

Electron-transporting PAHs with dual perylenediimides: syntheses and semiconductive characterizations†

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Zhuoran Zhang, Ting Lei, Qifan Yan, Jian Pei* and Dahui Zhao*

An effective method was developed to prepare triphenyleno[1,2,3,4-*ghi*]-perylenediimide derivatives, via ICl-induced annulation, dehalogenation, followed by photocyclization. A perylenediimide (PDI) dimer featuring a terphenyl bisethynylene linker was thereby transformed into a benzo[*k*]tetraphene fused with two benzoperylenediimides. These PDI derivatives exhibited electron mobility up to $0.079\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ in solution-processed thin film transistors.

Solution-processed organic field-effect transistors (OFETs) have attracted tremendous interest due to the appealing merits of low cost, large flexible devices.¹ In addition to charge transporting ability, the film-forming property of active materials is another critical factor governing the device performance of solution-processed OFETs. Amorphous films with optimal homogeneity are more often attained from conjugated polymers.² Compared with the polymeric materials, small organic molecules bestow superior charge carrier mobility by virtue of the more ordered molecular packing structures. Additionally, small molecules are easier to purify, thus offering more stable device performance and reproducible production quality. However, the evident crystallization propensity of small molecules typically curtails the homogeneity of solution-processed films, which greatly limits their performance in OFETs.³ Thus, developing organic molecules possessing properly balanced tendencies to form ordered molecular packing structures and to achieve thin films with long-range homogeneity upon solution processing is a pivotal issue for acquiring high-performance OFET materials. Large polycyclic aromatic hydrocarbons (PAHs) with flexible side chains at the periphery are promising candidates to manifest such properties.

A low LUMO level is an indispensable requisite for air-stable n-channel semiconductive materials. Due to its electron-deficient characteristic, PDI emerged as a useful structure in designing new electron-transporting organic semiconductors.⁴

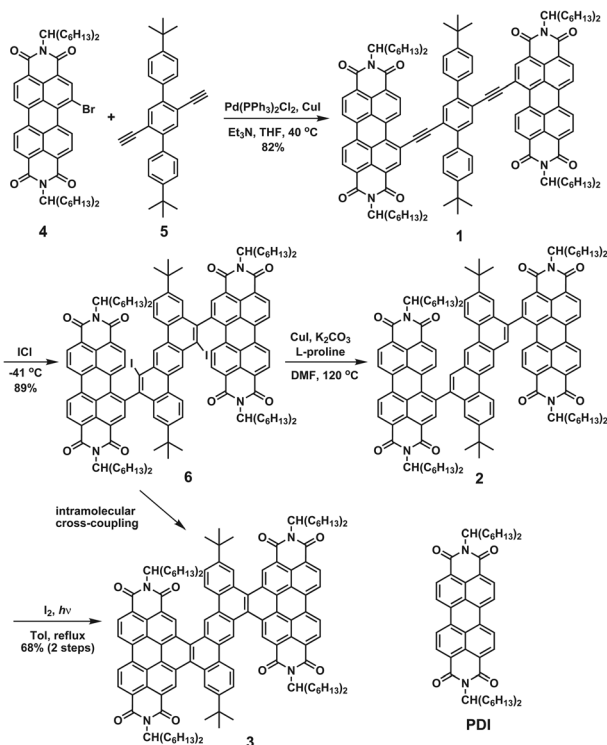
Various PDI derivatives were synthesized exhibiting attractive optical and electronic properties.^{5–8} PAH derivatives comprising multiple interconnected PDI units with a low-lying LUMO are promising high-performance n-type semiconductors.^{9,10} The preparation of relevant molecules generally involves coupling PDI units with various conjugative linkages.^{5–7} To obtain polycyclic skeletons, efficient ligation and fusion protocols, particularly those applicable to electron-deficient aromatic substrates, are necessary. Iodonium-induced cyclization, developed by Swager *et al.* and Larock *et al.*, is an effective annulation protocol, producing iodo-substituted polycyclic molecules.^{11,12} Recently, the scope of the ICl-annulation protocol was further expanded to electron-deficient substrates in our laboratory, establishing a facile synthetic approach to achieving larger PAHs from PDI.¹³

We now report the syntheses of a series of new electron-deficient PAHs 1–3, which are all obtained using PDI as the main modular unit (Scheme 1). Compound 1 is a PDI dimer featuring terphenyl bisethynylene as the linker to join two PDI units. PAH 2, a different PDI dimer having a benzo[*k*]tetraphene linker, is obtained when ICl-induced annulation is carried out on 1, followed by dehalogenation. Subsequently, photocyclization of 2 accomplishes a large PAH 3, which comprises a central benzo[*k*]tetraphene structure fused with two benzo[*ghi*]perylenediimide moieties. The good solubility and film-forming property displayed by all three molecules allow the fabrication of OFETs through solution processing. Molecules 1 and 3 afford electron mobility up to 0.079 and $0.014\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, respectively. The results demonstrate the great potential of synthesized molecules to serve as n-type semiconductors. Moreover, the synthetic methodologies developed herein provide effective tools for making new, various electron-deficient PAHs.

Specifically, molecule 1 is a PAH containing a terphenyl group bearing two PDI units tethered to the central phenyl ring through acetylene spacers. The molecule was synthesized *via* double Sonogashira cross-coupling of bromo-substituted PDI 4 with di(4-*tert*-butylphenyl)diethynylbenzene 5¹⁴ (Scheme 1). Compound 1 was designed to undergo ICl-induced annulation subsequently. According to previous studies, addition of ICl to the triple bonds in 1 could possibly proceed along two different cyclization pathways.^{12,13} That is, the annulation could take place with either the terphenyl or PDI groups. Since *tert*-butylphenyl was much more electron-rich and reactive

Beijing National Laboratory for Molecular Sciences, the Key Laboratories of Polymer Chemistry and Physics and of Bioorganic Chemistry and Molecular Engineering of the Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China. E-mail: dhzhao@pku.edu.cn, jianpei@pku.edu.cn; Fax: +8610 62751708; Tel: +8610 62753973

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Scheme 1 Syntheses of studied compounds.

toward electrophilic addition than electron-deficient PDI, we expected that double cyclization on the terphenyl moiety could be achieved selectively by controlling the reaction temperature. After several trials at different temperatures, molecule **6** was found to be most efficiently generated at about -40 °C, by treating **1** with two equivalents of ICl, with an isolated yield of 89%. No significant by-product was observed under such conditions. In the literature, the ICl annulation could be triggered at a much lower temperature of -78 °C for alternative substrates.¹⁵ A higher temperature was required for the reaction of compound **1**, most likely because the C \equiv C triple bonds in **1** were deactivated by the electron-withdrawing PDI units. Whereas when this reaction was carried out at higher temperatures, e.g. near room temperature, evident side reactions were found to occur.

At first we attempted to obtain the final product **3** directly from **6** via intramolecular Ullmann-type C–H transformation or Heck coupling reaction.^{7,16–19} Unfortunately, no direct cyclization product was observed. Instead, reductive dehalogenation occurred under the applied conditions and afforded product **2** (Scheme 1).²⁰ The ¹H NMR spectrum of the resultant reaction mixture revealed that two major products with nearly identical chemical structures were generated with similar quantities. Nonetheless, only one of them (**2a**) was isolatable, the structure of which was fully characterized and confirmed. The other product, **2b**, which was of slightly lower polarity as shown by thin layer chromatography, was unstable under ambient conditions. The two molecules, **2a** and **2b**, were suspected to be stereoisomers of each other according to their very similar ¹H NMR spectra. This hypothesis was further corroborated by the observation that the unstable product **2b** was partially converted to the stable product **2a** upon heating at 120 °C in DMF under a nitrogen atmosphere. The isomerism of **2a** and **2b** is speculated to result from the severe

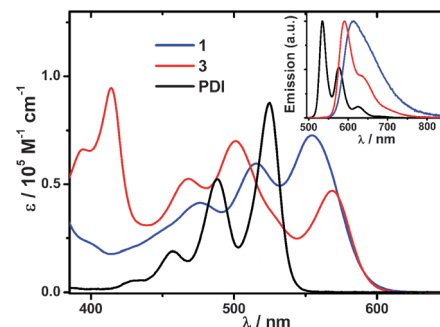


Fig. 1 UV-Vis absorption (in CH₂Cl₂) and emission spectra (inset, in CHCl₃) of **1** and **3**, in comparison with those of PDI.

steric congestion near the bay region of the PDI groups (see Fig. S11 (ESI[†]) for DFT calculated structures).

After screening a set of different conditions, compound **3** was eventually attained by exposing a solution of **2a** to UV-light irradiation at room temperature. The conversion of this photocyclization process was about 60%. Nonetheless, no such cyclization reaction was observed for **2b** under the same conditions. In light of the fact that isomer **2b** could be converted to **2a** at elevated temperature under oxygen-free conditions, we designed an experiment to optimize the overall reaction yield by combining the isomerization and photocyclization steps in one pot. Specifically, a mixture of **2a** and **2b** was irradiated by UV light in refluxed toluene under an N₂ atmosphere. This strategy effectively improved the total yield from 18% to 68% for the two steps.

Compounds **1** and **3** both showed broad absorptions spanning nearly the entire visible region. The absorption onsets of **1** and **3** shifted bathochromically by ca. 50 nm compared to that of PDI (Fig. 1), resulting from their extended π -skeletons. Molecule **3** manifested a band shape similar to that of coronenediimide,^{13,21} consistent with its cyclized structure. The absorption maximum λ_{max} of **2a** did not differ significantly from that of PDI (Fig. S1, ESI[†]), but the band shape became much broadened and featureless. This reflects the sterically encumbered nature of **2a**. Compounds **1** and **3** displayed relatively high emission quantum yields of 0.66 and 0.72, with emission maxima λ_{max} of 614 and 591 nm, respectively. Molecule **3** displayed a smaller Stokes shift and more pronounced vibrational structures, in agreement with its more rigid π -scaffold. The cyclic voltammograms (CV) of **1** and **3** both exhibited two reversible reduction waves (Fig. S3 and S4, ESI[†]). The half-wave reduction potentials were determined to be $-1.08/-1.30$ V for **1** and $-1.26/-1.48$ V for **3** (Table 1).

OTFT devices were then fabricated using these newly synthesized molecules, with a top-gate/bottom-contact configuration. The semi-conductive layer was deposited by spin-casting dichlorobenzene solutions of respective compounds (at 8 mg mL⁻¹) on patterned

Table 1 Photophysical, electrochemical, and FMO data of **1** and **3**

	$\lambda_{\text{max}}/\text{nm}$	E_g^a/eV	E_{r1}^b/V	E_{r2}^b/V	LUMO ^c /eV	HOMO ^d /eV
PDI	525	2.30	-1.05	—	-3.74	-6.04
1	557	2.13	-1.08	-1.30	-3.72	-5.85
3	569	2.10	-1.26	-1.48	-3.54	-5.64

^a Band gap calculated from the absorption onset in optical spectra. ^b The 1st and 2nd half-wave reductive potentials (vs. Fc/Fc⁺) measured by CV in CH₂Cl₂. ^c LUMO energy levels calculated from E_{r1} . ^d HOMO energy levels estimated based on CV-determined LUMO and optical band gaps.

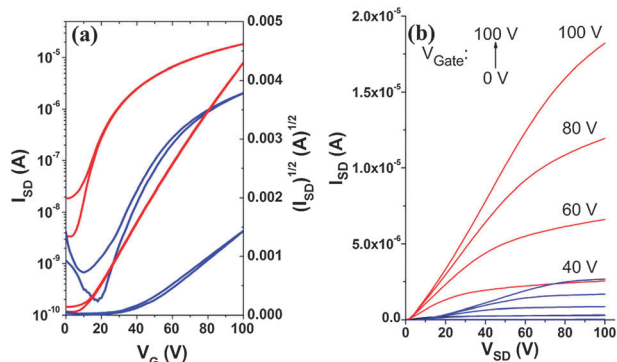


Fig. 2 The transfer (a, $V_{SD} = 100$ V) and output characteristics (b) of **1** (red) and **3** (blue), measured from OFET devices ($L = 5$ μm , $W = 100$ μm) fabricated with CYTOP on the top (capacitance $C_i = 3.7$ nF cm^{-2}).

Au(source/drain electrodes)/SiO₂/Si substrates in the glove box. After thermal annealing the obtained organic films at 160 °C for about 10 min, a poly(perfluorobutenylvinylether) CYTOP solution was spin-coated on top of the organic films to serve as the dielectric layer (ca. 500 nm thick). Then an aluminum layer was thermally evaporated to act as the gate electrode. All devices were tested under ambient conditions. The highest electron mobility detected for molecule **1** reached 0.079 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ (Fig. 2). Compound **3** exhibited an electron mobility of 0.014 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, whereas **2a** possessed a much lower electron mobility of $5.7 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$.

Subsequently, thin-film morphologies of **1–3** were characterized. The film preparation conditions were identical to those applied for OFET fabrication. The AFM images confirmed the amorphous nature of all three examined materials, as no obvious crystalline domains were observed (Fig. 3). However, disparate smoothness was observed for different films, which well correlated with their respective semiconductive performance. Specifically, molecules **1** and **3** both manifested relatively smooth surfaces with minimum roughness, but the homogeneity of the former was still superior to that of the latter. In contrast, an evidently more bumpy and rough surface was displayed by molecule **2a**, explaining its less optimal transistor performance.

While all three molecules exhibited sufficient solubility allowing for solution processing of OFETs, the differences in molecular structure and film morphology were evident. The significant steric encumbrance in **2** apparently hindered effective intermolecular stacking of the molecule. Although compound **3** possessed a larger PAH skeleton, the non-planar conformation likely curtailed its ability to form long-range ordered structures. Compound **1**, possessing properly balanced structural rigidity (pivotal for π -conjugation and molecular stacking) and flexibility (hampering large-scale

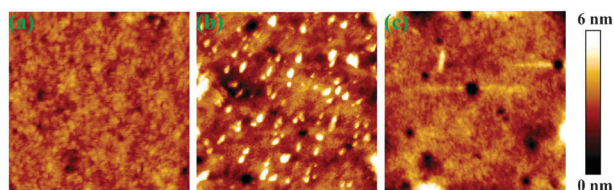


Fig. 3 AFM height images ($1 \mu\text{m} \times 1 \mu\text{m}$) of thin films of compounds **1–3** after thermal annealing at 160 °C: (a) **1**, (b) **2a**, (c) **3**.

crystallization), along with a lower LUMO, exhibited the most desirable film morphology and semiconductive capacity.

In conclusion, a new synthetic protocol was developed for preparing triphenyleno[1,2,3,4-*ghi*]perylene-3,4,9,10-tetracarboxylic diimide derivatives, involving a sequence of ICl-induced cyclization, dehalogenation, and photocyclization reactions. Using this method, PAH **3** featuring a benzo[*k*]tetraphene moiety fused with two benzoperylene-3,4,9,10-tetracarboxylic diimides was prepared from terphenyl bisethynylene PDI dimer **1**. The electron-deficient characteristics of these PDI derivatives, in combination with the optimal film-forming ability, entailed desirable electron-transporting performance in solution-processed OFET devices. Electron mobilities up to 0.079 and 0.014 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ were achieved for **1** and **3**, respectively. The work presented herein has offered both new structures and potent synthetic tools for developing large, electron-deficient PAH-based electron-transporting semiconductors.

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