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ARTICLE TYPE

Synthesis and optical reactivity of 6,13-α-diketoprecursors of 2,3,9,10-tetraalkylpentacenes in solution, film and crystals

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Tetraalkylpentacenes having alkyl chains at 2,3,9,10-positions (**Et-PEN**, **Pr-PEN** and **Hex-PEN**) were prepared from their precursors **Et-PDK**, **Pr-PDK** and **Hex-PDK** respectively. Photoreactions proceeded both in solutions, thin-films, and crystals, thus the properties of **Et-PDK** in films can be studied despite the instability of the pentacenes in solution. **Et-PEN** showed significantly different aggregation-nature compared with the parent pentacene. The hole mobilities of **Et-PEN** and **Pr-PEN** in films were 3.4×10^{-6} and 8.1×10^{-7} cm^2 V^{-1} s^{-1}, respectively, determined by space-charge-limited current measurement, comparable with the order 10^{-6} cm^2 V^{-1} s^{-1} of the electron mobility of Alq$_3$.

Introduction

Over the past 15 years, synthesis of organic semiconducting materials is one of the most active areas of organic chemistry.[1] Among various novel organic semiconducting materials reported so far,[2] pentacene is still one of the most attractive materials due to its inherent high carrier mobility in organic field-effect transistors (OFETs).[3] From the point of view of material development, various synthetic methods[4] have been reported while synthetic study of pentacene derivatives are still not enough due to its instability and insolubility. We have previously reported 6,13-α-diketo pentacene (**PDK**), which can be converted to parent pentacene by photo-induced decarbonylation-reaction[5] (Strating-Zwanenberg reaction) in solution or thin film state (Figure 1).[6] Our group reported the fabrication of pentacene-based OFETs using **PDK** with 0.86 cm^2/Vs of hole-mobility in top-contact device and this value is comparable with that of vapour-deposited pentacene.[7] **PDK** was also applied to the printable pn-type organic photovoltaics (OPVs) of pentacene and fullerenes.[8] This photo-conversion method is also powerful tool for the synthesis of novel acene derivatives[9] including substituted acenes and higher acenes[10].

In order to expand the capability of this photo-conversion methodology, 2,3,9,10-tetraalkylpentacenes were selected as synthetic targets. 2,3,9,10-Tetraalkylpentacenes are fascinating materials for their applications to soluble organic semiconducting materials, liquid-crystalline pentacenes, supramolecular-pentacenes and so on. In that sense, 2,3,9,10-tetraalkylpentacenes are one of the good candidates for the purpose, since the hole mobilities can be controlled by the chain length of the substituents and crystalinities. However the lack of general synthetic method of 2,3,9,10-tetraalkylated pentacenes[11], due to the instability at 6,13-positions, prohibits its wider applications. Bao and co-workers have reported the synthesis and OFET application of 2,3,9,10-tetramethylpentacenes[12] while synthetic methods applied by them were inadequate for the synthesis of the other 2,3,9,10-tetraalkylpentacenes due to the inaccessibility of 2,3,9,10-tetraalkylpentacenequinones. In order to establish the general synthetic route toward 2,3,9,10-tetraalkylpentacenes, we have considered applying the photo-conversion method. Thus photoreaction of 2,3,9,10-tetraalkylpentacene-precursors (**R-PDKs**, **Et-PDK**: R = C_2H_5, **Pr-PDK**: C_3H_7 or **Hex-PDK**: C_6H_{13}) would afford 2,3,9,10-tetraalkylpentacenes (**R-PEN**: **Et-PEN**: R = C_2H_5, **Pr-PEN**: C_3H_7 or **Hex-PEN**: C_6H_{13}) as shown in Figure 1. Herein we will report the synthesis and optical reactivities of **PDKs**, and mobilities of the films of **R-PENs** obtained from the corresponding **R-PDKs** by spin-coating and irradiation.

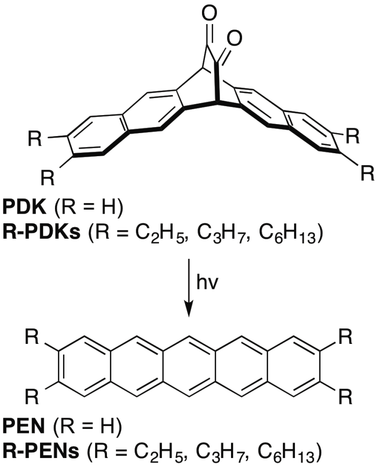
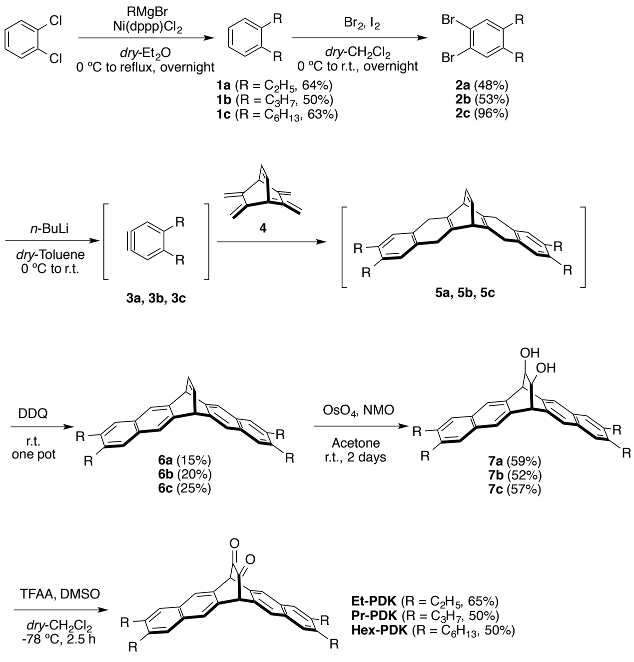


Figure 1. Photochemical synthesis of **PEN** and **R-PENs** from **PDKs**.

Results and Discussion

Synthesis

Synthesis of **Et-PDK**, **Pr-PDK** and **Hex-PDK** are shown in Scheme 1. Kumada-coupling reaction of alkyl magnesium bromides with 1,2-dichlorobenzene under Ni catalyst afforded 1,2-dialkylbenzenes **1**.[13] Bromination of **1** afforded 1,2-dialkyl-4,5-dibromobenzenes **2**. Modern precursors for aryne such as 2-(trimethylsilyl)phenyl-trifluoromethanesulfonate or 2-(iodo)phenyl-trifluoromethanesulfonate would allow milder and selective cycloaddition, but introduction of two alkyl chains to such precursors is very difficult, thus compounds **2** are the only practical precursors of 1,2-dialkyl-4,5-benzynes. Diels-Alder reaction of benzynes **3**, those were prepared in situ from **2** and n-BuLi, with exo-methylene **4** afforded Diels-Alder adducts **5**. Adducts **5** were unstable under air thus one-pot oxidation to pentacene skeletons **6** by DDQ was applied. Purity of **6a** was found almost 35% by HPLC analysis. The high reactivity of aryne **3a** attributed the low purity. Pure **6a** was obtained by multiple-recrystallization by hexane. Purification of **6b** and **6c** was difficult by recrystallization due to their high solubility. Attempts to purify **6b** and **6c** using middle-pressure liquid chromatography, gel permeation chromatography and normal-phase HPLC also failed. Finally purification by recycle reversed-phase HPLC (COSMOSIL Cholester Packed Column, 10 mml I. D. × 250 mm), succeeded to afford pure **6b** and **6c**. OsO_4 oxidation of adducts **6** afforded diols **7** and the subsequent Swern oxidation afforded desired **Et-PDK**, **Pr-PDK** and **Hex-PDK**. Solubility of **Et-PDK** is high as > 60 mg/ml in CH_2Cl_2. Compared with **PDK**, solubility of **Et-PDK** was improved in all solvents, and especially in dichloromethane, toluene and THF as shown in Table S1. Solubility of **Pr-PDK** and **Hex-PDK** is also high. High solubility is an important property for the fabrication of solution-processed devices.



Scheme 1. Synthesis of **alkylated-PDKs**

The UV-Vis absorption spectra of **R-PDKs** in toluene are shown in Figure 2. **R-PDKs** show characteristic weak and broad forbidden n–π* absorptions at around 460 nm. No significant difference of absorptions by the change of alkyl chains was observed.

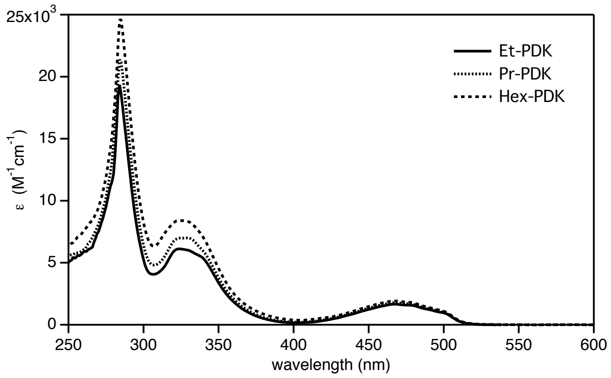


Figure 2. UV-vis absorption spectra of **R-PDKs** in toluene.

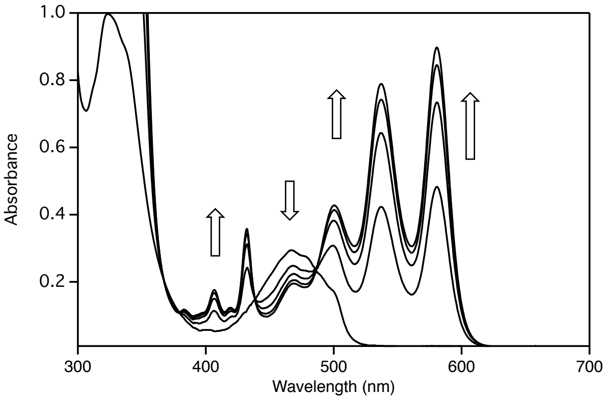


Figure 3. Photoreaction of **Et-PDK** in toluene under Ar atmosphere. The UV-vis absorption spectra were measured at 0, 10, 20, 30, and 40 min during the irradiation.

The photoreactions of **R-PDKs** to **R-PENs** were performed. The 0.2 mM solutions of **R-PDKs** in toluene were degassed by Ar bubbling for 10 min in the dark. Then the solutions were irradiated with a blue LED (StockerYale SpecBright™ Blue LED. wavelength: 470 nm, intensity: 2.5 mW/cm^2). The change in the absorption spectra was measured with an interval of 30 s during photoreaction. The change of UV–Vis spectra and time-profiles during the photoreaction under Ar-atmosphere is shown in Figure 3 and ESI†, Figure S1 for **Et-PDK**. Before irradiation, only the broad n–π* peak at around 467 nm was observed. As this peak decreased gradually, the new peaks at 580, 537, 500, 468, 432 and 407 nm assigned to **Et-PEN** were increased. Appearance of isosbestic points at 486, 439, 379 and 368 nm indicates the quantitative photo-conversion from **Et-PDK** to **Et-PEN**. According to the progress, the colour of the solution was changed from yellow to purple. The absorbance of pentacene became constant after 40-min irradiation. The solubility of **Et-PEN** is improved compared to parent pentacene, thus precipitation of **Et-PEN** during photoreaction was not observed. Photo-conversions of **Pr-PDK** to **Pr-PEN** or **Hex-PDK** to **Hex-PEN** are shown in ESI†, Figure S2 or S3. In both cases, the conversion proceeded smoothly in similar to the case of **Et-PDK**. And also precipitation of formed pentacenes **Pr-PEN** or **Hex-PEN** was not observed.

The photoreactions were further monitored by ^{1}H-NMR spectroscopy. Change of NMR spectra during photo-irradiation of **Et-PDK** under Ar atmosphere is shown in Figure 4. **Et-PDK** was placed in degassed CDCl$_3$ and was irradiated with the blue LED under Ar atmosphere. During the photoreaction, the singlet peak at 5.25 ppm (H^C) due to bridgehead protons of **Et-PDK** gradually decreased while new singlet peaks due to **Et-PEN** emerged at 7.70 (H^D), 8.55 (H^E), and 8.88 (H^F) ppm. From the results of absorption and ^{1}H-NMR spectral changes, quantitative photo-conversion was confirmed. The alkylated pentacenes are not enough stable for isolation. The colour of **Et-PEN** solution was bleached in 3 min under air.

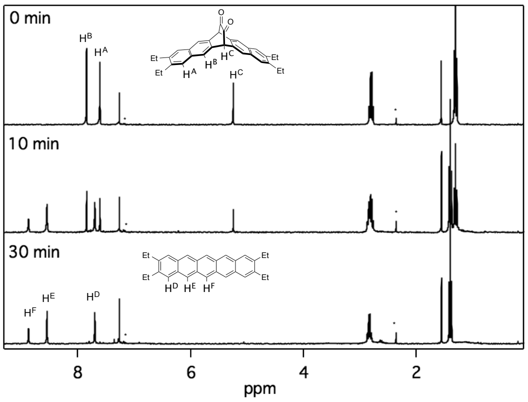


Figure 4. Change of ^{1}H-NMR spectrum during photoreaction of **Et-PDK** in CDCl$_3$ under Ar atmosphere. *: toluene.

Absorption and fluorescence spectra of the obtained **Et-PEN**, **Pr-PEN** and **Hex-PEN** in toluene are shown in Figure 5, ESI† Figures S4 and S5. Compared to the parent pentacene, red-shifts of absorption were not observed. The absolute fluorescence quantum yields were 0.08 for **Et-PEN**, 0.10 for **Pr-PEN** and 0.09 for **Hex-PEN**. These values are comparable with the reported value 0.09 of pentacene in cyclohexane.[14]

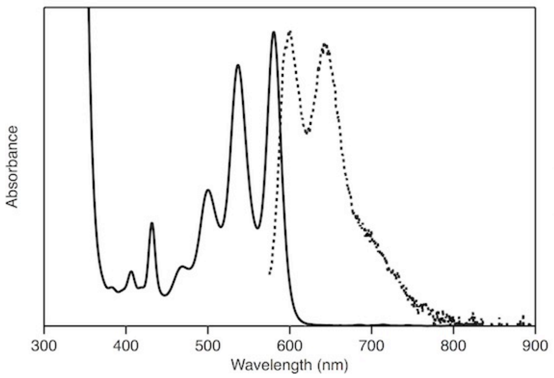


Figure 5. Absorption (black line) and fluorescence (black dotted-line, excited at 537 nm) spectra of **Et-PEN** in toluene.

In order to confirm the complete conversion of **R-PDKs** to **R-PENs** in thin films, photoreactions were monitored by IR and UV-Vis measurement. Thin films were prepared by drop casting of **Et-PDKs** in CHCl$_3$ (20 mg / ml) to washed glass-substrates. Photoreactions were conducted under Ar atmosphere. Conversion was monitored by IR measurement of films, in which the characteristic absorption of carbonyl moiety at 1728 and 1745 cm^{-1} was completely disappeared after the 90 min of photo-conversion (Figure 6). The change of UV–vis spectra of **Et-PDK** in thin film under Ar atmosphere is shown in Figure 7. Before irradiation, only the broad n–π^* peak at around 400-525 nm was observed. Absorption of **Et-PDK** was completely disappeared and new absorption that is characteristic for **Et-PEN** at around 400~625 nm was appeared after 90 min photo-irradiation. Photoreactions of **Pr-PDK** or **Hex-PDK** to **Pr-PEN** or **Hex-PEN** in films are also shown in ESI†, Figure S6, S7, S8 and S9. The absorption spectrum of **Et-PEN** in thin film is significantly different from that of **PEN** (Figure 7). In the case of **Et-PEN**, absorption spectrum of the thin film is similar to that in the solution. In the case of **PEN** film, absorption around 600~700 nm, which is originated from aggregation of **PEN**, was observed. This difference indicates the weak intermolecular interaction of **Et-PEN** in the film compared with **PEN**.

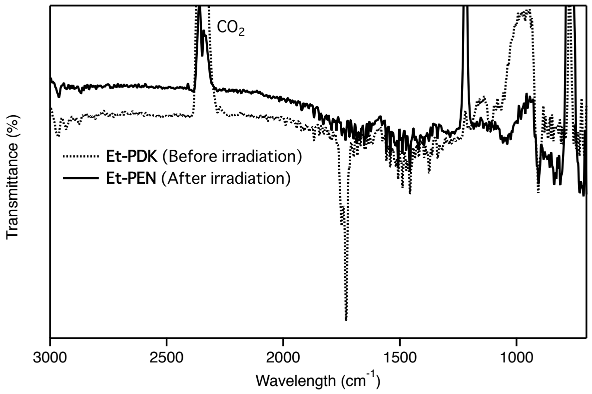


Figure 6. Change on IR spectra before- and after-photoreaction of **Et-PDK** in thin film.

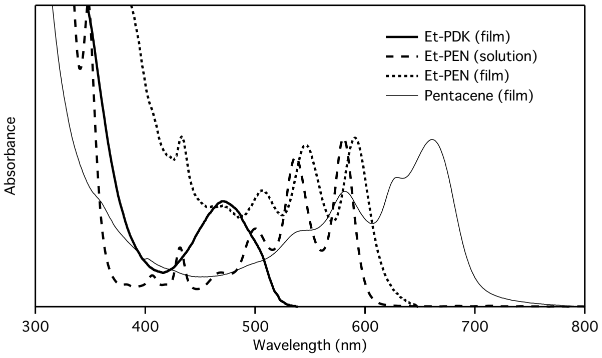


Figure 7. Absorption spectra of **Et-PEN** in solution or thin film and absorption of **PEN** in thin film.

Difference of aggregation nature was also measured by fluorescence from solid **Et-PEN** or **PEN** (Figure 8). Changes of fluorescence during photo-conversion of **Et-PDK** or **PDK** to **Et-PEN** or **PEN** in solid state were monitored. Fluorescence spectrum from solid **Et-PEN** is similar to that in the solution and no aggregation was observed after 30 min irradiation. In sharp contrast to **Et-PEN**, **PEN** shows additional fluorescence around 650~800 nm, which is originated from aggregated pentacene, during photo-conversion. This indicates non-substituted pentacene molecules have strong π-π stacking in crystals but ethyl groups distract the π-π interaction. Difference of π-π stacking nature is remarkably observed in colour of crystals as shown in Figure 8. **Et-PEN** is red crystal while **PEN** is dark-blue crystal due to strong interaction, depending on the π-π interaction between molecules.

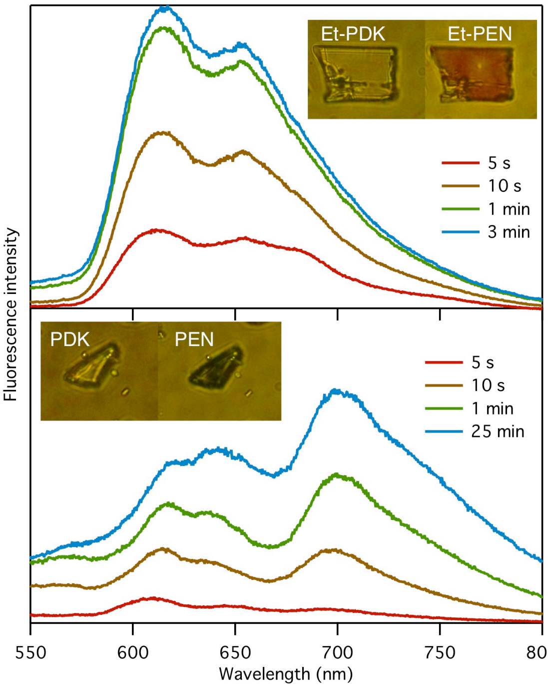


Figure 8. Solid-state fluorescence of **Et-PEN** (top) and **PEN** (bottom)

In order to further pursuit the difference of aggregation nature, crystal growing of **PEN** and **Et-PEN** was measured by AFM. Change of AFM images during photo-conversion from **PDK** to **PEN** is shown in Figure 9. Before photo-irradiation, flat and uniform film of **PDK** was observed. After 5 min irradiation, small pentacene crystals arose and those were growing up with further irradiation. The small crystals gradually grow in height and width then fused to neighboring micro crystals. Thus, total numbers of grain were decreased with increasing of grain size (Figure 9). In the case of **Et-PDK**, flat and uniform film of **Et-PDK** was also observed before photo-irradiation with 0.563 nm of roughness. However crystal growth of **Et-PEN** was not observed during irradiation and film was still flat after 60 min (Figure 10), although the photo-conversion occurred similarly as confirmed by UV-vis and IR measurement.

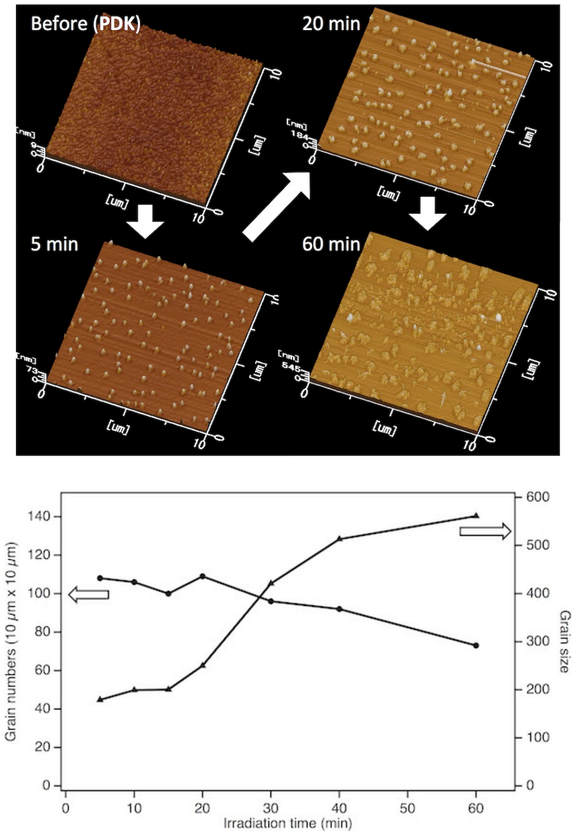


Figure 9. Changes of AFM images (10μm×10μm) during photoreaction of **PDK** to **PEN** (top) and the change of grain numbers (circles) and size (triangles) during photoreaction of **PDK** to **PEN** (bottm)

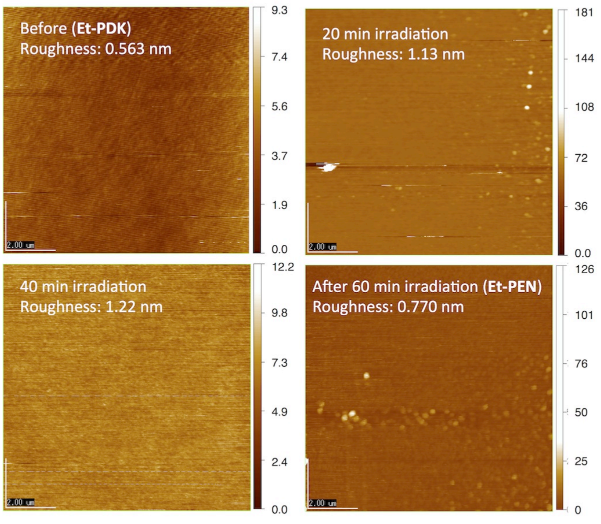


Figure 10. Changes of AFM images (10μm×10μm) during photoreaction of **Et-PDK** to **Et-PEN**.

The mobilities of **Et-PEN** and **Pr-PEN** prepared from the precursors by irradiation using metal halide lamp were measured by space-charge-limited current (SCLC) measurements (ESI†, Figure S10).[15] The film thickness of **Et-PEN** and **Pr-PEN** was about 45 and 60 nm, respectively. The film surface was flat and smooth, which enables the film to be measured by SCLC method. With the same irradiation condition, **PEN** film prepared from **PDK** was not smooth enough and the mobility could not be measured. The mobilities of **Et-PEN** and **Pr-PEN** were obtained as 3.4×10^{-6} and 8.1×10^{-7} $cm^2 V^{-1} s^{-1}$, respectively, which are comparable with the order 10^{-6} $cm^2 V^{-1} s^{-1}$ of the electron mobility of Alq_3, a typical electron transporting material.[16] The lower hole mobilities of **Et-PEN** and **Pr-PEN** compared with general hole transporting materials are probably due to the amorphous properties of the films. In general carrier mobility of hole-transporting material is higher than that of electron transporting material,[17] but the carrier balance between hole and electron transporting abilities are important for the organic electroluminescence (EL) materials. Thus **Et-PEN** and **Pr-PEN** can be good candidates for the p-type materials in combination with general electron transporting materials like Alq_3.

Conclusions

In this paper, the photochemical synthesis of 2,3,9,10-tetraalkylpentacenes and their properties were discussed. By using these precursors, the first synthesis of 2,3,9,10-tetraalkylpentacenes **Et-PEN**, **Pr-PEN**, and **Hex-PEN** was achieved. Synthesized pentacene derivatives were characterized by UV-Vis, fluorescence, and ^{1}H-NMR spectroscopy. Since the photoconversion proceeded in films the properties of **Et-PDK** in films can be studied despite the instability of the pentacenes in solution. Irradiation-induced conversions in thin films were confirmed by IR and UV-vis spectra of the film, but the AFM measurement of **Et-PEN** film showed clear difference of crystallinity from non-substituted pentacene film. In the **PEN** film, the growth of pentacene-crystal pillars was clearly observed, however no crystals grew in the **Et-PEN** film. Such low aggregation nature of **Et-PEN** was also confirmed by fluorescence measurement of solid. Due to the low crystalinity, **Et-PEN** and **Pr-PEN** showed hole mobilities of 3.4×10^{-6} and 8.1×10^{-7} $cm^2 V^{-1} s^{-1}$, respectively, by SCLC measurement. Such moderate mobilities might be suitable for the hole transporting materials of organic EL.

Acknowledgments

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Experimental Section

General Methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded on JEOL JNM-AL300 or a JNM-ECX400 spectrometer using tetramethylsilane as an internal standard. ESI mass spectra were measured on JEOL JMS-MS T100LC spectrometer. Melting points were measured with a J-Science Group RFS-10. IR spectra were measured on a JASCO FT/IR-4200. UV-Vis absorption spectra were measured on a JASCO UV/VIS/NIR Spectrophotometer V-670. Fluorescence spectra and fluorescence quantum yields were measured on a Hamamatsu Absolute PL Quantum Yield Measurement System C9920-02. AFM images were measured on JEOL JSPM-5200. SCLC measurement was performed on the device of [ITO (200 nm)/ PEDOT:PSS (20 nm) / R-PEN / MoO_3 (5 nm) / Au (50nm)].

Photoreaction

Photoreactions in solutions were performed with a blue LED (StockerYale SpecBright™ Blue LED. wavelength: 470 nm, intensity: 2.5 mW/cm2) and were monitored on Ocean Optics DH-2000-BAL and HR4000. Photoreactions in thin films were performed with metal halide lamp (NPI, PCS-MH375RC, intensity: 5750 lm).

Synthesis

All solvents and chemicals were reagent grade quality, obtained commercially and used without further purification except as noted. For spectral measurements and photoreaction, spectral-grade toluene was used. Thin-layer chromatography (TLC) and column chromatography were performed on Art. 5554 (Merck KGaA) and Silica Gel 60N (Kanto Chemical Co.), respectively.

General Procedure for the Synthesis of 1,2-Dialkylbenzenes

1,2-Diethylbenzene 1a: Under argon atmosphere, alkylmagnesium bromide (0.88 mol in 240 ml Et_2O) was added dropwise to the stirred mixture of 1,2-dichlorobenzene (36.0 ml, 0.318 mol) and $Ni(dppp)Cl_2$ (1.0g) in *dry*-Et_2O (160 ml) at 0 ºC. The reaction was carefully allowed to warm to room temperature and stirred for 30 min. Then, the reaction was then heated to reflux and stirred for overnight. After cooling the reaction mixture to 0 ºC, 6M-HCl was added dropwise. Organic phase was diluted with Et_2O and was washed with H_2O, water and brine, dried over Na_2SO_4, then concentrated under reduced pressure to give the crude product. Crude product purified by distillation to afford the product. Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.19-7.12 (m, 4H), 2.66 (q, J = 7.6 Hz, 4H), 1.22 ppm (t, J = 7.6 Hz, 6H).

1,2-Dipropylbenzene 1b: Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.23-7.10 (m, 4H), 2.59 (t, J = 7.9 Hz, 4H), 1.75-1.55 (m, 4H), 0.99 ppm (t, J = 7.3 Hz, 6H).

1,2-Dihexylbenzene 1c: Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.16-7.09 (m, 4H), 1.62-1.52 (m, 4H), 1.41-1.28 (m, 12H), 0.89 ppm (t, J = 6.6 Hz, 6H).

General Procedure for the Synthesis of 1,2-Dibormo-4,5-dialkylbenzenes 2

Under argon atmosphere, Br_2 (72 g, 0.45 mol) was added dropwise to the stirred mixture of starting material (0.203 mol) and I_2 (2.6 g) in CH_2Cl_2 (240 ml) at 0 ºC. The reaction was allowed to warm to room temperature and stirred for overnight. Then, the reaction was quenched by *aq*-$NaHSO_3$. Organic phase was washed with *aq*-$NaHCO_3$, water and brine, dried over Na_2SO_4, then concentrated under reduced pressure to give the crude product. Crude product purified by distillation to afford the product.

1,2-Dibormo-4,5-diethylbenzene 2a: Colourless oil; ^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.38 (s, 2H), 2.57 (q, *J* = 7.5 Hz, 4H), 1.20 ppm (t, *J* = 7.5 Hz, 6H).

1,2-Dirbormo-4,5-dipropylbenzene 2b: Colourless oil; ^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.37 (s, 2H), 2.50 (t, *J* = 7.8 Hz, 4H), 1.65-1.50 (m, 4H), 0.97 ppm (t, *J* = 7.3 Hz, 6H).

1,2-Dirbormo-4,5-dihexylbenzene 2c: Colourless oil; ^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.36 (s, 2H), 2.51 (t, *J* = 7.9 Hz, 4H), 1.57-1.48 (m, 6H), 1.38-1.26 (m, 20H), 0.93-0.85 ppm (m, 10H).

General Procedure for the Synthesis of Diels-Alder adducts

Diels-Alder adduct 6a: Under argon atmosphere, *n*-BuLi (1.0 ml, 1.65 M in hexane) was added dropwise to the stirred mixture of starting material **2a** (0.476g, 1.62 mmol) and *exo*-methylene **4** (60.0 mg, 0.38 mmol) in *dry*-toluene (2.5 ml) at 0 ºC. The reaction was allowed to warm to room temperature and stirred for 3 h. Then, the reaction was cooled to 0 ºC and DDQ (0.20 g) was added at one-portion. After 15 min stirring, the reaction was quenched by addition of silica gel. The reaction mixture was filtrated off and washed with CHCl$_3$. The filtrates were concentrated under reduced pressure to give the crude product. Crude product was purified by column chromatography (CHCl$_3$: hexane = 1: 6) and recrystallization with hexane to afford the pure-product (23.7 mg, 0.057 mmol, 15%). White powder; m. p. 185.5-186.2 ºC; ^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.60 (s, 4H), 7.46 (s, 4H), 6.99 (m, 2H), 5.23 (m, 2H), 2.74 (q, *J* = 7.5 Hz, 8H), 1.25 ppm (t, *J* = 7.5 Hz, 12H); ^{13}C-NMR (75 MHz, CDCl$_3$): δ = 141.5, 140.1, 138.2, 130.3, 125.6, 120.3, 50.1, 25.4, 15.1 ppm; IR (ATR): *ν* = 3000, 2933, 2871, 899, 778 cm^{-1}; HRMS (EI): *m*/*z* calculated for $C_{32}H_{32}$ [M$^+$]: 416.2504, found for 416.2503.

Diels-Alder adduct 6b: Prepared as reported for **6a**, starting from **2b** and obtaining pure **6b** (20%) by recycle reverse-phase HPLC (COSMOSIL Cholester Packed Column, Acetonitrile, 4ml /min). White powder; m. p. 36.5 ºC; ^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.58 (s, 4H), 7.43 (s, 4H), 6.99 (m, 2H), 5.23 (m, 2H), 2.67 (t, *J* = 7.7 Hz, 8H), 1.63 (dq, *J* = 15.1, 7.5 Hz, 8H), 0.97 ppm (t, *J* = 7.3 Hz, 12H); ^{13}C-NMR (75 MHz, CDCl$_3$): δ = 141.5, 138.7, 138.2, 130.3, 126.7, 120.3, 50.2, 34.9, 24.2, 14.1 ppm; IR (ATR): *ν* = 2963, 2928, 2868, 1218, 1091, 910, 776 cm^{-1}; HRMS (ESI$^+$): *m*/*z* calculated for $C_{36}H_{40}Na$ (M$^+$+Na): 495.3027, found for 495.3026.

Diels-Alder adduct 6c: Prepared as reported for **6a**, starting from **2c** and obtaining pure **6c** (25%) by recycle reverse-phase HPLC (COSMOSIL Cholester Packed Column, Acetonitrile: THF = 4:1, 4ml /min). Colourless viscous oil; ^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.58 (s, 4H), 7.43 (s, 4H), 6.99 (m, 2H), 5.25-5.20 (m, 2H), 2.68 (t, *J* = 7.8 Hz, 8H), 1.61-1.54 (m, 8H), 1.39-1.27 (m, 24H), 0.88 ppm (t, *J* = 6.9 Hz, 13H); ^{13}C-NMR (75 MHz, CDCl$_3$): δ = 141.4, 139.0, 138.2, 130.3, 126.7, 120.3, 50.2, 32.8, 31.8, 31.2, 29.4, 22.6, 14.1 ppm; IR (ATR): *ν* = 2962, 2924, 2854, 1219, 904, 770 cm^{-1}; HRMS (ESI$^+$): *m*/*z* calculated for $C_{48}H_{64}Na$ (M$^+$+Na): 663.49057, found for 663.49028.

General Procedure for the Synthesis of Pentacene-diols

Tetraethylpentacene-diol 7a: Under argon atmosphere, OsO$_4$ (1.0 ml, 0.02 M in *t*-BuOH) was added to the stirred mixture of **6a** (50 mg, 0.12 mmol) and *N*-methylmorpholine *N*-oxide (NMO) (50 mg, 0.42 mmol) in acetone (2.0 ml) at room temperature. The reaction was stirred for 2 days. Then, the reaction was quenched by *aq*-Na$_2$S$_2$O$_4$. The reaction mixture was extracted with EtOAc. Combined organic extracts were washed with H$_2$O, water and brine, dried over Na$_2$SO$_4$, and concentrated under reduced pressure to give the crude product. Crude product was purified by column chromatography (CHCl$_3$) and GPC to afford the pure-product (31.9 mg, 0.071 mmol, 59%). White powder; m. p. 224.2-225.7 ºC; ^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.76 (s, 2H), 7.70 (s, 2H), 7.58 (s, 2H), 7.56 (s, 2H), 4.59-4.57 (t, 2H), 4.18-4.16 (m, 2H), 2.82-2.74 (m, 8H), 1.33-1.24 ppm (m, 12H); ^{13}C-NMR (75 MHz, CDCl$_3$): δ = 140.65, 140.59, 136.6, 135.0, 131.43, 131.41, 125.7, 124.35, 124.33, 122.35, 122.32, 68.5, 51.08, 51.05, 25.5, 15.0 ppm; IR (ATR): *ν* = 2964, 2940, 2873, 1217, 1057, 1013, 906, 766; HRMS (ESI$^+$): *m*/*z* calculated for $C_{32}H_{34}O_{32}$ (M$^+$): 450.2558, found for 450.2559.

Tetrapropylpentacene-diol 7b: Prepared as reported for **7a**, starting from **6b** (1.98 mmol) and obtaining pure **7b** (1.03 mmol, 52%). White powder; m. p. 79.3-80.5 ºC; ^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.73 (s, 2H), 7.67 (s, 2H), 7.55 (s, 2H), 7.53 (s, 2H), 4.58-4.56 (m, 2H), 4.23-4.12 (m, 2H), 2.75-2.66 (m, 8H), 1.72-1.59 (m, 8H), 1.05-0.96 ppm (m, 12H); ^{13}C-NMR (75 MHz, CDCl$_3$): δ = 139.32, 139.27, 136.6, 134.9, 131.38, 131.33, 126.8, 124.4, 122.4, 68.5, 51.1, 34.9, 24.18, 24.15, 14.2 ppm; IR (ATR): *ν* = 2956, 2930, 2863, 1216, 1057, 1071, 1012, 909, 773; HRMS (ESI$^+$): *m*/*z* calculated for $C_{32}H_{34}O_{32}Na$ (M$^+$+Na): 529.3082, found for 529.3082.

Tetrahexylpentacene-diol 7c: Prepared as reported for **7a**, starting from **6c** (1.93 mmol) and obtaining pure **7c** (0.78 mmol, 57%). Colourless viscous oil; ^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.72 (s, 2H), 7.66 (s, 2H), 7.54 (s, 2H), 7.52 (s, 2H), 4.57-4.54 (m, 2H), 4.18-4.12 (m, 2H), 2.72 (t, *J* = 7.7 Hz, 8H), 1.67-1.57 (m, 8H), 1.42-1.31 (m, 24H), 0.89 ppm (t, *J* = 6.7 Hz, 12H); ^{13}C-NMR (75 MHz, CDCl$_3$): δ = 139.57, 139.53, 136.5, 134.9, 131.38, 131.32, 126.7, 124.4, 122.3, 68.5, 51.1, 32.8, 31.8, 31.16, 31.12, 29.4, 22.6, 14.1 ppm; IR (ATR): *ν* = 2960, 2926, 2857, 1219, 1077, 1013, 906, 776; HRMS (ESI$^+$): *m*/*z* calculated for $C_{48}H_{66}O_2Na$ (M$^+$+Na): 697.4960, found for 697.4961.

General Procedure for the Synthesis of Diketone-Precursors

Et-PDK: Under argon atmosphere, TFAA (3.6 ml) was added to the stirred solution of *dry*-DMSO (3.6 ml) in *dry*-CH$_2$Cl$_2$ (25.5 ml) at -78 ºC over 10 min. After being stirred at same temperature for 15 min, **7a** (0.619 g, 1.374 mmol) in *dry*-CH$_2$Cl$_2$ (12.8 ml) was added to the reaction over 20 min. After 2.5 h stirring at -60 ºC, the reaction was cooled to -78 ºC and *N*,*N*-diisopropylethylamine (DIPEA) (12.8 ml) was added dropwise to the reaction. The reaction was stirred at -78º C for 1.5 h and then allowed to warm to room temperature over 30 min. 3 M-HCl was added to the reaction and the organic phase was extracted with CH$_2$Cl$_2$. The combined organic extracts were washed with water and brine, dried over Na$_2$SO$_4$, concentrated under reduced pressure to give the crude product. Crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$: hexane = 3:2 to 3:1) to afford the product as yellow powder (0.400 g, 0.895 mmol, 65 %). Orange powder; m. p. 270.3-271.4 ºC; ^{1}H-NMR (300 MHz, CDCl$_3$): δ = 7.85 (s, 4H), 7.61 (s, 4H), 5.24 (s, 2H), 2.80 (q, *J* = 7.5 Hz, 8H), 1.30 ppm (t, *J* = 7.5 Hz, 12H); ^{13}C-NMR (100 MHz, CDCl$_3$); δ = 185.6, 142.2, 132.6, 131.2, 126.0, 124.5, 60.6, 25.6, 14.9 ppm; IR (ATR): *ν* = 2973, 2933, 2873, 1750, 1731, 1223, 1112, 920, 773; HRMS (ESI$^+$): *m*/*z* calculated for $C_{32}H_{30}O_2$ (M$^+$): 446.2245, found for 446.2245.

Pr-PDK: Prepared as reported for **Et-PDK**, starting from **7b**

(0.790 mmol) and obtaining pure **Pr-PDK** (0.398 mmol, 50%). Orange powder; m. p. 101.1-102.0 ºC; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.82 (s, 4H), 7.59 (s, 4H), 5.23 (s, 2H), 2.73 (t, J = 7.8 Hz, 8H), 1.68 (dq, J = 15.1, 7.5 Hz, 8H), 1.01 ppm (t, J = 7.3 Hz, 12H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 185.7, 140.8, 132.5, 131.2, 127.1, 124.5, 60.6, 35.0, 24.1, 14.3 ppm; IR (ATR): v = 2963, 2933, 2876, 1750, 1731, 1219, 1106, 913, 773; HRMS (ESI$^+$): m/z calculated for $C_{36}H_{38}O_2Na$ (M^++Na): 525.2769, found for 525.2769.

Hex-PDK: Prepared as reported for **Et-PDK**, starting from **7c** (1.01 mmol) and obtaining pure **Hex-PDK** (0.506 mmol, 50%). Orange viscous oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 4H), 7.58 (s, 4H), 5.23 (s, 2H), 2.74 (t, J = 7.8 Hz, 8H), 1.64 (dt, J = 15.2, 7.6 Hz, 8H), 1.42-1.31 (m, 24H), 0.89 ppm (t, J = 6.9 Hz, 12H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 185.7, 141.1, 132.5, 131.1, 127.0, 124.5, 60.6, 32.9, 31.8, 31.0, 29.5, 22.7, 14.2 ppm; IR (ATR): v = 2949, 2927, 2857, 1750, 1732, 1216, 911, 776; HRMS (ESI$^+$): m/z calculated for $C_{48}H_{62}O_2Na$ (M^++Na): 693.4647, found for 693.4647.

Notes and references

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