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Photochemical synthesis of tetraaryl-substituted pentacenes

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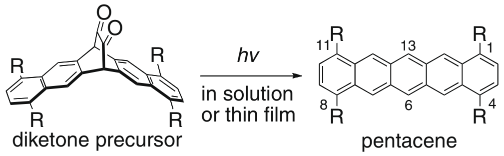
ABSTRACT

The syntheses of 1,4,8,11-tetraphenylpentacene and 1,4,8,11-tetra(2′-thienyl)pentacene are described via photodecarbonylation of the corresponding α-diketone precursors.

Pentacene is one of the most fascinating molecules for organic electronic devices because of its high carrier mobility.[1,2] Various pentacene-based organic field-effect transistors (OFETs) have been reported to show carrier mobilities greater than 1.0 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ value of which is comparable with that of amorphous silicon.[3] The main drawbacks of pentacene, however, are its poor solubility in common organic solvents and facile photodegradation in air.[4] Introduction of substituents to pentacene increases the solubility and stability efficiently.[5] The most common method for the synthesis of such substituted pentacenes is based on nucleophilic addition of aryl-lithiums[6] or magnesium bromides[7] to pentacene 6,13-quinone followed by reductive aromatization. 6,13-Bis(trialkylsilylethynyl)-pentacenes[8] and 6,13-connected pentacene oligomers[9] were successfully obtained and their optical or OFET properties were exemplified. Although various synthetic methods for substituted pentacenes have been reported,[10] a few methods for the synthesis of 1,4,8,11-substituted pentacenes have also been reported.[11] This may be due to the inaccessibility of pentacene 1,4,8,11-diquinone.[12] Miller et al. reported the formation of 1,4,8,11-tetraphenylpentacene by the reduction of the corresponding quinone, which was, in turn, prepared by the Diels–Alder reaction of benzoquinone with 4,7-diphenylbenzo[*c*]furan.[13] In our previous studies, we reported the synthesis of pentacene from its diketone precursor (Scheme 1, **1c** to **2c**)[14] by application of the photodecarbonylation of dicarbonyl-bridged anthracene.[15] We successfully applied this conversion reaction for solution-processed device-fabrication of OFET.[16] Recently, Neckers' group has reported to prepare the substituted pentacenes and higher acenes by this method.[17] This method is based on the Diels–Alder reaction of 5,6,7,8-tetramethylenebicyclo[2.2.2]oct-2-ene with arynes. We planned to prepare soluble pentacene derivatives by the application of this preparation method. In this Letter, we report the synthesis of diketone precursors of 1,4,8,11-tetraarylpentacene and their photochemical conversion.

The synthesis of the diketone precursors is shown in Scheme 2. 3,6-Dibromophthalic anhydride[18] (**3**) was converted to *N*-hydroxy-3,6-dibromophthalimide (**4**) quantitatively and then tosylated to *N*-tosyl-3,6-dibromophthalimide (**5**) with tosyl chloride and triethylamine in 95% yield. Lossen rearrangement of **5** with NaOH cleanly afforded 3,6-dibromoanthranilic acid (**6**) in 85% yield. Esterification of **6** with diazomethane followed by Suzuki–Miyaura coupling reaction with phenylboronic acid afforded 3,6-diphenysubstituted anthranilic ester **8a** in 90% yield. Hydrolysis of **8a** with TMSONa afforded anthranilic acid **9a** in 90% yield.[19] As previously reported,[14] the Diels–Alder reaction of an aryne generated in situ from **9a** with 5,6,7,8-tetramethylenebicyclo[2.2.2]oct-2-ene followed by oxidation with DDQ gave tetraphenylethenopentacene **10a** in 54% yield. $\mathrm{OsO_4}$-mediated dihydroxylation afforded tetraphenylethanopentacene diol **11a** in 73% yield. Swern oxidation of **11a** afforded the phenyl-substituted diketone precursor **1a** in 45% yield. In a similar manner, **1b** was obtained in 22% overall yield from **8b**.

The UV–vis absorption spectra of diketone precursors **1a** and **1b** in toluene are shown in Figure 1. The precursors show characteristic weak and broad n–π* absorptions at ca. 460 nm. The photoreactions of diketone precursors to pentacenes were performed. The solution of diketone precursor in toluene was degassed by Ar bubbling for 20 min in the dark and then the solution was irradiated with a blue LED. The change in the absorption spectra was measured at an interval of 30 s during photoreaction.



1a (R = Ph)
1b (R = 2-thienyl), **1c** (R = H)

2a - 2c

Scheme 1. Photochemical synthesis of pentacenes.

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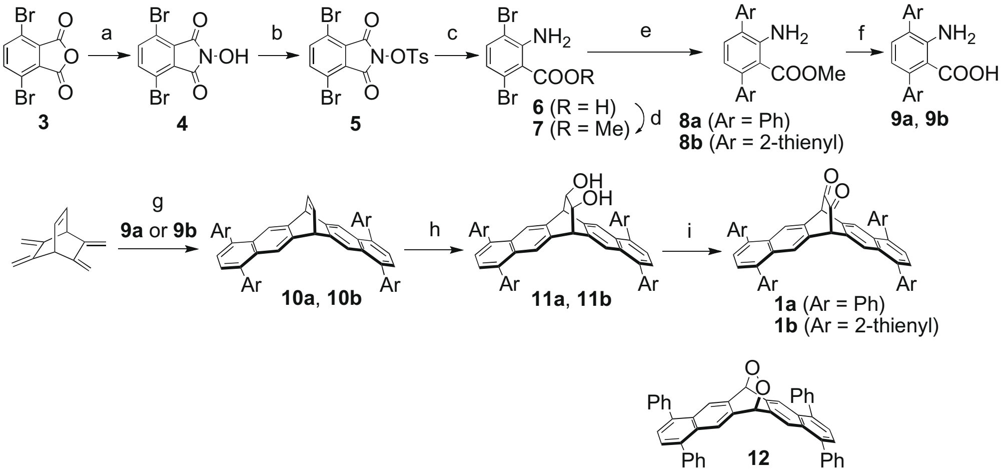

Scheme 2. Reagents and conditions: (a) $NH_2OH{\cdot}HCl$, *dry*-pyridine, rt to 95 °C, 5 h; quant; (b) TsCl, Et_3N, THF, rt, 1 h; 95%; (c) NaOH, THF, H_2O, 60 °C, 3 h; 80%; (d) Diazald®, KOH, THF, 0 °C to rt, overnight; quant (e) $ArB(OH)_2$, Na_2CO_3, $Pd(PPh_3)_4$, DME, H_2O, reflux; **8a**: 90%; **8b**: 92%; (f) TMSONa (in THF), *dry*-THF, reflux, overnight; **9a**: 90%; **9b**: 94%; (g) isoamyl nitrite, *dry*-THF, 60 °C to reflux, 1.5 h; DDQ, *dry*-CH_2Cl_2, rt, overnight; **10a**: 54%; **10b**: 58%; (h) OsO_4, NMO, THF, rt, overnight; **11a**: 73%; **11b**: 63%; (i) *dry*-DMSO, TFAA, Et_3N, *dry*-CH_2Cl_2, −60 °C, 1.5 h; **1a**: 45%; **1b**: 63%.

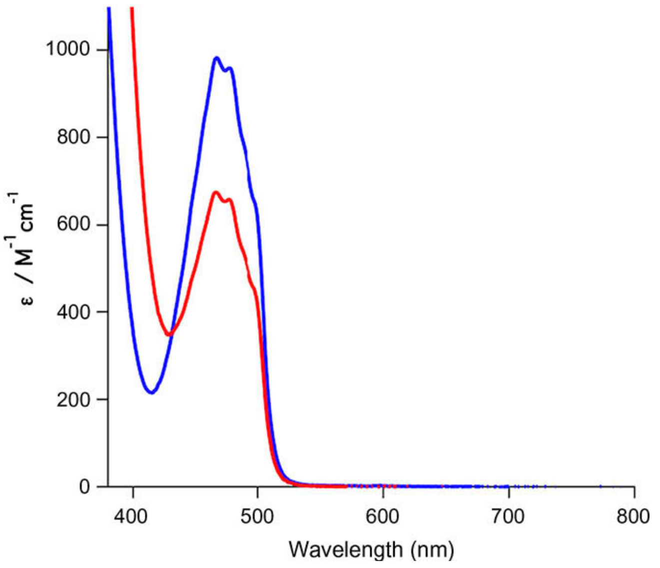

Figure 1. UV–vis spectra of **1a** (blue line) and **1b** (red line) in toluene.

The change of UV–vis spectra during the photoreaction of **1a** under Ar or O_2 is shown in Figure 2, and the time profiles of the change are shown in Figure S1. Before irradiation, only the broad n–π* peak at 465 nm was observed. As this peak decreased gradually,the new peaks at 480, 515, 554, and 600 nm assigned to tetraphenylpentacene **2a** increased. According to the progress, the color of the solution was changed from yellow to purple. The absorbance of pentacene became constant after 60-min irradiation. Similarly, diketone precursor **1b** was converted to tetra(2′-thienyl)pentacene **2b** as shown in Figure S2. The solubility of **2a** and **2b** is improved compared to that of **2c**, because precipitation of pentacenes was not observed during the photoirradiation under these conditions.[14b] The reactivity of the obtained pentacenes with oxygen is very high since they do not have substituents at 6 and 13-positions (Fig. S3).

Absorption and fluorescence spectra of the obtained pentacenes **2a** and **2b** in toluene are shown in Figure 3. The absorbance maximums of pentacenes were red shifted to 23 nm for **2a** and 32 nm

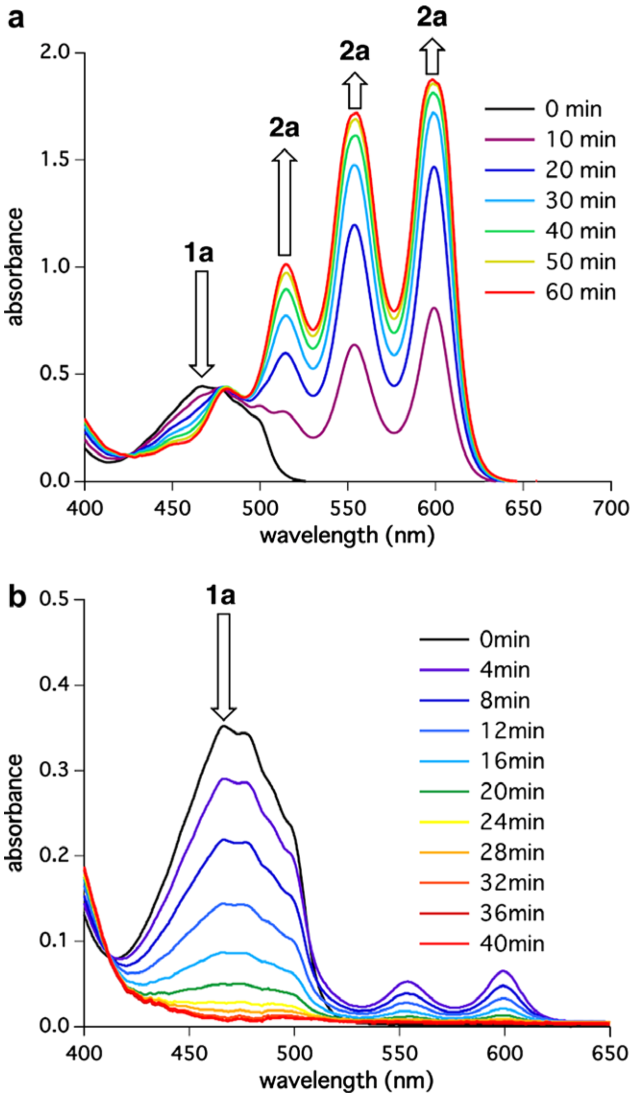

Figure 2. UV–vis spectra during the photoreaction of **1a** in toluene (a) under Ar (4.5×10^{-4} M) or (b) O_2 (3.6×10^{-4} M).

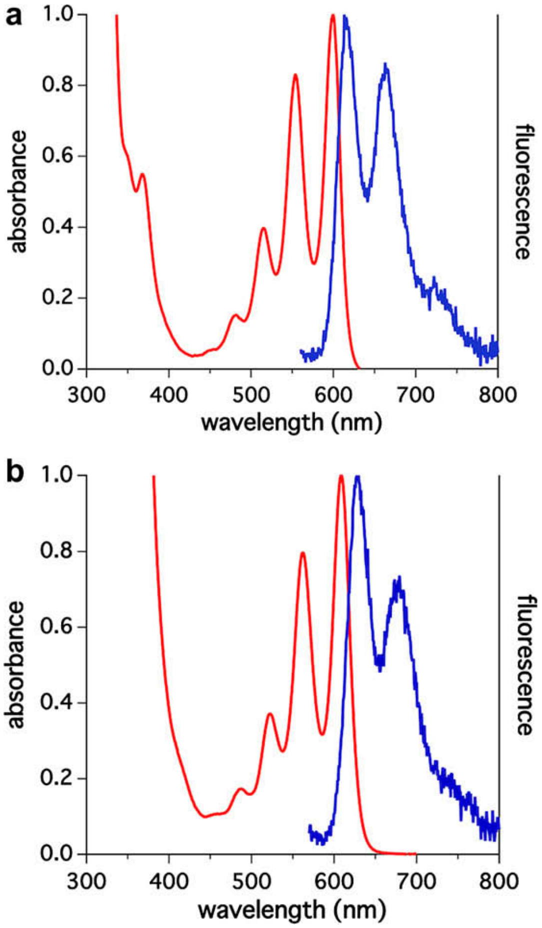

Figure 3. Normalized UV–vis spectra (red lines) and fluorescence spectra (blue lines) of **2a** (a) and **2b** (b) in toluene.

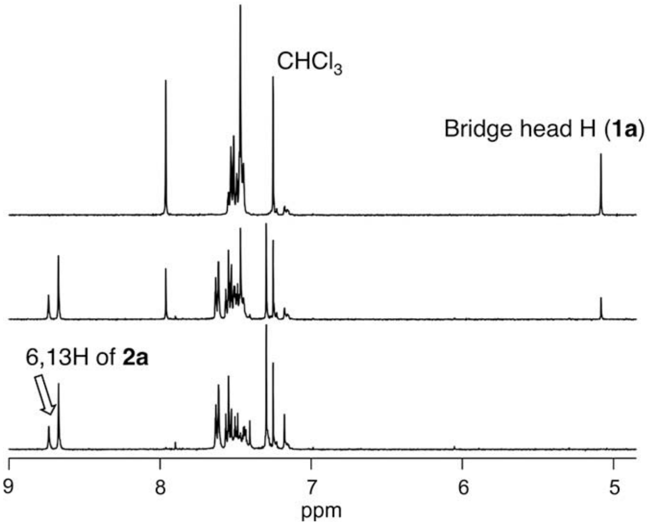

Figure 4. ^{1}H NMR spectra during the photoreaction of **1a** in $CDCl_3$ under Ar: Top: before irradiation; Middle: during irradiation; Bottom: after irradiation.

for **2b** in comparison with the unsubstituted pentacene **2c**. The absolute fluorescence quantum yields of pentacenes were 0.19 for **2a** and 0.16 for **2b**.

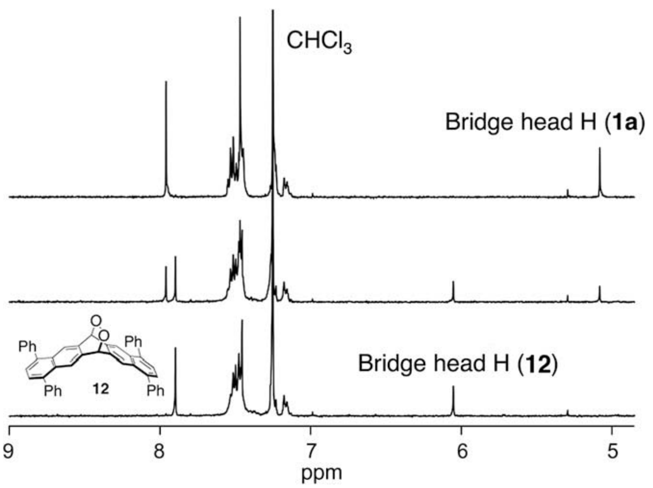

Figure 5. ^{1}H NMR spectra during the photoreaction of **1a** in $CDCl_3$ under O_2: Top: before irradiation; Middle: during irradiation; Bottom: after irradiation.

When the photoreaction of diketone precursor **1a** was conducted in toluene under O_2, peaks at 465 nm gradually decreased in the same way but peaks for pentacene at 554 and 600 nm first appeared and then decreased rapidly due to the reaction of the formed pentacene with oxygen giving 6,13-endoperoxide pentacene (Figs. 2b and S1).[20]

The photoreactions were further monitored by ^{1}H NMR spectroscopy under either Ar or O_2 condition. Diketone precursor **1a** was placed in degassed $CDCl_3$ and was irradiated with blue LED under Ar. During the photoreaction, the singlet peak at 5.08 ppm due to bridgehead protons of **1a** gradually decreased while new singlet peaks due to pentacene **2a** emerged at 8.74, 8.67, and 7.30 ppm (Fig. 4). The new singlet peaks correspond to protons on the 6, 13 carbons, 5, 7, 12, 14 carbons, and 2, 3, 9, 10 (peri) carbons of **2a**, respectively. The TOF-MS spectrum of the reaction is shown in Figure S4. The parent peak of pentacene **2a** was observed at 582. The peak was also observed at 1164, which corresponded to a pentacene dimer. When the photoreaction was performed under O_2 conditions, the diketone singlet at 5.08 ppm decreased with the emergence of new singlets at 7.90 and 6.05 ppm assignable to the peri and bridgehead protons of pentacene 6,13-endoperoxide **12** (Fig. 5).[17d,e]

In summary, the first syntheses of 1,4,8,11-tetraphenylpentacene (**2a**) and 1,4,8,11-tetra(2′-thienyl)pentacene (**2b**) are described using a photodecarbonylation method. The newly synthesized pentacenes are difficult to prepare by conventional methods. They were characterized by UV–vis, fluorescence, and ^{1}H NMR spectroscopy. The 1,4,8,11 substitution pattern will influence molecular packing in crystalline thin films making these molecules interesting candidates for further electronic characterization. Preparation and evaluation of solution-processed devices are under way and will be reported elsewhere.

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Supplementary data

Experimental procedures and characterization data for all new compounds. Detail photoreaction data for **1a** and **1b** are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.01.009.

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