]

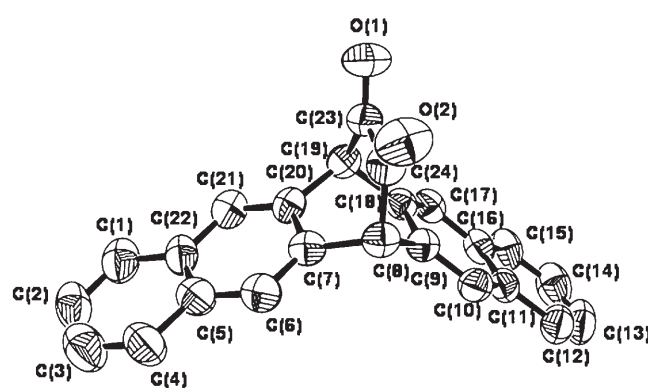
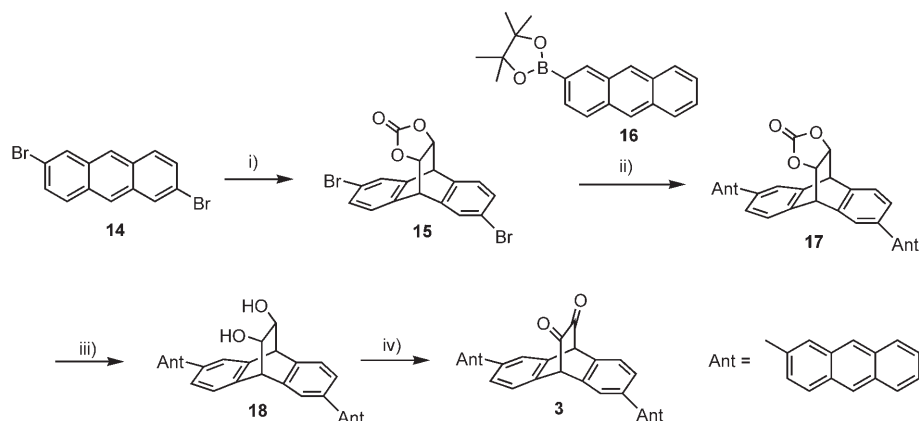


Figure 1. ORTEP drawing of the X-ray structure of α -diketone **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: O(1)–C(23), 1.191(4); O(2)–C(24), 1.197(4); C(7)–C(8), 1.520(4); C(8)–C(9), 1.513(5); C(18)–C(19), 1.518(4); C(19)–C(20), 1.518(4); C(8)–C(24), 1.501(4); C(19)–C(23), 1.511(4); C(23)–C(24), 1.558(5). Selected angles [$^\circ$]: O(1)–C(23)–C(19), $127.6(3)$; O(1)–C(23)–C(24), $121.4(3)$; O(2)–C(24)–C(23), $122.6(3)$; O(2)–C(24)–C(8), $126.8(3)$.



Scheme 2. Synthesis of diketone **3**. Reagents and conditions: i) vinylene carbonate, xylene, autoclave, 180 °C, 3 d, 72 %. ii) $[\text{Pd}(\text{PPh}_3)_4]$, toluene, aqueous Na_2CO_3 , reflux, 18 h, 25 %. iii) aqueous NaOH , dioxane, reflux, 1 h, 85 %. iv) trifluoroacetic anhydride, dry DMSO, dry CH_2Cl_2 , $-60 \rightarrow -70^\circ\text{C}$, 1.5 h, 81 %.

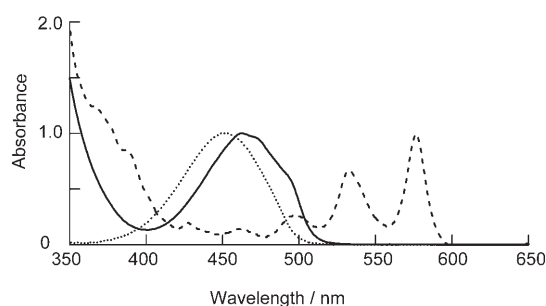


Figure 2. Absorption spectra of α -diketone **1** (solid line), reference diketone **4** (dotted line), and pentacene **5** (broken line) in toluene.

The typical photolysis of α -diketone to pentacene was performed as follows: the α -diketone **1** (6.64 mg) was dissolved in 10 mL of toluene in a 20 mL round-bottomed flask. After bubbling Ar through the solution for 15 min, the solution was irradiated by using a super-high-pressure mercury lamp (500 W), through a blue filter (>390 nm) and a Na_2SO_4 aqueous solution, which acted as UV and IR cut-off filters, respectively. The color of the photolyzed solution changed from yellow to fluorescent orange-pink within a few minutes, after which purple precipitates appeared. The irradiation was continued for 35 min until the solution turned colorless. The purple precipitate was collected by filtration to give pentacene in 74 % yield. The pentacene was identified by recording EI-mass and absorption spectra. The NMR spectrum could not be observed because of the low solubility of pentacene in common organic solvents.^[19] The solvent of the filtrate was removed under reduced pressure and the residue was assigned by ^1H NMR to be a mixture of mainly 6,13-pentacene-endoperoxide (**19**)^[20] and 6,13-pentacenequinone (**20**).^[4]

To monitor the photoreaction process, the change in the UV-visible absorption spectra was measured at intervals during photolysis. The 5.25×10^{-1} mm solution of α -diketone **1** in toluene under an Ar atmosphere was irradiated with light at 460 nm. The results are shown in Figure 3a. The ab-

sorption peaks at 465 and 470 nm at 0 min correspond to α -diketone **1**. During irradiation, these peaks decreased gradually, and at the same time new peaks at 495, 530, and 578 nm, which are characterized as pentacene, increased.^[21] Although the diketone peaks simply decreased during the reaction, the pentacene peaks increased for 25 min, and then started to decrease. At the same time, purple precipitates started to appear in the solution. The reaction mechanism was investigated by recording

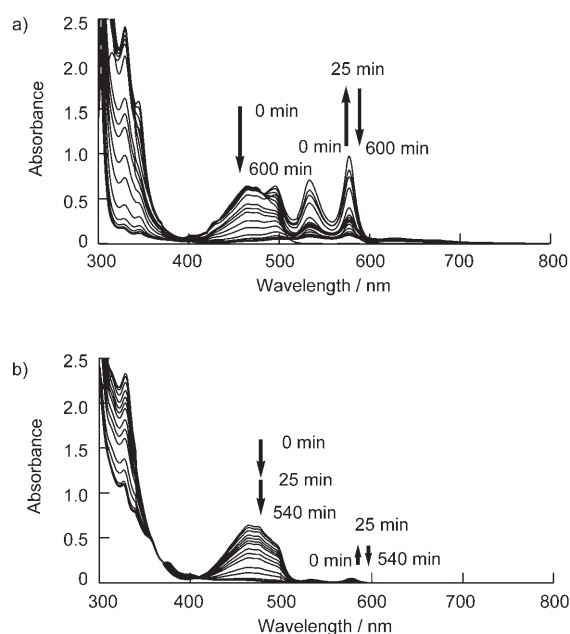


Figure 3. The change in the absorption spectra during photolysis ($\lambda_{\text{EX}} = 460$ nm) of α -diketone **1** in toluene under a) Ar and b) O_2 atmospheres.

the time profiles of the absorbance at 465 and at 577 nm, as shown in Figure 4, even though a quantitative interpretation of the results of the UV-visible absorption spectra could be difficult owing to the precipitates that appeared during the reaction. Because both the α -diketone **1** and pentacene **5** absorb at 465 nm (see Figure 2), the profile of the diketone was obtained by compensating for the contribution of pentacene at 465 nm by using Equation (1),

$$\text{Abs}(\text{diketone}; 465) = \text{Abs}(465) - \text{Abs}(577) \times 0.128 \quad (1)$$

in which $\text{Abs}(\text{diketone}; 465)$ is the absorbance of α -diketone **1** at 465 nm, $\text{Abs}(465)$ is the observed absorbance at 465 nm, $\text{Abs}(577)$ is the observed absorbance of pentacene

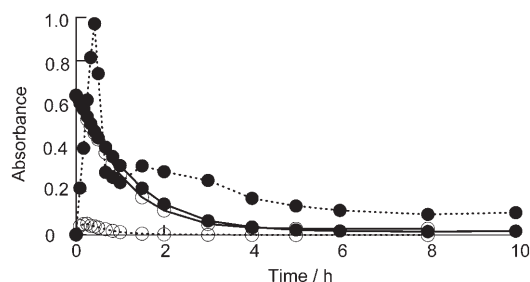


Figure 4. Time profiles of the absorbance at 465 (solid lines) and 577 nm (dotted lines) during photolysis ($\lambda_{\text{EX}}=460$ nm) of α -diketone **1** in toluene under Ar (closed circles) and O_2 (open circles) atmospheres.

5 at 577 nm, and 0.128 is the ratio of the absorbance of pentacene **5** at 465 nm and 577 nm obtained from Figure 2. Although the diketone peaks simply decreased during the reaction, the pentacene peaks increased until 25 min into the reaction, after which they started to decrease. After 25 min, the precipitation of pentacene was observed and the purple precipitates increased gradually. This result indicates that pentacene had been supersaturated until 25 min, and then precipitation began. At 30 min, a broad absorption over 600 nm started to appear, and did not disappear until the end of the reaction (Figure 3a). Because the pentacene amorphous films are known to give a red-shifted absorption,^[21] the broad absorption band seems to correspond to the stacked pentacene that deposited on the glass surface of the UV cell.

The same measurement was performed on an O_2 -saturated toluene solution of α -diketone **1**. Under the O_2 atmosphere, the pentacene was not obtained and the color of the solution changed from yellow to pale yellow during the irradiation. The spectral change is shown in Figure 3b. The diketone peaks at 465 and 470 nm were observed at the beginning of the reaction and gradually decreased. The rate of decrease of the diketone under an O_2 atmosphere was almost the same as that under an Ar atmosphere (Figure 4), which indicated that photolysis of α -diketone **1** proceeded via a singlet excited state. Pentacene peaks at 495, 530, and 578 nm were observed only weakly until 15 min, after which they decreased, and were not observed after 90 min (Figure 3b). These results suggest that, in the presence of oxygen, pentacene was generated, but it was soon converted into other products.

To identify the product under an O_2 atmosphere, the photoreaction was performed in CDCl_3 in an NMR tube.^[12] The CDCl_3 solution of α -diketone **1** was bubbled with O_2 gas in advance of the irradiation. The result is shown in Figure 5. Before the irradiation, only the peaks corresponding to α -diketone **1** (7.94, 7.84, 7.52, and 5.31 ppm) were observed. During the irradiation by the light of 460 nm, these peaks

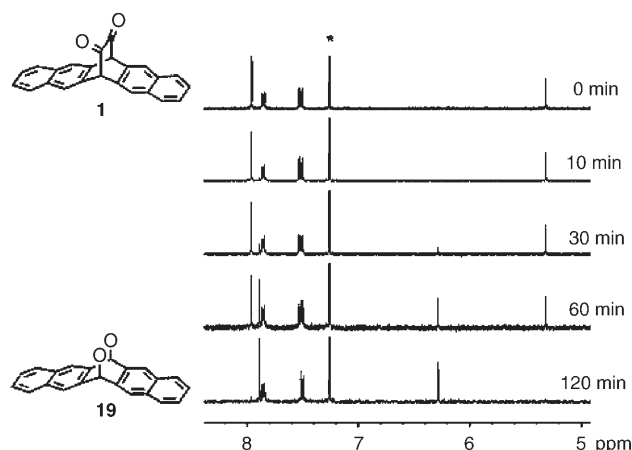
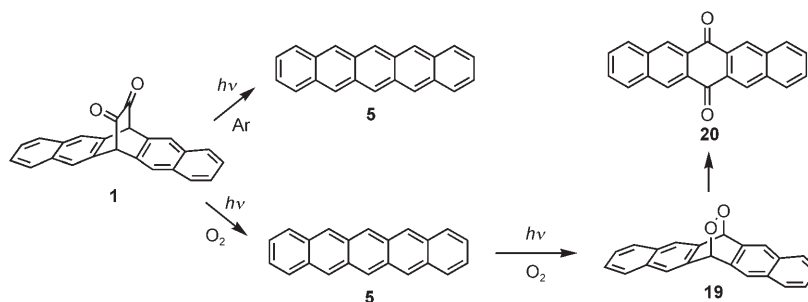


Figure 5. Changes in the NMR spectrum during photolysis of diketone **1** in CDCl_3 under an O_2 atmosphere. The reaction was monitored at 0, 10, 30, 60, and 120 min. $\lambda_{\text{EX}}=460$ nm; O_2 atmosphere. The peak of solvent is marked with *.

gradually decreased, and after 2 h, they had been completely consumed. On the other hand, the peaks belonging to 6,13-endoperoxide **19** (7.89, 7.85, 7.51, and 6.29 ppm) appeared at 30 min and increased until the end of the reaction.^[20,22] According to the NMR spectra, only 6,13-endoperoxide was observed, and 1,4- or 5,14-endoperoxides were not observed, which is in accordance with the results reported by Rigaudy et al.^[20] The UV-visible absorption spectra of the endoperoxide **19** correlated well with the absorption spectrum of the photolysis product under the O_2 -saturated atmosphere stated above. In addition, the peaks of pentacene could not be observed by NMR analysis, although they were apparent from UV-visible measurements during the first 25 min (Figure 3b). The results indicate that, in an O_2 atmosphere, α -diketone **1** produced pentacene photochemically, but this pentacene reacted immediately with an O_2 molecule to give endoperoxide **19** quantitatively. The photoaddition of singlet oxygen to acenes is well known to give endoperoxides by [4+2]-cycloadditions.^[23] Because pentacenequinone **20**, which was observed in the filtrate as a byproduct of photolysis under an Ar atmosphere, was not observed from the NMR measurements reported here, it was probably obtained by the oxidation of **19** during the workup and the rate of the reaction of **19** to **20** was slower than that of pentacene **5** to **19**. From these results, the reaction mechanism can be summarized, as shown in Scheme 3.



Scheme 3. Photolysis of α -diketone **1** in the presence and absence of oxygen.

To investigate the formation process of singlet oxygen, nanosecond transient absorption measurements on the photolysis of α -diketone **1** in toluene under an Ar atmosphere were performed (Figure 6). The transient absorption spec-

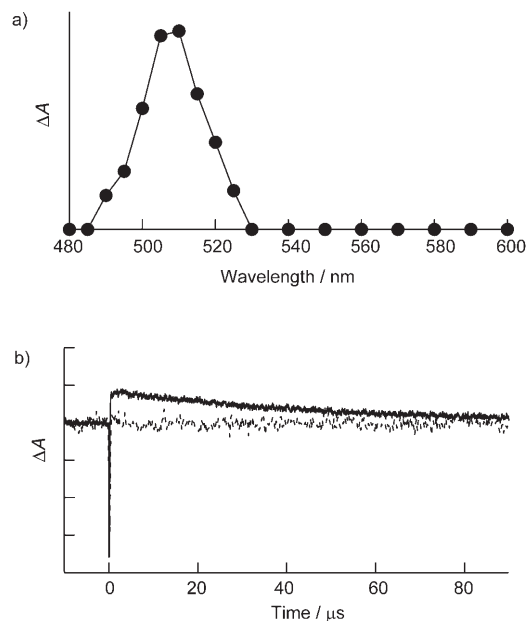
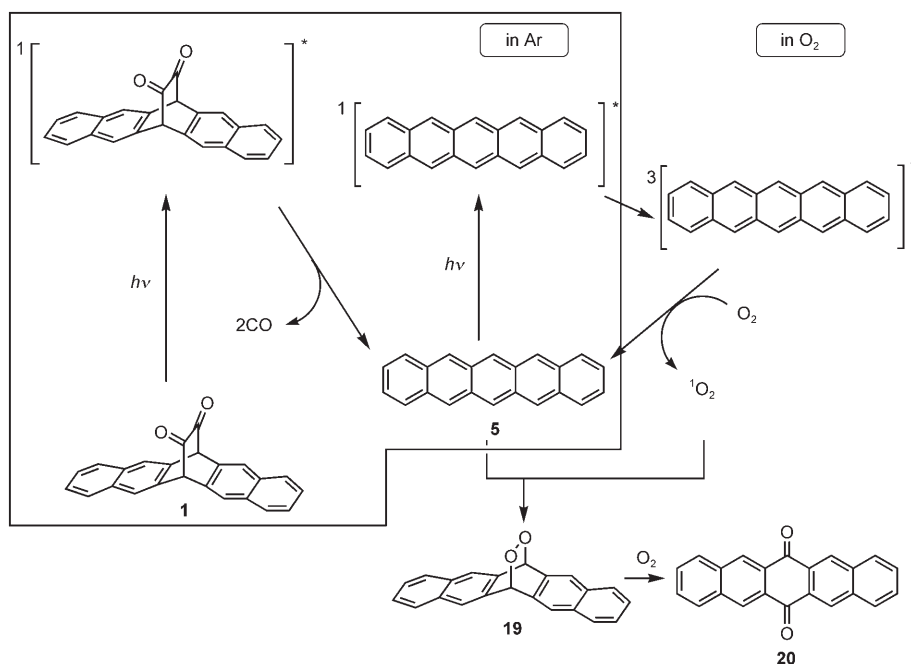


Figure 6. a) Transient absorption spectrum at the delay time of 3.0 μ s after excitation, observed upon photolysis of α -diketone **1** in toluene under an Ar atmosphere. b) Time evolutions of the transient absorption at 510 nm observed upon photolysis of α -diketone **1** in toluene under Ar (solid line) and O_2 (dotted line) atmospheres.

trum observed for this system at the delay time of 3.0 μ s after laser excitation (around 460 nm) is shown in Figure 6a. The absorption had a peak of 510 nm, which correlated well with the reported T–T absorption of pentacene.^[24] The time profile of the absorbance at 510 nm is shown in Figure 6b. The lifetime of the transient absorption was 48.48 (± 0.15) μ s, and this transient absorption disappeared completely as oxygen was bubbled into the solution. These results suggest that the transient absorption at around 510 nm was due to the T–T absorption of the excited triplet state of pentacene, and it was quenched effectively by the presence of oxygen. Therefore, the expected photoreaction mechanism can be summarized,

as shown in Scheme 4. Once pentacene **5** was obtained by the photoreaction of α -diketone **1**, the following occurred: i) the generated pentacene was easily excited by photoirradiation and formed a triplet excited state in high yield (through the intersystem crossing from the singlet excited state); ii) the triplet state of pentacene caused photosensitization and generated singlet oxygen (1O_2) from the ground-state triplet oxygen by energy transfer; and subsequently, iii) 1O_2 reacted with ground-state pentacene to give endoperoxide **19**. These phenomena suggest that, although the photoreaction was performed after 20 min of bubbling with Ar, the oxygen adduct could still be observed because the reactivity of pentacene to 1O_2 was very high, and pentacene reacted effectively with slightly contaminated O_2 . This high reactivity of pentacene with oxygen might be the obstacle for the widespread use of pentacene in related applications.

Photolysis of diketone compounds of dibromo derivative (2) and 2,6-trianthrylene (3): Photolysis of the dibromo derivative **2** was also performed under the same experimental conditions as the photoreaction of α -diketone **1**. The toluene solution of diketone **2** (1.26 mM) was bubbled with Ar in the dark for 20 min before irradiation. Upon irradiation with light of over 390 nm by using a super-high-pressure mercury lamp (500 W), the color of the solution started to change from yellow to colorless, and no fluorescence was observed during the reaction. Purple precipitates started to appear just after irradiation, and after 35 min, the solution became completely colorless. The precipitates were filtered to give a mixture of 2,9- and 2,10-dibromopentacenes **6**, which were identified from the EI-mass spectrum, in 79% yield. The reaction was monitored by measuring UV-visible absorption spectra (Figure 7a). Although the $n\text{--}\pi^*$ absorption of the di-



Scheme 4. Schematic mechanism of photolysis of α -diketone **1**.

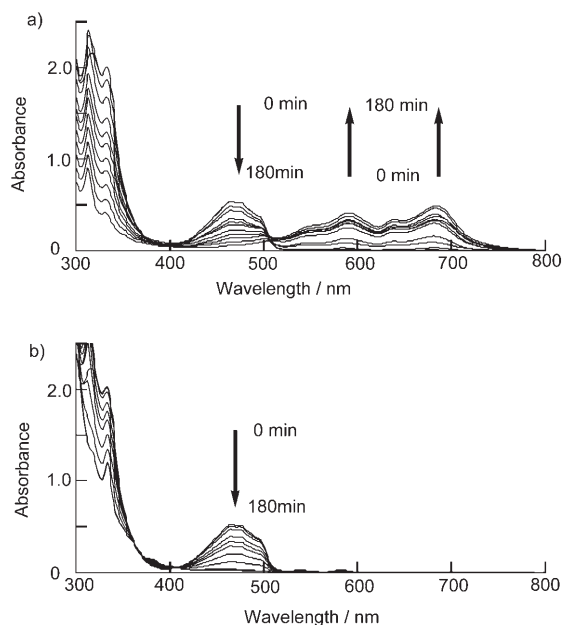


Figure 7. The changes in the absorption spectra during photolysis ($\lambda_{\text{EX}} = 460$ nm) of α -diketone **2** in toluene under a) Ar and b) O₂ atmospheres.

ketone at 465 nm decreased gradually, the widespread absorption from 450 nm to 800 nm increased. At the same time, purple precipitates appeared on the surface of the UV cell. The time profiles at 465, 583, and 684 nm are shown in Figure 8. The peak at 465 nm decreased gradually, and at the same time, the peaks at 583 and 684 nm increased, to give similar curves. These results show that the solubility of dibromopentacene is quite low, and the peaks that appeared at 550, 591, 640, and 684 nm would correspond to the stacked dibromopentacene. This molecular stacking induced the self-quenching of the fluorescence state of pentacene, which explains why no fluorescence was observed during the present photoreaction. In the presence of oxygen, photolysis of the precursor gave a mixture of 2,9-dibromo- and 2,10-dibromopentacene-6,13-endoperoxide **21**, identified by NMR and EI-mass spectra, in place of dibromopentacene, which was similar to the photoreaction of diketone **1** (Figure 7b).

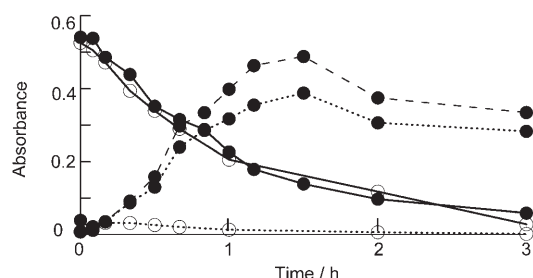


Figure 8. Time profile of the absorbance at 465 (solid lines), 583 (dotted lines), and 684 nm (broken line) during photolysis ($\lambda_{\text{EX}} = 460$ nm) of α -diketone **2** in toluene under Ar (closed circles) and O₂ (open circles) atmospheres.

A photoreaction of trianthrylene diketone **3** was also performed under the same conditions. The color of the solution changed from pale yellow to yellow under an Ar atmosphere, and yellow precipitates appeared. The precipitates could not be identified by NMR spectroscopy because of their low solubility,^[14] however, a TOF-MS measurement revealed the parent peak (see Figure S2 of the Supporting Information) of trianthrylene. Monitoring the reaction by recording absorption spectra was difficult, because both the starting material and the photolysis product have similar UV-visible absorption spectra. However, these results suggest that photolysis of diketone **3** gave trianthrylene.

Photolysis of deposited α -diketone **1 on glass:** The α -diketone **1** was deposited on glass by employing a spin-coating method under an Ar atmosphere. It was then photoirradiated by using a metal-halide lamp in a dry box.^[12] The UV-visible absorption spectra of the deposited film before and after photoirradiation are shown in Figure 9. Before irradiation,

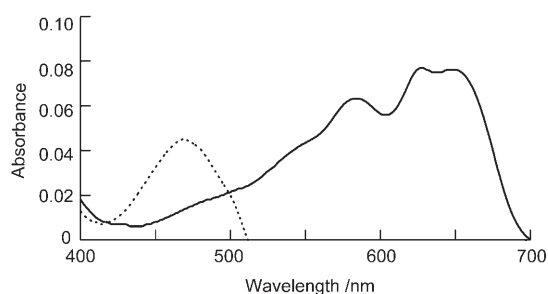


Figure 9. Absorption spectra of a spin-coated film of α -diketone **1** before (broken line) and after (solid line) photoirradiation by using a metal-halide lamp in a dry box.

tion, the color of the deposited film was yellow, and the typical $n-\pi^*$ absorption was observed at 470 nm. After irradiation, the color of the film changed from yellow to purple, and the $n-\pi^*$ absorption at 470 nm disappeared. At the same time, the peaks at 585, 627, and 648 nm appeared, which were about 70 nm red-shifted from the pentacene peaks in toluene (see Figure 2), and are similar to those reported in the literature.^[21] Upon irradiation in air, the film color changed from yellow to colorless. Because this result corresponded with the photoreaction of α -diketone **1** in solution under an O₂ atmosphere, the oxygen adduct of pentacene was formed in air.

Conclusion

We have succeeded in both the preparation of novel photochemical precursors of pentacene (**1**), and in their photochemical conversion to pentacene in good yield, both in solution and on glass. The reaction mechanism of photolysis of the α -diketone precursor was investigated. The dibromo-substituted pentacene and trianthrylene could also be prepared by pho-

tolysis of the corresponding precursors, **2** and **3**, respectively. These results suggest that this photolysis reaction is very useful for the preparation of a variety of acenes with low solubility from soluble diketone precursors in a single step, both in solution and in a film condition, and, therefore, could contribute to the development of acenes with high mobilities.

Experimental Section

General: Melting points were measured by using a Yanaco M500-D melting point apparatus. ^1H NMR and ^{13}C NMR spectra were recorded by using a JEOL JNM-AL 400 spectrometer with tetramethylsilane as an internal standard. IR spectra were measured by using a Hitachi 270–30 with KBr disks. FAB and DI-EI mass spectra were measured by using a JEOL JMS-MS700 V spectrometer. MALDI-TOF mass spectra were measured by using a Voyager DE Pro (Applied Biosystems). Elemental analyses were performed by using a Yanaco MT-5 elemental analyzer. Nanosecond transient absorption measurements were made by using a conventional nanosecond laser-photolysis system (UNISOKU TSP-1000 based). A dye-laser (UNISOKU TSP-611) operated with a coumarin-110 ethanol solution excited by a Nd-YAG laser (Continuum Surelight-I, THG 355 nm, 2 Hz) was used as the excitation light source (around 460 nm) for the transient absorption experiment.

Materials: All solvents and chemicals were of reagent grade quality, obtained commercially, and used without further purification, except as noted. For photoreactions or spectral measurements, spectral grades of toluene and chloroform were purchased from Nacalai Tesque. Thin-layer chromatography (TLC) and column chromatography were performed by using Art. 5554 (Merck) and Silica Gel 60N (Kanto Chemical), respectively.

Photoreactions: The photoreactions were performed by using Pyrex round-bottomed flasks under an Ar atmosphere. Typically, a solution of diketone **1** in toluene (2.0 mm) was irradiated through a thermal cut-off filter and a blue filter to cut out UV light (transmission range > 390 nm) by using a super-high-pressure mercury lamp (Hamamatsu Photonics, 500 W). To monitor the reaction by recording UV/Vis spectra, the diketone solution (0.53 mm) in a quartz UV cell was irradiated with monochromatic excitation light through a monochromator (Ritsu MC-10N) by using a 500 W Xenon lamp (Ushio XB-50102 AA-A). The deposition of a diketone on glass was performed by using a standard spin-coating method (Oshigane, SC-200, 1000 rpm, 30 s) using a diketone solution dissolved in CHCl_3 . The film was irradiated by using a metal-halide lamp (Nippon P. I. PCS-UMX250, 330 W) in a dry box.

Acknowledgements

The authors are grateful to Prof. Nagao Azuma of Ehime University for his help with using a super-high-pressure mercury lamp for the photoreactions, and to Prof. Shin-ichi Nagaoka of Ehime University for his help in operating a conventional nanosecond laser-photolysis system. This work was partially supported by Canon Inc., and by Grants-in-Aid for the Scientific Research C (16550016) and Scientific Research on Priority Areas "Application of Molecular Spins: Nanomagnets to Biological Spin Systems" (Area No. 769, 15087104) from the Japanese Ministry of Education, Culture, Sports, Science, and Technology (MEXT). In addition, H.Y. would like to thank the Hayashi Memorial Foundation for Female Natural Scientists for their financial support.

- [1] F. Würthner, *Angew. Chem.* **2001**, *113*, 1069–1071; *Angew. Chem. Int. Ed.* **2001**, *40*, 1037–1039.

- [2] A. Kraft, *ChemPhysChem* **2001**, *2*, 163–165.
 [3] C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv. Mater.* **2002**, *14*, 99–117.
 [4] O. D. Jurchescu, J. Baas, T. T. M. Palstra, *Appl. Phys. Lett.* **2004**, *84*, 3061–3063.
 [5] a) D. Knipp, R. A. Street, B. Krusor, R. Apte, J. Ho, *J. Non-cryst. Solids* **2002**, 299–302, 1042–1046; b) H. Klauk, M. Halik, U. Zschieschang, F. Eder, G. Schmid, C. Dehm, *Appl. Phys. Lett.* **2003**, *82*, 4175–4177; c) J. A. Nichols, D. J. Gundlach, T. N. Jackson, *Appl. Phys. Lett.* **2003**, *83*, 2366–2368; d) N. Kitamura, T. Imada, Y. Arakawa, *Appl. Phys. Lett.* **2003**, *83*, 3410–3412.
 [6] a) T. Takahashi, M. Kitamura, B. Shen, K. Nakajima, *J. Am. Chem. Soc.* **2000**, *122*, 12876–12877; b) J. E. Anthony, J. S. Brooks, D. L. Eaton, S. R. Parkin, *J. Am. Chem. Soc.* **2001**, *123*, 9482–9483; c) J. E. Anthony, D. L. Eaton, S. R. Parkin, *Org. Lett.* **2002**, *4*, 15–18; d) C. D. Sheraw, T. N. Jackson, D. L. Eaton, J. E. Anthony, *Adv. Mater.* **2003**, *15*, 2009–2011; e) M. J. Joung, J. H. Ahn, S. Y. Kang, K. H. Baek, S. D. Ahn, L. M. Do, C. A. Kim, G. H. Kim, I. K. You, S. M. Yoon, K. S. Suh, *Bull. Korean Chem. Soc.* **2003**, *24*, 1862–1864; f) M. M. Payne, S. A. Odom, S. R. Parkin, J. E. Anthony, *Org. Lett.* **2004**, *6*, 3325–3328; g) M. M. Payne, S. R. Parkin, J. E. Anthony, C.-C. Kuo, T. N. Jackson, *J. Am. Chem. Soc.* **2005**, *127*, 4986–4987; h) S. H. Chan, H. K. Lee, Y. M. Wang, N. Y. Fu, X. M. Chen, Z. W. Cai, H. N. C. Wong, *Chem. Commun.* **2005**, 66–68.
 [7] a) H. Meng, M. Bendikov, G. Mitchell, R. Helgeson, F. Wudl, Z. Bao, T. Siegrist, C. Kloc, C.-H. Chen, *Adv. Mater.* **2003**, *15*, 1090–1093; b) Y. Sakamoto, T. Suzuki, M. Kobayashi, Y. Gao, Y. Fukai, Y. Inoue, F. Sato, S. Tokito, *J. Am. Chem. Soc.* **2004**, *126*, 8138–8140.
 [8] a) A. R. Brown, A. Pomp, D. M. de Leeuw, D. B. M. Klaassen, E. E. Havinga, P. Herwig, K. Müllen, *J. Appl. Phys.* **1996**, *79*, 2136–2138; b) P. T. Herwig, K. Müllen, *Adv. Mater.* **1999**, *11*, 480–483; c) A. Afzali, C. D. Dimitrakopoulos, T. L. Breen, *J. Am. Chem. Soc.* **2002**, *124*, 8812–8813; d) N. Vets, M. Smet, W. Dehaen, *Tetrahedron Lett.* **2004**, *45*, 7287–7289.
 [9] K. P. Weidkamp, A. Afzali, R. M. Tromp, R. J. Hamers, *J. Am. Chem. Soc.* **2004**, *126*, 12740–12741.
 [10] A. Afzali, C. D. Dimitrakopoulos, T. O. Graham, *Adv. Mater.* **2003**, *15*, 2066–2069.
 [11] a) J. Strating, B. Zwanenburg, A. Wagenaar, A. C. Udding, *Tetrahedron Lett.* **1969**, *10*, 125–128; b) D. Stülze, T. Weiske, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1993**, *125*, 75–79; c) H. Chen, J. L. Holmes, *Int. J. Mass Spectrom. Ion Processes* **1994**, *133*, 111–119; d) M. B. Rubin, M. Kapon, *J. Photochem. Photobiol. A* **1999**, *124*, 41–46.
 [12] H. Uno, Y. Yamashita, M. Kikuchi, H. Watanabe, H. Yamada, T. Okujima, T. Ogawa, N. Ono, *Tetrahedron Lett.* **2005**, *46*, 1981–1983.
 [13] M. B. Rubin, *Top. Curr. Chem.* **1985**, *129*, 1–56.
 [14] K. Ito, T. Suzuki, Y. Sakamoto, D. Kubota, Y. Inoue, F. Sato, S. Tokito, *Angew. Chem.* **2003**, *115*, 1191–1194; *Angew. Chem. Int. Ed.* **2003**, *42*, 1159–1162.
 [15] H. Uno, H. Watanabe, Y. Yamashita, N. Ono, *Org. Biomol. Chem.* **2005**, *3*, 448–453.
 [16] Molecular packing in the crystal structure of diol **10** is shown in Figure S1 of the Supporting Information.
 [17] M. M. Wright, M. E. Welker, *J. Org. Chem.* **1996**, *61*, 133–141.
 [18] CCDC 270597 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
 [19] M. Nagano, T. Hasegawa, M. Norikatsu, J. Yamaguchi, K. Itaka, H. Fukumoto, T. Yamamoto, H. Koinuma, *Jpn. J. Appl. Phys. Part 2*, **2004**, *43*, L315–L316.
 [20] D. Sparfel, F. Gobert, J. Rigaudy, *Tetrahedron* **1980**, *36*, 2225–2235.
 [21] Y. Kamura, I. Shirotani, H. Inokuchi, Y. Maruyama, *Chem. Lett.* **1974**, 627–630.
 [22] The same reaction was performed in an Ar atmosphere, and NMR spectroscopy was used in an attempt to monitor the pentacene peaks. Although the color of the reaction mixture changed to purple during photoirradiation, precipitates of pentacene appeared during

the NMR measurements, and no peaks of the pentacene were observed.

- [23] a) J.-M. Aubry, B. Mandard-Cazin, M. Rougee, R. V. Bensasson, *J. Am. Chem. Soc.* **1995**, *117*, 9159–9164; b) A. R. Wartini, H. A. Staab, F. A. Neugebauer, *Eur. J. Org. Chem.* **1998**, 1161–1170; c) X. Zhou, M. Kitamura, B. Shen, K. Nakajima, T. Takahashi, *Chem. Lett.* **2004**, *33*, 410–411.

- [24] a) C. Hellner, L. Lindqvist, P. C. Roberge, *J. Chem. Soc. Faraday Trans. 2* **1972**, *68*, 1928–1937; b) K. A. Nguyen, J. Kennel, R. Pachter, *J. Chem. Phys.* **2002**, *117*, 7128–7136.

Received: May 23, 2005
Published online: August 1, 2005