Photochemical Formation of Substituted Pentacenes

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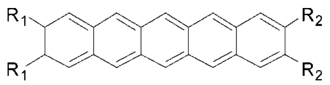
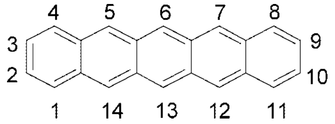


8a: R_1 = 2-methylphenyl, R_2 = H;
8b: R_1 = 4-*tert*-butylphenyl, R_2 = H;
14a: R_1 = R_2 = 2-methylphenyl;
14b: R_1 = R_2 = 4-*tert*-butylphenyl

Substituted pentacenes (**8a**, **8b**, **14a**, and **14b**) were prepared by Strating−Zwanenburg photodecarbonylation of diones (**7a**, **7b**, **13a**, and **13b**). The compounds are red and stable in the solid state under inert atmosphere as well as in degassed solutions, but not in air. Each is soluble in common organic solvents where, unless protected, they are oxygen sensitive.

Introduction

Pentacene emerged in the early 1990s[2] as *the* candidate among organic semiconductors to be used in "plastic" electronics.[3] It has the most nearly ideal thin film characteristics so far observed among p-type semiconductors[4] and the highest charge carrier (hole) mobilities of any small molecule.[5,6] Pentacene, however, is sensitive to oxygen, difficult to purify, and rather insoluble in many organic solvents.[7] There are few reports of modified pentacene derivatives substituted at positions other than 6 and 13 positions,[8,9] because the classic preparative methods for preparing polyacenes reported by Clar,[10] and later Bailey,[11] do not allow for routine structural modification. These methods used Meerwein Pondorf Verley reduction of dione assemblies that, as well, led to incorrect conclusions about heptacene.[12] More recent syntheses of pentacenes have employed the elimination of 6 and 13 functional groups from dihydro precursors other than carbonyl groups[13] though Ono's group did report using the Strating−Zwanenburg reaction to synthesize pentacene- and bromine-substituted derivatives.[9a,b]



Given the immense possibilities of poly(acenes), we have explored flexible photochemical routes to 2,3,9,10-substituted pentacenes. Photochemical reactions[14] can be carried out at ambient conditions, are hands off, and provide the opportunity

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[1] Contribution No. 672 from the Center for Photochemical Sciences.

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[8] In that pentacenes have such good charge carrier properties, subsequent preparation of substituted pentacenes, e.g., 6,13-bis(triisopropylsilylethynyl)-pentacene, which are stable and have acceptable field mobilities was reported.

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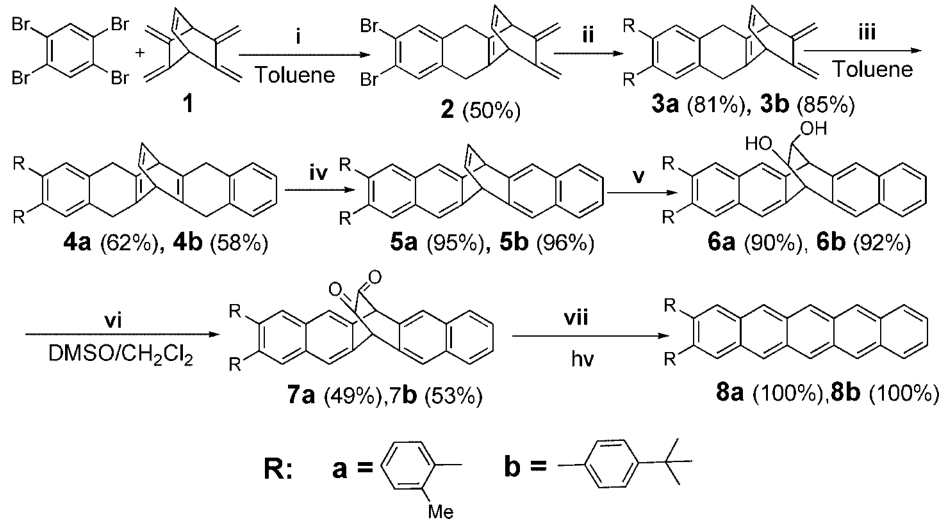
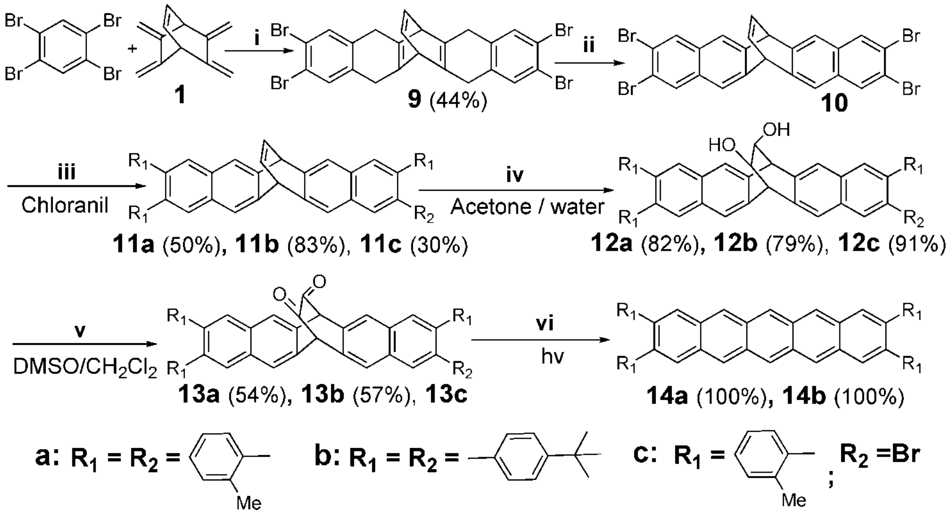
SCHEME 1. Pentacenes: Unsymmetrical 2,3-Disubstitution[a]



[a] Reagents and conditions: (i) *n*-BuLi, −50 to −60 °C; (ii) Suzuki coupling reaction, Cs_2CO_3, $Pd(PPh_3)_4$ (catalyst); (iii) *n*-BuLi, 1,2-dibromobenzene, −50 to −60 °C; (iv) Chloranil, refluxing in dry toluene; (v) OsO_4, MMO, water/acetone, $Na_2S_2O_4$; (vi) Swern oxidation, trifluoroacetic anhydride, −70 °C; (vii) 395 nm light or light ≥450 nm.

SCHEME 2. Pentacenes: 2,3,9,10 Multiple Substitutions[a]



[a] Reagents and conditions: (i) *n*-BuLi, toluene, −50 to −60 °C; (ii) refluxing in dry toluene, 2 h; (iii) Suzuki coupling reaction, Cs_2CO_3, $Pd(PPh_3)_4$ (catalyst); (iv) OsO_4, MMO, $Na_2S_2O_4$; (v) Swern oxidation, trifluoroacetic anhydride, −70 °C; (vi) 395 nm light or light ≥450 nm.

to produce images and, in the current case, to prepare the poly(acene) in situ. The conditions used in the case of heptacene[15−17] point to just a few of the advantages of the Strating−Zwanenburg photoprocess.

Results and Discussion

Scheme 1 was used for the syntheses of 2,3-disubstituted pentacenes which we called “one-sided”, and Scheme 2 was used for 2,3,9,10-tetrasubstituted pentacenes, i.e. “two-sided”. Both use the critical pentaene **1** with subsequent “naphthyne” cycloadditions to build the pentacene ring, Suzuki coupling to affect appropriate substitutions, chloranil aromatization, and osmium tetraoxide followed by modified Swern oxidation to produce the appropriate bridged diones. The routes are distinguished by the critical intermediate dibromide **2** and tetrabromide **9**. The specific experimental processes, of which the “benzyne” step proved most problematic (low yields because of water-sensitivity of BuLi and the poor solubility of the intermediate compound), are detailed in the Experimental Section or the Supporting Information. Each dione was found to be exceedingly photosensitive requiring protection from light both during and after synthesis.

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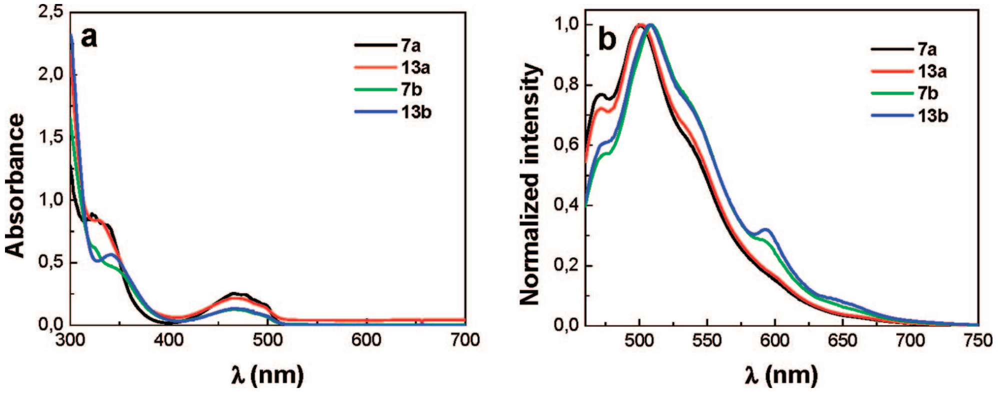

FIGURE 1. Absorption (a) and emission (b) spectra of diones in toluene (λ_{Ex} = 450 nm); [**7a**] = 2 × 10^{-4} M; [**13a**] = 2.5 × 10^{-4} M; [**7b**] = 1 × 10^{-4} M; [**13b**] = 1 × 10^{-4} M.

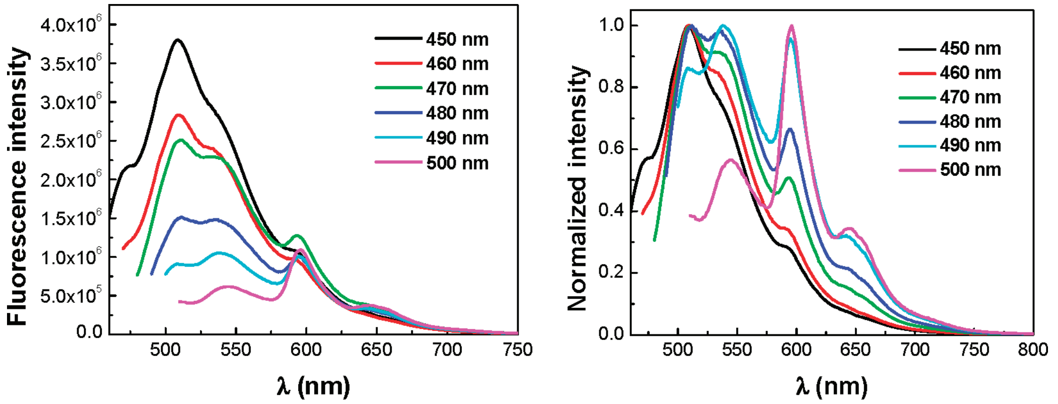

FIGURE 2. Emission spectra of **7b** at different excitation wavelengths in toluene (5 × 10^{-5} M).

TABLE 1. The Properties of Diones

compds	ϵ/M^{-1} cm^{-1} ($\lambda_{n\text{-}\pi^*}$/nm)^a	λ_{Em}/nm^a	FT−IR/ν (cm^{-1})
7a	1165 (465)	500	2922.4 (br), 1734.6, 1580.2, 1471.7, 1398.3, 1191.9, 1099.9, 904.2, 733.1, 614.1
7b	1083 (466)	508	2960.4, 2866.7, 1735.0, 1512.6, 1459.4, 1395.2, 1362.4, 1265.0, 1194.7, 1109.5, 1015.9, 954.8, 912.3, 886.5, 830.9, 747.6, 689.7
13a	845 (466)	500	3015.5, 2920.9, 1734.4, 1475.5, 1452.2, 1377.7, 1263.4, 1188.7, 1111.6, 1024.3, 951.2, 913.4, 758.7, 728.8
13b	1337 (468)	508	2958.8, 2867.5, 1735.7, 1513.7, 1477.2, 1394.4, 1362.2, 1267.8, 1195.5, 1111.3, 1014.8, 993.6, 955.4, 911.0, 872.4, 830.5, 748.9

^{a} Absorption and emission in toluene.

Properties: Diones 7a, 7b, 13a, and 13b. Diones **7a**, **7b**, **13a**, and **13b** (**13c** is unstable and decomposed during separation on a column) absorb between 420 and 510 nm in toluene showing characteristically broad n−π* bands. Absorption maxima appear at 465 (ϵ = 1165), 466 (ϵ =1083), 466 (ϵ = 845), and 468 nm (ϵ = 1337), respectively (Figure 1a). A fluorescence emission at 500 nm was observed in toluene for 2-methylphenyl-substituted diones, **7a** and **13a** (Figure 1b), while 4-*tert*-butylphenyl substituted diones, **7b** and **13b**, also showed two small peaks around 600 and 650 nm assigned to the emission of photolysis products, the pentacenes, besides the maximum at 508 nm.

The diones are exceedingly photosensitive, so the longer the excitation wavelength, the more obvious the emission of the pentacene (Figure 2). Almost all the emission originates from the pentacene with 500 nm excitation light in the case of **7b** with some **8b** (the photolysis product of **7b**) produced during measurement of the fluorescence.

The molar extinction coefficient (ϵ, in toluene) of the diones and infrared data are given in Table 1. Each diketone has a characteristic C=O peak around 1735 cm^{-1}.

Photodecarbonylation Reactions. This Strating−Zwanenburg decarbonylation was originally attractive as a potential approach to the now predicted to be unstable O=C=C=O.[15] Consequently in the Okhrimenko−Mondal report, decarbonylation was shown to be from the singlet state of the dione with no evidence *in transient UV experiments* as a first approximation for any reaction intermediate precedent to poly(acene). As these authors point out, the matter of biradical intermediates in the Strating−Zwanenburg reaction is not spoken to by transient UV spectroscopic methods, and must be addressed by TRIR. Under steady state conditions, both 395 nm light from an LED or continuous wavelength light (≥450 nm) worked well for the Strating−Zwanenburg photodecarbonylation, the results of which can be recorded by either NMR or UV−vis spectrometers. For example, if a

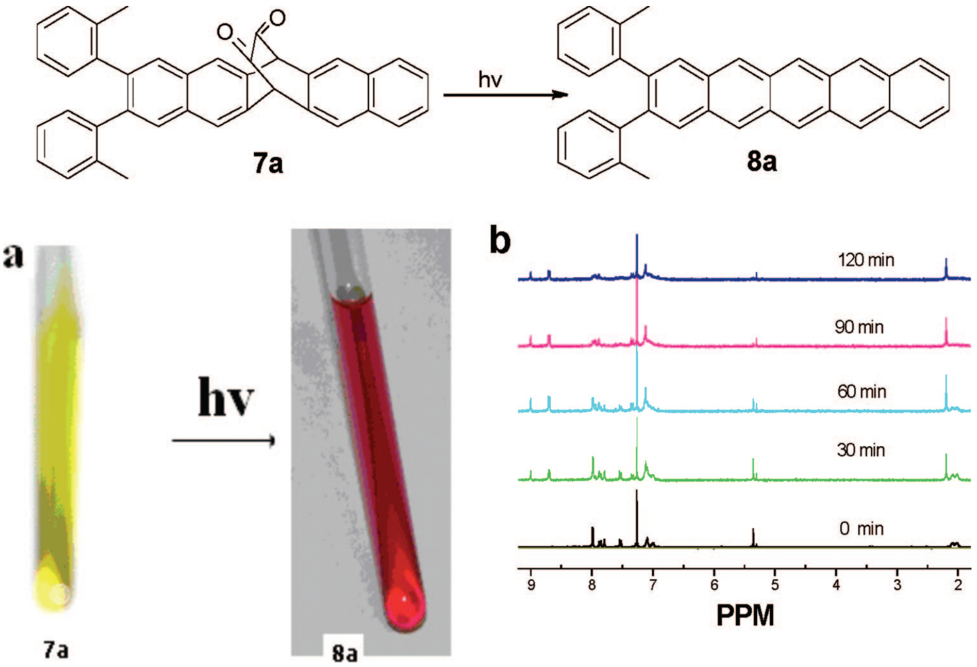

FIGURE 3. Transformation of **7a** to **8a** in sealed and degassed systems: (a) colors of **7a** $CDCl_3$ solution before and at the end of irradiation; (b) the evolution of ^1H NMR signals of **7a** with the irradiation.

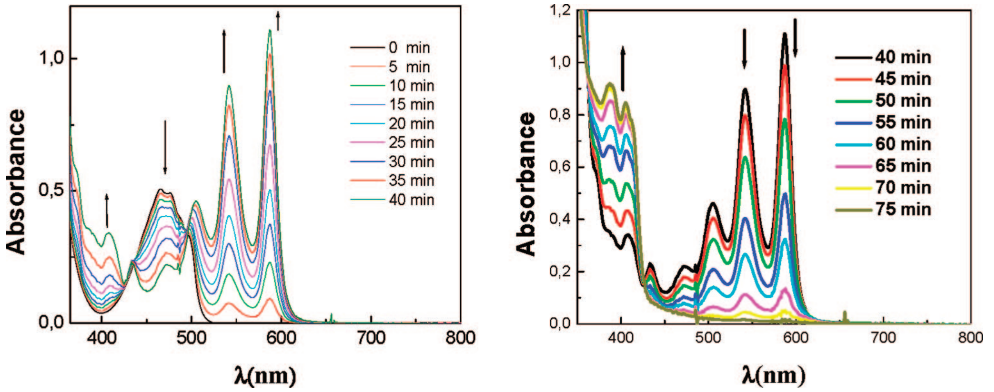

FIGURE 4. UV−vis spectra changes of **7a** during the irradiation in toluene (3×10^{-5} M).

$CDCl_3$ solution of **7a** in a sealed NMR tube was completely degassed by freeze−pump−thaw cycles before photolysis, the solution turned red from yellow during the photolysis while recorded changes in the NMR spectra reflect the transformation from diketone to pentacene, Figure 3.

Pentacenes without modification at the 6 and 13 positions are reported either to dimerize ([4 + 4] cycloaddition) or be oxidized to the 6,13-endoperoxide[9a−c,k] in solution with the appearance of new ^1H NMR peaks (6 and 13 positions) at ~5.06 ppm for the dimer and ~6.29 ppm for the endoperoxide. In our experiments, no new peaks were observed in the 5.0−7.0 ppm region, though peaks resulting from the 6 and 13 protons of the diketones gradually decreased as the irradiation progressed to completion in 2 h (±). Subsequently, the spectrum remained unchanged even following an additional 1 h of irradiation. The pentacenes thus formed also remain for almost one month in the sealed tube, indicating that they do not react via the reactive central ring by dimerization. The molecular weight of each pentacene was observed by DIP-MASS (see the Supporting Information) and the elemental composition confirmed by HRMS. After evaporating the solvent from the samples irradiated in an NMR tube, **8a** and **14a** were obtained as brown solids and **8b** and **14b** as red solids.

If a solution of a pentacene is transferred to an open cell it turns colorless (or pale yellow) resulting, as we show, from endoperoxide formation. Irradiating a degassed toluene solution of **7a** in a cuvette produced new, structured absorption bands from 385 to 625 nm with maxima at 408, 505, 542, and 587 nm (Figure 4). The latter three peaks, assigned to the $\pi-\pi^*$ transition of **8a**,[9a,k] increased for 40 min of photolysis, then decreased gradually, disappearing completely after 75 min. The peak around 400 nm is assigned to the endoperoxide (confirmed by MALDI-TOF analysis), which became the sole product after 80 min of irradiation in the cuvette, which cannot be firmly sealed like the special NMR tube.

To confirm that the peak around 400 nm belonged to the endoperoxide, a solution of **7b** saturated with oxygen was irradiated and the results recorded by UV−vis spectroscopy (Figure 5a). After irradiation, MALDI-TOF analysis confirmed the peaks around 400 nm originate from endoperoxide and during the irradiation no peaks for **8b** were observed, indicating **8b** from the photolysis immediately reacts with oxygen.

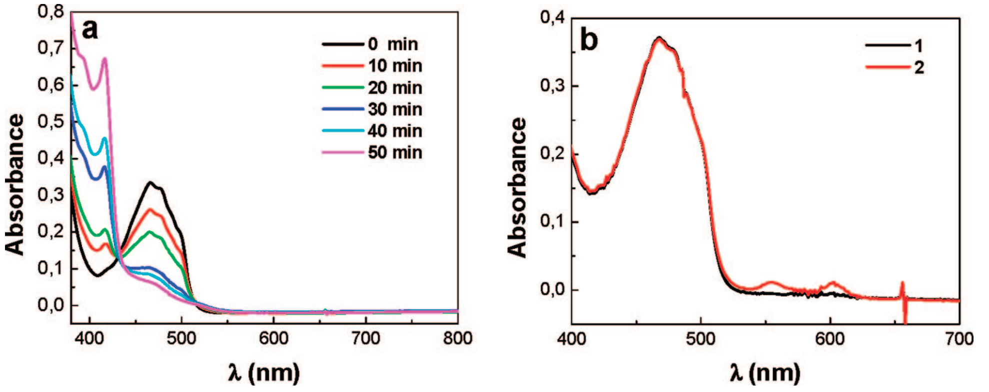

FIGURE 5. (a) Absorption spectra of **7b** (3×10^{-4} M) at different irradiation (395 nm) times in oxygen-saturated toluene; (b) absorption spectra of **7b** (3×10^{-4} M) in degassed toluene solution [before (line 1) and after (line 2) the fluorescence measurement].

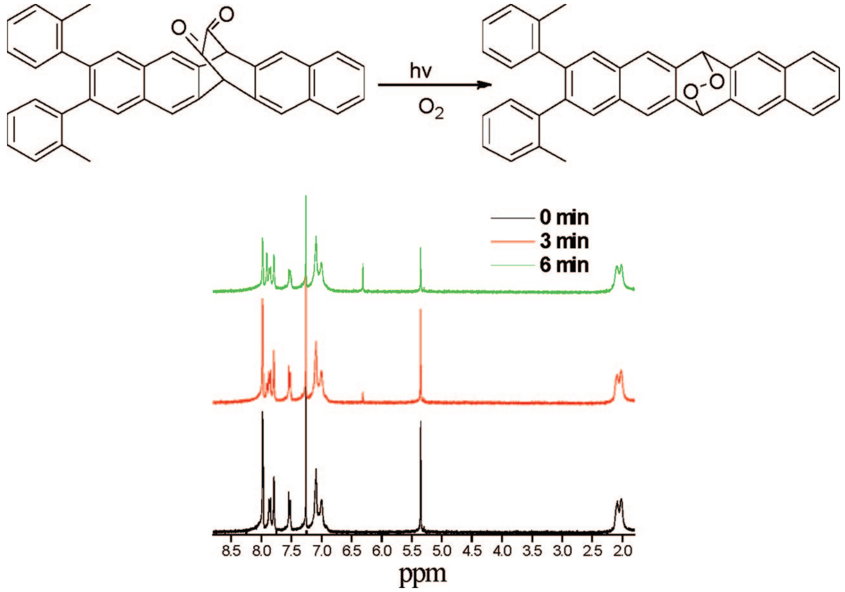

FIGURE 6. NMR spectra of the endoperoxide of **8a** in oxygen-saturated $CDCl_3$ solution.

However, in the solution containing **7b**, the absorbance persists almost an hour, meaning the step from **7b** to **8b** is the slow but predominant process. Transformation to pentacene can be affected even by the weak light of a fluorometer during measurement (Figure 5b).

The formation of endoperoxide can also be detected from the NMR spectra (Figure 6). A $CDCl_3$ solution of **7a** in an NMR tube was saturated with oxygen for 20 min following which the tube was irradiated. Before the irradiation, the protons of the bridge carbon atoms appear at 5.35 ppm in the ^{1}H NMR spectrum. As a result of the irradiation, the diketone NMR signal decreases and a new peak ascribed to the protons of the carbon atoms attached to the oxygen bridge at 6,13 positions in the endoperoxide appears at about 6.32 ppm. MALDI-TOF analysis also supports formation of endoperoxide in the oxygen-purged solution.

As we have previously demonstrated with both hexacene and heptacene, PMMA matrices stabilize reactive poly(acenes) substantially. The absorption and emission spectra of **7a** in a PMMA matrix were similar to those in solution though the absorption became broader and an approximate 20 nm red shift occurred in the emission peak (Figure 7a). Photolysis of **7a** in PMMA matrix also produces **8a** (Figure 7b). Thus **8a** is very stable in PMMA matrix and the spectra remain unchanged after 3 h of irradiation.

Pentacenes. The absorption and fluorescence spectra of pentacenes **8a**, **8b**, **14a**, and **14b** are shown in Figure 8. Their photophysical parameters are listed in Table 2. The emissions of **8a** and **14a** are nearly the same, whereas there is an obvious red shift (11 nm for the first peak and 24 nm for the second peak) observed for **8b** and **14b**.

Excitation spectra of **8a**, **8b**, **14a**, and **14b** (Figure 9) are similar to their absorption spectra, meaning emission mainly occurs from their singlet excited states (S^1) and that there are no spurious products in the system.

Conclusion

We report the facile photodecarbonylation of pentacene diones **7a**, **7b**, **13a**, and **13b** to pentacenes **8a**, **8b**, **14a**, and **14b**. The pentacenes are stable to dimerization and as isolated solids (under inert atmosphere), but they form endoperoxides with oxygen in solution. The facile synthetic approach will be useful on surfaces as the drive toward plastic electronics goes forward.

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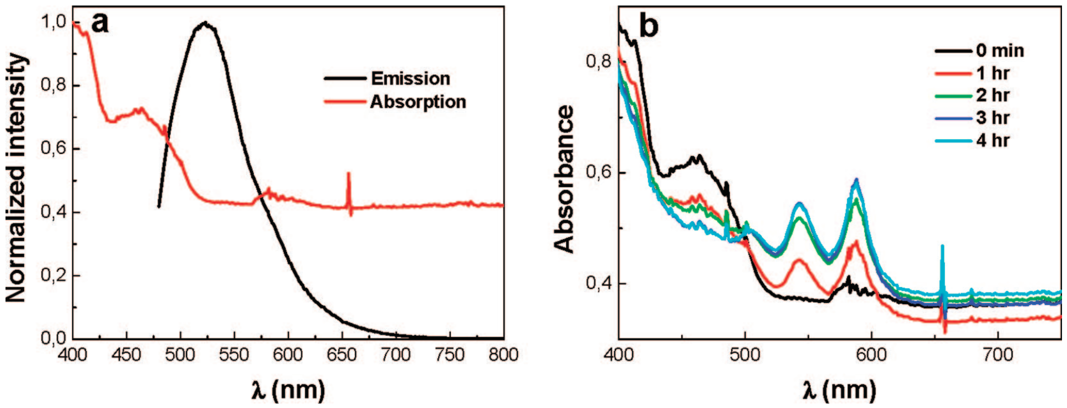

FIGURE 7. Absorption and emission (λ_{Ex} = 470 nm) spectra (a) of **7a** and its absorption changes (b) with irradiation time (light ≥450 nm) in PMMA matrix.

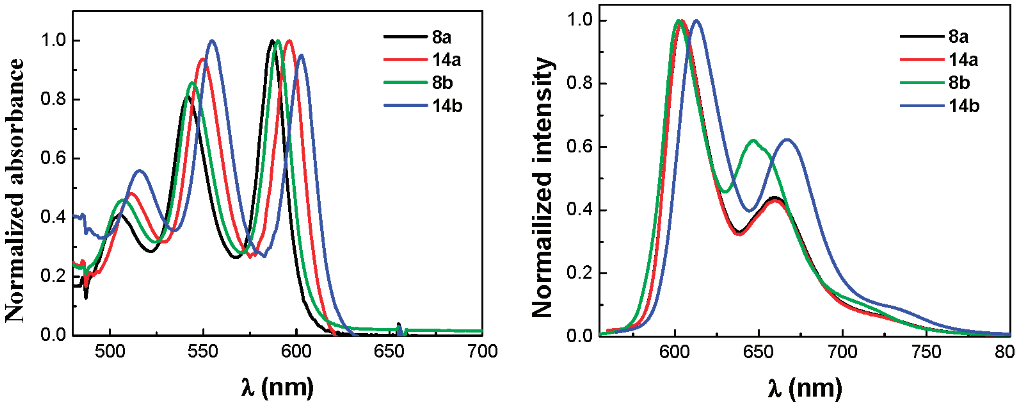

FIGURE 8. Normalized absorption and emission spectra of **8a**, **8b**, **14a**, and **14b** in toluene (λ_{Ex} = 550, 550, 545, and 555 nm, respectively).

TABLE 2. The Photophysical Properties of Pentacenes Obtained

compds	ϵ/M^{-1} cm^{-1} (λ/nm)[a]	λ_{Em}/nm[a]	$Ø_{fl}$[b]
8a	14330 (505), 28220 (542), 34790 (587)	605, 660	0.027
8b	12260 (507), 2287 (544), 26660 (590)	602, 646	0.088
14a	10150 (511), 19680 (550), 20920 (596)	605, 660	0.049
14b	10060 (516), 17960 (555), 17080 (603)	613, 668	0.067

[a] Absorption and emission in toluene. [b] Measured in toluene with Rose Bengal in basic ethanol as the ref 18.

Experimental Section

Bicyclo[2.2.2]oct-2,3,5,6,7-pentaene (1). **1** was prepared according to a literature procedure.[19]

2,3-Dibromo-5,6,9,10-tetrahydro-6,9-etheno-7,8-dimethyleneanthracene (2). *n*-BuLi (1.6 M in hexane) (0.88 mL, 1.41 mmol) was added dropwise under argon to 60 mL of a dry toluene solution containing **1** (200 mg, 1.28 mmol) and 1,2,4,5-tetrabromobenzene (505 mg, 1.28 mmol) at −50 to −60 °C. After being stirred for 6 h at this temperature, the reaction mixture was warmed slowly to rt followed by another 1 h of stirring. Methanol (5 mol) was then added to quench the excess of *n*-BuLi, solvents were removed on a rotary evaporator, and the resulting solid mixture was applied to a silica gel column for purification. Elution was started with hexanes and ended with 10% (vol) of dichloromethane (DCM) in hexanes. The collected fractions were evaporated to isolate the desired compound (250 mg, yield 50%). Mp 142−143 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.462 (s, 4H), 3.95 (m, 2H), 4.872 (s, 2H), 5.092 (s, 2H), 6.482 (m, 2H), 7.375 (s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 30.9, 52.2, 101.9, 121.6, 133.4, 133.6, 135.2, 143.6; mass spectrum (DIP-MS) *m*/*z* M$^+$ 390 (50), 375 (20), 310 (30), 230 (55), 104 (100); HRMS (EI) *m*/*z* calcd for $C_{18}H_{14}Br_2$ 387.9463 (M$^+$), found 387.9467.

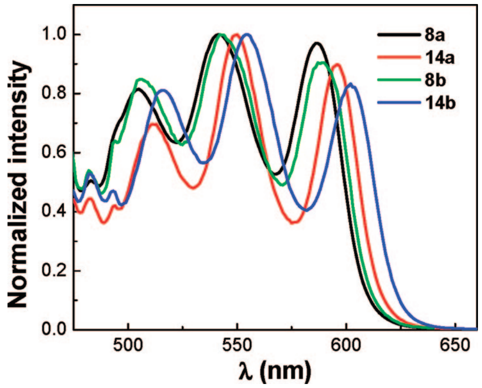

FIGURE 9. Excitation spectra or **8a**, **8b**, **14a**, and **14b** in toluene (λ_{Em} = 643, 660, 650, and 670, respectively).

2,3-Di(2-methylphenyl)-5,6,9,10-tetrahydro-6,9-etheno-7,8-dimethyleneanthracene (3a). Into a 100-mL 2-necked round-bottomed flask was placed **2** (200 mg, 0.51 mmol), *o*-tolylboronic acid (210 mg, 1.53 mmol), Cs_2CO_3 (602 mg, 1.8 mmol), 40 mL of toluene, and 20 mL of water. After this the reaction mixture was degassed for 30 min with argon with strong stirring, then $Pd(PPh_3)_4$ (20 mg, 0.017 mmol) was introduced; this was followed by 48 h of reflux. The reaction mixture was cooled to rt, the solvent was evaporated on a rotary evaporator, and the residue was applied to a silica gel column for purification. The column was washed with a gradient eluent (starting with hexane and ending with 20% DCM (vol) in hexane). Condensation of the fraction provided the pure compound **3a** (170 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.039 (s, 6H), 3.598 (s, 4H), 3.964 (m, 2H), 4.877 (s, 2H), 5.097 (s, 2H), 6.501 (m, 2H), 6.960−7.078 (m, 10H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 20.7, 34.7, 57.4, 101.5, 124.8, 126.7, 129.7, 130.7, 132.5, 133.7, 134.0, 135.7, 138.7, 144.1; mass spectrum (DIP-MS) *m/z* M$^+$ 412 (100), 397 (40), 325 (40); HRMS (EI) *m/z* calcd for $C_{32}H_{28}$ 412.2191 (M$^+$), found 412.2188.

2,3-Di(2-methylphenyl)-5,6,7,12,13,14-hexahydro-6,13-ethenopentacene (4a). *n*-BuLi (1.6 M in hexane) (0.69 mL, 1.1 mmol) was added dropwise under argon to 50 mL of a dry toluene solution containing **3a** (200 mg, 0.49 mmol) and 1,2-dibromobenzene (236 mg, 1 mmol) at −50 to −60 °C. After 3 h of stirring, the reaction mixture was warmed slowly to rt. Then 3 mol of methanol was added to quench the reaction. Following removal of the solvents the crude residue was applied to a silica gel column for purification. Elution (hexane to 25% (vol) DCM in hexane) was used to wash the column. White pure **4a** (149 mg) was obtained (yield 62%) from the fraction. Mp 178−180 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.028 (s, 6H), 3.612 (s, 4H), 4.329 (m, 2H), 6.873−7.104 (m, 16 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 32.9, 34.5, 54.4, 124.8, 125.9, 126.7, 128.9, 129.9, 130.9, 133.0, 134.6, 135.8, 138.5, 139.4, 140.5; mass spectrum (DIP-MS) *m/z* M$^+$ 488 (100), 398 (25), 347 (25), 180 (70); HRMS (EI) *m/z* calcd for $C_{38}H_{32}$ 488.2503 (M$^+$), found 488.2519.

2,3-Di(2-methylphenyl)-6,13-dihydro-6,13-ethenopentacene (5a). A dry toluene solution containing 244 mg of **4a** (0.5 mmol) and chloranil (246 mg, 1 mmol) was refluxed in a 100-mL round-bottomed flask for 2 h. The reaction mixture was then cooled to rt and solvent was evaporated on a rotary evaporator. The reaction residue was dissolved in 50 mL of DCM and washed with 2 N NaOH solution (2 × 10 mL) and ultimately with brine (1 × 10 mL). The organic layer was dried (anhydrous $MgSO_4$), filtered, and evaporated. The crude product was further purified by column chromatography on silica gel to give **5a** (white solid, 230 mg, 95%). The elution started with hexane and ended with 30% (vol) DCM in hexane. Mp 263−265 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) = 2.065 and 2.131 (d, 6H), 5.407 (m, 2H), 7.054−7.129 (b, 10 H), 7.445 (m, 2H), 7.719−7.819 (m, 8H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 34.7, 50.3, 121.0, 121.4, 124.1, 125.7, 127.0, 127.5, 129.1, 130.6, 131.9, 136.0, 138.3, 142.1, 142.7; mass spectrum (DIP-MS) *m/z* 484 (100); HRMS (EI) *m/z* calcd for $C_{38}H_{28}$ 484.2191 (M$^+$), found 484.2190.

2,3-Di(2-methylphenyl)-6,13-dihydro-6,13-ethanopentacene-15,16-diol (6a) and 2,3-di(4-*tert*-butylphenyl)-6,13-dihydro-6,13-ethanopentacene-15,16-diol (6b). Osmium tetroxide [1 mL solution of 2.5% (w)] in *tert*-butyl alcohol was added to 100 mL of a mixed solution of acetone and water (1:5 in volume) containing 250 mg of 4-methylmorpholine *N*-oxide (2.14 mmol) in a 500-mL round-bottomed flask. After 10 min of stirring, an acetone solution containing 0.5 mmol of **5a** or **5b** (242 mg or 284 mg) was introduced and a suitable amount of acetone added to make the solution transparent. The reaction mixture was then stirred at rt for 48 h. Sodium dithionite (400 mg) was added to this reaction mixture, then it was stirred for another 20 min to yield a heterogeneous solution. The suspension in the mixture was removed by filtering it through a pad of cerite and washing the pad with acetone. The solvent from the filtered solution was evaporated on a rotary evaporator, and the residue was applied to a silica gel column and washed with gradient eluent. For **6a** (**6b**), the eluent started from hexane and ended with 25% (30%) ethyl acetate in hexane. The collected solvent was evaporated to provide the pure compound (white solid, yield 90% for **6a** 92% for **6b**). Data for **6a**: Mp 193−195 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.987−2.097 (m, 8H), 4.224 (s, 2H), 4.653 (s, 2H), 6.990−7.072 (d, 8H), 7.428 (m, 2H), 7.720−7.858 (m, 8H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.2, 51.3, 68.5, 123.1, 123.4, 124.8, 125.4, 126.0, 127.0, 127.7, 129.8, 131.7, 132.8, 135.9, 137.4, 137.8, 140.4, 144.3; mass spectrum (DIP-MS) *m/z* (M$^+$ − $C_2H_4O_2$) 458 (100); MALDI-TOF 541 (M$^+$ + Na); HRMS (ESI) *m/z* calcd for $C_{38}H_{30}O_2$ 541.2144 (M$^+$ + Na), found 541.2139. Data for **6b**: Mp 188−190 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.290 (s, 18), 2.336 (br, 2H), 4.074 (br, 2H), 4.608 (s, 2H), 7.015−7.045 (m, 4H), 7.181−7.248 (m, 4H), 7.429 (m, 2H), 7.767−7.843 (m, 8H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 31.3, 34.4, 51.3, 68.4, 123.4, 124.4, 125.0, 125.9, 127.7, 128.8, 129.6, 131.9, 132.8, 136.2, 137.4, 138.6, 139.5, 149.3; mass spectrum (DIP-MS) *m/z* (M$^+$ − $C_2H_4O_2$) 543 (100), 557 (20); MALDI-TOF 626 (M$^+$ + Na); HRMS (ESI) *m/z* calcd for $C_{44}H_{42}O_2$ 625.3083 (M$^+$ + Na), found 625.3079.

Preparation of 2,3-Di(2-methylphenyl)-6,13-dihydro-6,13-ethanopentacene-15,16-dione (7a) and 2,3-Di(4-*tert*-butylphenyl)-6,13-dihydro-6,13-ethanopentacene-15,16-dione (7b). Under argon atmosphere trifluoroacetic anhydride (3 mL) was added dropwise to a stirred solution of dry dimethyl sulfoxide (DMSO, 1.2 mL) in 30 mL of DCM kept at −50 to −60 °C. After 15 min, a solution (1.2 mL of dry DMSO in 15 mL of DCM) of **6a** (150 mg, 0.29 mmol) or **6b** (200 mg, 0.33 mmol) was added very slowly. The resulting mixture was stirred for 2 h after which 2 mL of diisopropylethylamine was introduced dropwise and this reaction mixture was stirred for another 2 h. The mixture was maintained at reduced temperature under argon for the entire time after which the resulting bright yellow solution was warmed to rt and extracted with DCM followed by washing the organic layer with water. Evaporation of solvent provided crude product, **7a**, which was purified by recrystallization with DCM and hexane (pale yellow solid, 73 mg, yield 49%). Pure yellow **7b** (105 mg, yield 53%) was obtained following separation on a silica gel column eluted with DCM. Data for **7a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.019 and 2.085 (6H), 5.350 (s, 2H), 6.999 and 7.091 (8H), 7.526 (m, 2H), 7.790, 7.843 and 7.853 (8H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 20.3, 60.7, 124.9, 125.1, 125.4, 127.1, 127.2, 127.9, 129.3, 129.8, 131.4, 131.9, 132.3, 132.6, 133.7, 135.7, 140.8, 185.1; mass spectrum (DIP-MS) *m/z* (M$^+$ − C_2O_2) 458 (100); HRMS (ES) *m/z* calcd for $C_{38}H_{26}O_2$ 515.2011(MH$^+$), found 515.1993. Data for **7b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.298 (s, 18), 5.327 (s, 2H), 7.088−7.320 (m, 8H), 7.522 9M, 2H), 7.856−7.965 (m, 8H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 17.7, 20.6, 46.9, 110.8, 111.2, 111.6, 113.2, 114.3, 115.2, 115.7, 118.1, 118.8, 119.7, 124.1, 126.6, 135.8, 171.4; mass spectrum (DIP-MS) *m/z* (M$^+$ − C_2O_2) 543 (100), 410 (60); HRMS (EI) *m/z* calcd for $C_{44}H_{38}O_2$ 598.28718 (M$^+$), found 598.21775.

2,3,9,10-Tetrabromo-5,6,7,12,13,14-hexahydro-6,13-ethenopentacene (9). To a solution containing **1** (200 mg, 1.28 mmol) and 1,2,4,5-tetrabromobenzene (1.06 g, 2.69 mmol) in 60 mL of dry toluene was added 1.85 mL of *n*-BuLi in hexane (1.6 M) dropwise at −50 to −60 °C. The procedure was similar to that described for the preparation of **2**. Elution was begun with hexane and ended with 20% DCM in hexane. The purified compound was obtained in a yield of 350 mg (44%). Mp 295−296 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.506 (s, 8H), 4.276 (m, 2H), 6.840 (m, 2H), 7.365 (s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 32.4, 53.8, 121.6, 133.4, 135.4, 139.2, 139.8; mass spectrum (DIP-MS) *m/z* M$^+$ 624 (40), 544 (10), 464 (10), 384 (8), 151 (100); HRMS (EI) *m/z* calcd for $C_{24}H_{16}Br_4$ 625.79413 (M$^+$), found 625.79255.

2,3-Dimethylphenyl(4-*tert*-butylphenyl)pentacene 8a (8b) and 2,3,9,10-Tetramethylphenyl(4-*tert*-butylphenyl)pentacene 14a (14b). Transparent diketone (**7a**, **7b**, **13a**, **13b**) solutions (5 mg in about 0.7 mL of $CDCl_3$) in Norell Young valve NMR tubes were degassed by using freeze−pump−thaw cycles in the dark. Subsequently the sealed, oxygen-free diketone solutions were irradiated with an UV-LED lamp (395 ± 25 nm) or high-pressure mercury lamp (a filter was used to cut off the light below 450 nm) as the light source. During the irradiation, the ^{1}H NMR signal (around 5.3 ppm) of the 6 and 13 positioned protons of the diketone were monitored to follow the transformation from diketone to pentacene. Reaction completion was indicated by the disappearance of 6 and 13 proton signals of the diketone. The pentacenes were obtained as follows: Following the complete disappearance of the diketone signals, the tube was transferred to a dry box and solvent was removed in vacuum. There were no apparent side products (NMR) so we estimate 100% yield. The dried pentacenes were redissolved in either C_6D_6 or $CDCl_3$ and the NMR spectra recorded. Data for **8a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.187 (s, 6 H), 7.051−7.109 (m, 8H), 7.314−7.353

(m, 2H), 7.881−7.959 (m, 4H), 8.701 (d, 4H), 9.004 (s, 2H); mass spectrum (DIP-MS) *m*/*z* M^+ 458 (100); HRMS (EI) *m*/*z* calcd for $C_{36}H_{26}$ 458.20345 (M^+), found 458.20348. Data for **8b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.326 (s, 18 H), 7.030−7.216 (m, 8H), 7.890−8.075 (m, 6H), 8.675 (d, 4H), 8.974 (s, 2H); mass spectrum (DIP-MS) *m*/*z* M^+ 543 (100); HRMS (EI) *m*/*z* calcd for $C_{42}H_{38}$ 542.29735 (M^+), found 542.29733. Data for **14a**: ^{1}H NMR (300 MHz, C_6D_6) δ 2.193 (s, 6H), 2.218 (s, 6H), 7.058−7.136 (w, 16H), 7.915 (s, 4H), 8.737 (s, 4H), 9.046 (s, 2H); mass spectrum (DIP-MS) *m*/*z* M^+ 638 (100); HRMS (EI) *m*/*z* calcd for $C_{50}H_{38}$ 638.29735 (M^+), found 638.29757. Data for **14b**: ^{1}H NMR (300 MHz, C_6D_6) δ 1.351 (s, 36H), 7.115−7.292 (m, 16H), 8.017 (s, 4H), 8.706 (s, 4H), 8.997 (s, 2H); mass spectrum (DIP-MS) *m*/*z* M^+ 807 (100), 675 (40); HRMS (EI) *m*/*z* calcd for $C_{62}H_{62}$ 807.48515 (M^+), found 807.48525.

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Supporting Information Available: General experimental procedures, synthesis, and characterization of **3b**, **4b**, **5b**, **10,** **11a**, **11b**, **11c**, **12a**, **12b**, **12c**, **13a**, **13b**, and **13c**, ^{1}H NMR spectra evolutions reflecting the production of pentacene (**8b**, **14a**, **14b**) endoperoxides, emission spectra of **7a**, **13a**, and **13b** under different excitation lights, ^{1}H, ^{13}C NMR spectra for synthesized compounds, MALDI-TOF spectra for diols and pentacene endoperoxides, FT-IR for diones, and DIP-MS for pentacenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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