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Synthesis and optical reactivity of 6,13-α-diketoprecursors of 2,3,9,10-tetraalkylpentacenes in solution, films 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 synthesis methods[4] have been reported while the study of the synthesis of pentacene derivatives is still limited due to pentacene's instability and insolubility. We have previously reported 6,13-α-diketo pentacene (**PDK**), which can be converted to the parent pentacene by photo-induced decarbonylation-reaction[5] (Strating–Zwanenberg reaction) in solution or thin film state (Fig. 1).[6] Our group reported the fabrication of pentacene-based OFETs using **PDK** with 0.86 cm^2 V^{-1} s^{-1} of hole mobility in a 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 a 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 synthesis 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 good candidates for the purpose, since the hole mobilities can be controlled by the chain length of the substituents and crystallinities. However the lack of a general synthesis method of 2,3,9,10-tetraalkylated pentacenes,[11] due to the instability at 6,13-positions, prohibits its wider applications.

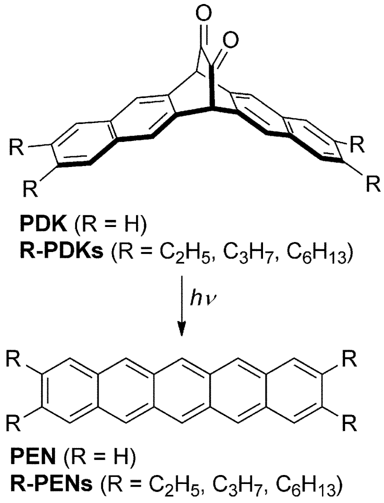

Fig. 1 Photochemical synthesis of **PEN** and **R-PENs** from **PDKs**.

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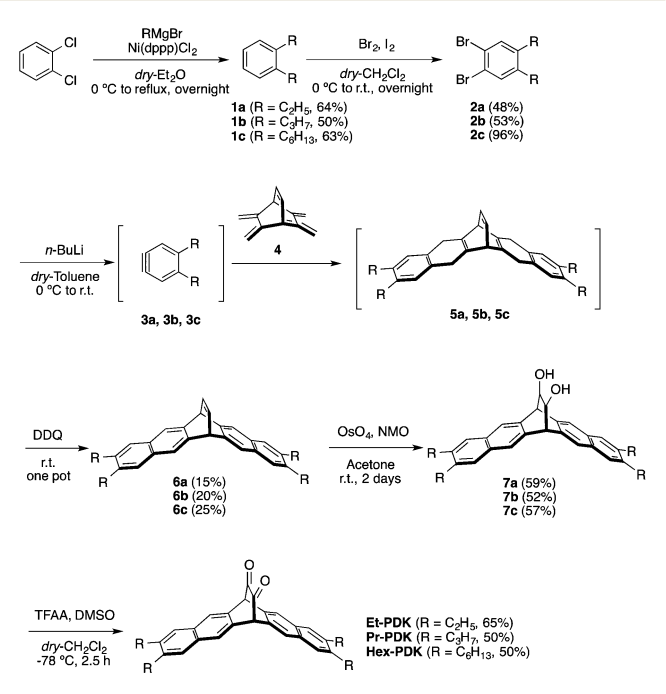
† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of the compounds, UV-vis absorption spectra during the photoreaction, IR spectra of the film, and hole mobilities of acenes measured by the SCLC method. See DOI: 10.1039/c3tc31824a

Bao and co-workers have reported the synthesis and OFET application of 2,3,9,10-tetramethylpentacenes[12] while synthesis methods applied by them were inadequate for the synthesis of other 2,3,9,10-tetraalkylpentacenes due to the inaccessibility of 2,3,9,10-tetraalkylpentacenequinones. In order to establish the general synthesis 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 Fig. 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.

Results and discussion

Synthesis

Synthesis of **Et-PDK**, **Pr-PDK** and **Hex-PDK** is shown in Scheme 1. Kumada-coupling reaction of alkyl magnesium bromides with 1,2-dichlorobenzene under a Ni catalyst afforded 1,2-dialkylbenzenes **1**.[13] Bromination of **1** afforded 1,2-dialkyl-4,5-dibromobenzenes **2**. Modern precursors for arynes 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**, which 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 to be almost 35% by HPLC analysis. The high reactivity of aryne **3a** attributed to the low purity. Pure **6a** was obtained by multiple-recrystallization with 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 as high as >60 mg ml^{-1} 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 R-PDKs.

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

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 an Ar atmosphere is shown in Fig. 3 and ESI, Fig. S1† for **Et-PDK**. Before irradiation, only the broad n–π* peak at around 467 nm was observed. As the intensity of this peak decreased gradually, the intensities of the new peaks at 580, 537, 500, 468, 432 and 407 nm assigned to **Et-PEN** 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 changed from yellow to purple. The absorbance of pentacene became constant after 40 min irradiation. The solubility of **Et-PEN** is improved compared to the parent pentacene, thus precipitation of **Et-PEN** during photoreaction was not

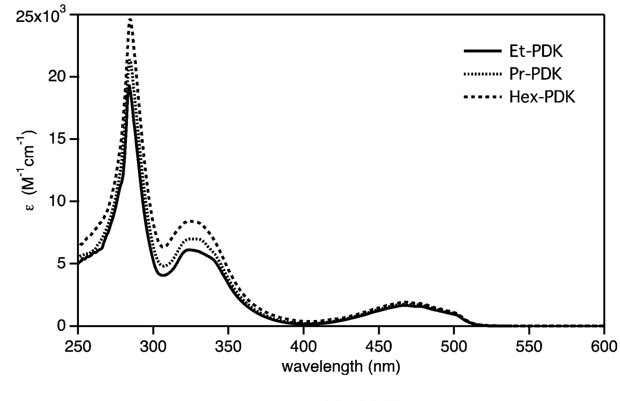


Fig. 2 UV-vis absorption spectra of R-PDKs in toluene.

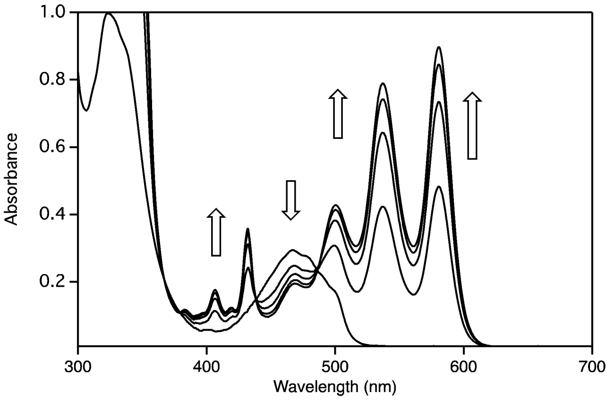


Fig. 3 Photoreaction of **Et-PDK** in toluene under an Ar atmosphere. The UV-vis absorption spectra were recorded at 0, 10, 20, 30, and 40 min during irradiation.

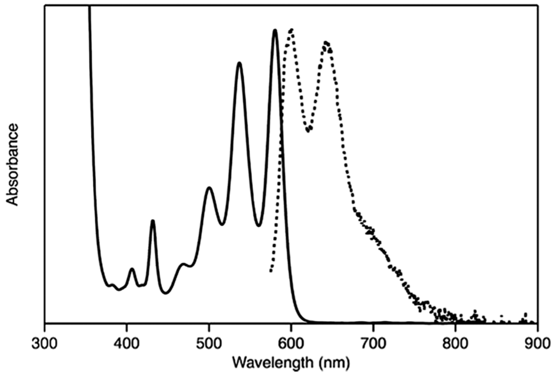


Fig. 5 Absorption (black line) and fluorescence (black dotted-line, excited at 537 nm) spectra of **Et-PEN** in toluene.

observed. Photo-conversions of **Pr-PDK** to **Pr-PEN** or **Hex-PDK** to **Hex-PEN** are shown in the ESI, Fig. S2 or S3.† In both cases, the conversion proceeded smoothly similar to the case of **Et-PDK**. And also precipitation of the formed pentacenes **Pr-PEN** or **Hex-PEN** was not observed.

The photoreactions were further monitored by ^{1}H-NMR spectroscopy. The changes in the NMR spectra during photo-irradiation of **Et-PDK** under an Ar atmosphere is shown in Fig. 4. **Et-PDK** was placed in degassed $CDCl_3$ and was irradiated with the blue LED under an Ar atmosphere. During the photo-reaction, 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 stable enough for isolation. The colour of **Et-PEN** solution was bleached in 3 min under air.

Absorption and fluorescence spectra of the obtained **Et-PEN**, **Pr-PEN** and **Hex-PEN** in toluene are shown in Fig. 5, ESI Fig. S4 and S5.† Compared to the parent pentacene, red-shift of absorption was 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]

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^{-1}) to washed glass substrates. Photoreactions were conducted under an Ar atmosphere. Conversion was monitored by IR measurement of films, in which the characteristic absorption of the carbonyl moiety at 1728 and 1745 cm^{-1} had completely disappeared after 90 min of photo-conversion (Fig. 6). The change of UV-vis spectra of **Et-PDK** in the thin film under an Ar atmosphere is shown in Fig. 7. Before irradiation, only a broad n–π* peak at around 400–525 nm was observed. Absorption of **Et-PDK** completely disappeared and new absorption that is characteristic of **Et-PEN** at around 400–625 nm 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 the ESI, Fig. S6–S9.† The absorption spectrum of **Et-PEN** in the thin film is significantly different from that of **PEN** (Fig. 7). In the case of **Et-PEN**, the absorption spectrum of the thin film is similar to that in the solution. In the case of the **PEN** film, absorption around 600–700 nm, which originates from aggregation of **PEN**, was observed. This

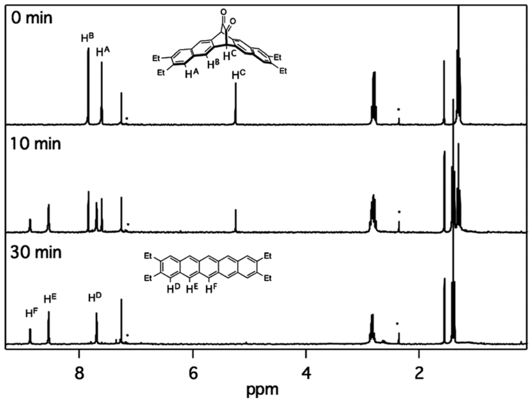


Fig. 4 Change of ^{1}H-NMR spectrum during photoreaction of **Et-PDK** in $CDCl_3$ under an Ar atmosphere. * toluene.

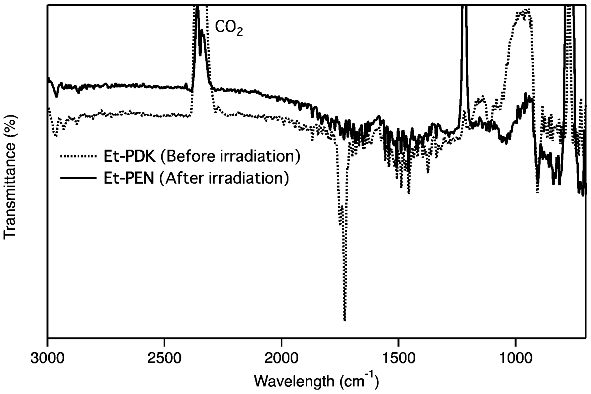


Fig. 6 IR spectra before and after photoreaction of **Et-PDK** in the thin film.

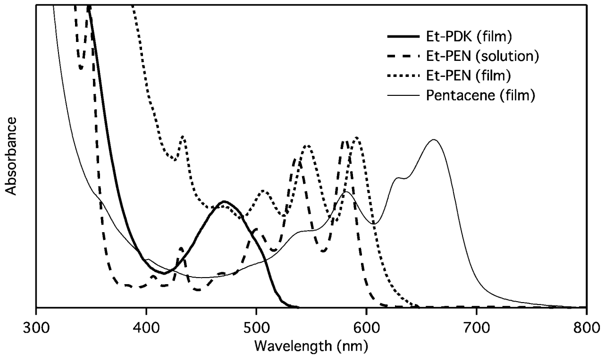


Fig. 7 Absorption spectra of Et-PEN in solution or thin film and absorption of PEN in the thin film.

difference indicates the weak intermolecular interaction of **Et-PEN** in the film compared with **PEN**.

The difference of aggregation nature was also measured by fluorescence from solid **Et-PEN** or **PEN** (Fig. 8). Changes of fluorescence during photo-conversion of **Et-PDK** or **PDK** to **Et-PEN** or **PEN** in the solid state were monitored. The 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 originates from the aggregated pentacene, during photo-conversion. This indicates that non-substituted pentacene molecules have strong π–π stacking in crystals, but ethyl groups disrupt the aggregation due to a π–π interaction between molecules. A difference of π–π stacking nature is remarkably observed in the colour of crystals as shown in Fig. 8. **Et-PEN** is a red crystal while **PEN** is a dark-blue crystal due to strong interaction, depending on the π–π interaction between molecules.

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

The mobilities of **Et-PEN** and **Pr-PEN** prepared from the precursors by irradiation using a metal halide lamp were measured by space-charge-limited current (SCLC) measurements (ESI, Fig. 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 the SCLC method. Under the same irradiation conditions, the **PEN** film

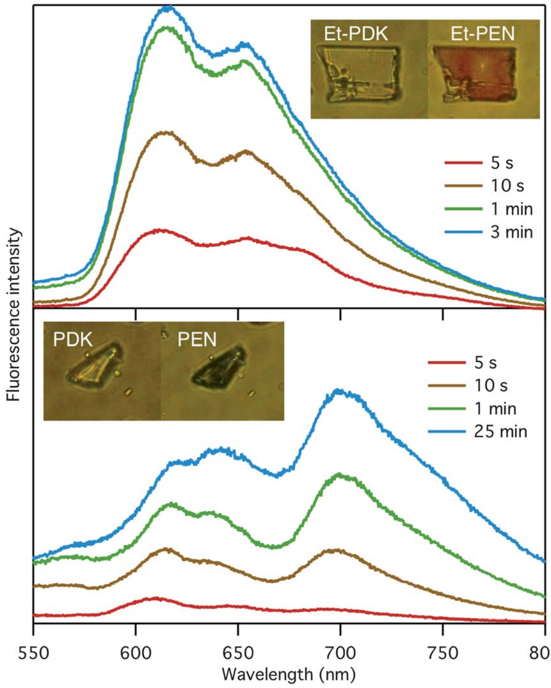


Fig. 8 Change of fluorescence in crystals of Et-PDK (top) and PDK (bottom) during the photoconversion to Et-PEN and PEN, respectively. Inset: Pictures of crystals of Et-PDK and PDK before and after the photoirradiation.

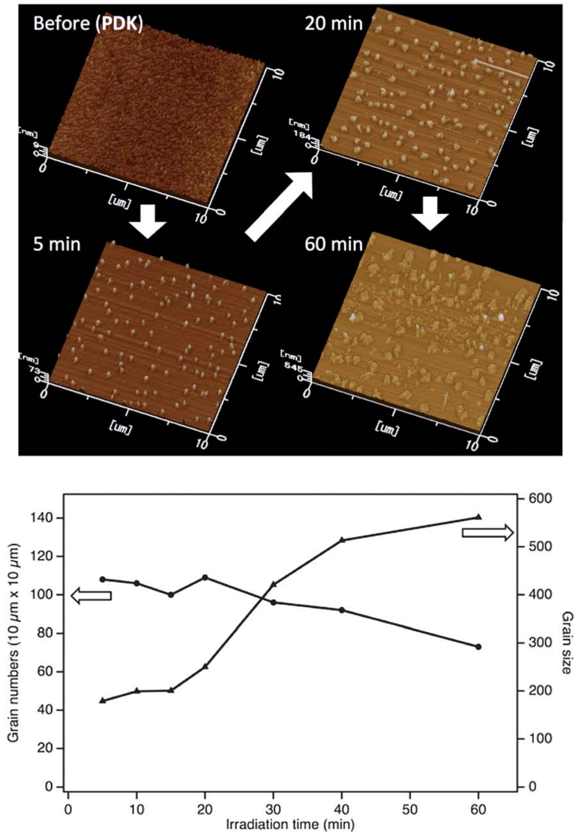


Fig. 9 Changes of AFM images (10 μm × 10 μm) during photoreaction of PDK to PEN (top) and the change of grain numbers (circles) and size (triangles) during photoreaction of PDK to PEN (bottom).

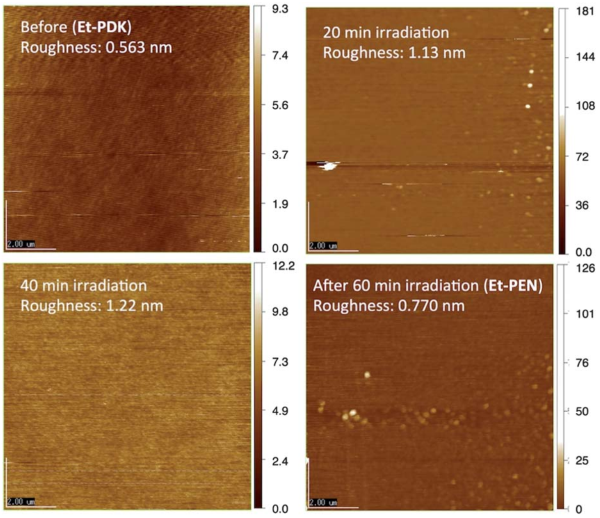


Fig. 10 Changes of AFM images (10 μm × 10 μm) during photoreaction of **Et-PDK** to **Et-PEN**.

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 the carrier mobility of hole-transporting materials is higher than that of electron transporting materials,[17] but the carrier balance between hole and electron transporting abilities is important for the organic electroluminescence (EL) materials. Thus **Et-PEN** and **Pr-PEN** can be good candidates for 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. The 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 the **Et-PEN** film showed a clear difference of crystallinity from the 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 a low aggregation nature of **Et-PEN** was also confirmed by fluorescence measurement of the solid. Due to the low crystallinity, **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.

Experimental section

General methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL JNM-AL300 or a JNM-ECX400 spectrometer using tetramethylsilane as an internal standard. ESI mass spectra were recorded on a JEOL JMS-MS T100LC spectrometer. Melting points were measured with a J-Science Group RFS-10. IR spectra were recorded on a JASCO FT/IR-4200. UV-vis absorption spectra were recorded on a JASCO UV/VIS/NIR Spectrophotometer V-670. Fluorescence spectra and fluorescence quantum yields were obtained on a Hamamatsu Absolute PL Quantum Yield Measurement System C9920-02. AFM images were taken on a 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 (50 nm)].

Photoreaction

Photoreactions in solutions were performed with a blue LED (StockerYale SpecBright™ Blue LED; wavelength: 470 nm, intensity: 2.5 mW cm^{-2}) and were monitored on an Ocean Optics DH-2000-BAL and HR4000. Photoreactions in thin films were performed with a metal halide lamp (NPI, PCS-MH375RC, intensity: 5750 lm).

Synthesis

All solvents and chemicals were of 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 an 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 an argon atmosphere, alkyl magnesium 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 $Ni(dppp)Cl_2$ (1.0 g) in dry-Et_2O (160 ml) at 0 °C. The reaction was carefully allowed to warm to room temperature and stirred for 30 min. Then, the reaction was heated to reflux and stirred overnight. After cooling the reaction mixture to 0 °C, 6 M-HCl was added dropwise. The organic phase was diluted with Et_2O, washed with H_2O, water and brine, dried over Na_2SO_4, and then concentrated under reduced pressure to give the crude product. The crude product was purified by distillation to afford the product. Colourless oil; ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 7.19–7.12$ (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, $CDCl_3$): $\delta = 7.23–7.10$ (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, $CDCl_3$): $\delta = 7.16–7.09$ (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 an 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 °C. The reaction was allowed to warm to room temperature and stirred overnight. Then, the reaction was quenched with aq-$NaHSO_3$. The organic phase was washed with aq-$NaHCO_3$, water and brine, dried over Na_2SO_4, and then concentrated under reduced pressure to give the crude product. The crude product was 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 an argon atmosphere, *n*-BuLi (1.0 ml, 1.65 M in hexane) was added dropwise to the stirred mixture of starting material **2a** (0.476 g, 1.62 mmol) and *exo*-methylene **4** (60.0 mg, 0.38 mmol) in dry-toluene (2.5 ml) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 3 h. Then, the reaction was cooled to 0 °C 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 filtered off and washed with $CHCl_3$. The filtrates were concentrated under reduced pressure to give the crude product. The 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; mp 185.5–186.2 °C; ^{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: 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, 4 ml min^{-1}). White powder; mp 36.5 °C; ^{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: 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, 4 ml min^{-1}). 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: 663.49028.

General procedure for the synthesis of pentacene-diols

Tetraethylpentacene-diol 7a. Under an 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 solution was stirred for 2 days. Then, the reaction was quenched with aq-$Na_2S_2O_4$. The reaction mixture was extracted with EtOAc. Combined organic extracts were washed with H_2O, water and brine, dried over Na_2SO_4, and concentrated under reduced pressure to give the crude product. The 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; mp 224.2–225.7 °C; ^{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: 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; mp 79.3–80.5 °C; ^{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: 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: 697.4961.

General procedure for the synthesis of diketone-precursors

Et-PDK. Under an argon atmosphere, TFAA (3.6 ml) was added to the stirred solution of dry-DMSO (3.6 ml) in dry-CH_2Cl_2 (25.5 ml) at −78 °C over 10 min. After being stirred at the same temperature for 15 min, **7a** (0.619 g, 1.374 mmol) in dry-CH_2Cl_2 (12.8 ml) was added to the reaction mixture over 20 min. After 2.5 h stirring at −60 °C, the reaction mixture was cooled to −78 °C and *N*,*N*-diisopropylethylamine (DIPEA) (12.8 ml) was added dropwise to the reaction mixture. The reaction mixture was stirred at −78 °C for 1.5 h and then allowed to warm to room temperature over 30 min. 3 M HCl was added to the reaction mixture and the organic phase was extracted with CH_2Cl_2. The combined organic extracts were washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure to give the crude product. The crude product was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 3 : 2 to 3 : 1) to afford the product as yellow powder (0.400 g, 0.895 mmol, 65%). Orange powder; mp 270.3–271.4 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 7.85$ (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, $CDCl_3$); $\delta = 185.6$, 142.2, 132.6, 131.2, 126.0, 124.5, 60.6, 25.6, 14.9 ppm; IR (ATR): $\nu = 2973$, 2933, 2873, 1750, 1731, 1223, 1112, 920, 773; HRMS (ESI$^+$): *m*/*z* calculated for $C_{32}H_{30}O_2$ (M^+): 446.2245, found: 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; mp 101.1–102.0 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 7.82$ (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, $CDCl_3$): $\delta = 185.7$, 140.8, 132.5, 131.2, 127.1, 124.5, 60.6, 35.0, 24.1, 14.3 ppm; IR (ATR): $\nu = 2963$, 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: 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, $CDCl_3$): $\delta = 7.82$ (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, $CDCl_3$): $\delta = 185.7$, 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): $\nu = 2949$, 2927, 2857, 1750, 1732, 1216, 911, 776; HRMS (ESI$^+$): *m*/*z* calculated for $C_{48}H_{62}O_2Na$ (M^+ + Na): 693.4647, found: 693.4647.

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