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Synthesis and Characterization of Polysubstituted Dibenzopyrenes as Charge-Transporting Materials

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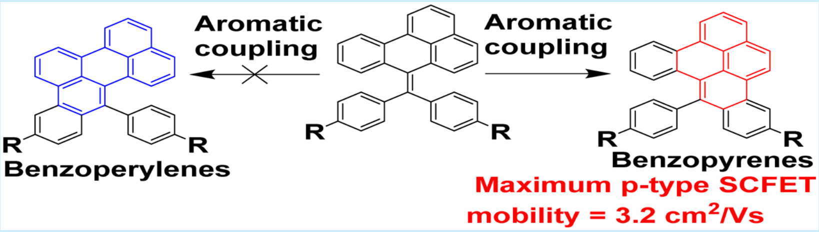
Supporting Information



ABSTRACT: A new class of benzopyrene-based semiconducting molecules is prepared and characterized. A four-step protocol involving Suzuki coupling and aromatic dehydrogenation reactions renders the new unsymmetrical framework. Introduction of various substituents at the dibenzopyrene framework modulates mainly the optoelectronic properties rather than the packing motif. Single-crystal field-effect transistors fabricated from these materials show a mobility ranging from 0.7 to 3.2 $cm^2/(V\ s)$. The highest mobility, 3.2 $cm^2/(V\ s)$, with an on/off ratio of 10^4–10^5 was achieved for 11-methoxy-8-(4-methoxyphenyl)dibenzo[*a*,*e*]pyrene.

The new era of flexible electronics is right around the corner, presumably due to the fast development of various organic electronic materials and devices. In these advancements, organic field-effect transistors (OFETs) are a critical component in most of the organic electronic devices.[1] Tremendous effort has been devoted to the search for high-performance field-effect transistor materials.[2] Much progress has been made in the quest for suitable organic materials for transistor applications, and general guidelines for molecular design have been proposed.[3] That is, a higher electronic coupling between neighboring molecules in the conducting channel as well as a lower reorganization energy for the molecule involved will be favored for charge transport in molecular materials. Toward that aim, extended conjugation and rigid aromatics are being explored. However, a clear structure–property correlation is elusive due to the complicated interplay of film morphology, molecular packing, as well as electron distribution in the frontier molecular orbitals, all of which affect the electronic coupling between neighboring molecules.[4] More systematic studies with new materials are needed to unravel the correlation between structure and properties.[5]

Polyfused aromatic hydrocarbons are widely used as transistor materials.[6] An extensive conjugate π-system and the π–π stacking interactions impart semiconducting properties to these molecules. For the same framework of molecules, the crystal packing as well as the molecular orbital levels may be perturbed by substitution with electron-donating or accepting functional groups of different sizes. As compared to symmetrical polyaromatics, the crystal packing for unsymmetrical ones are less predictable, so that a rational design of molecules with high π–π stacking interaction is difficult.[7] A post analysis of the single-crystal structure may sometimes provide a clue to the property observed.

After the seminal reports of Clar and Schiedt on unsymmetrical dibenzopyrene,[8] its derivatives or even the parent framework was seldom studied for general transistor applications. Recently, thin-film OFETs of pyrene-based materials were examined, giving some promising results.[9] These facts prompt us to design and synthesize a new series of benzopyrene-embedded derivatives carrying various functional groups and examine their potential in OFET application. The electronic properties and field-effect performances of selected derivatives show good potential for these molecules to be used in transistor applications.

The synthetic plan of the derivatives is illustrated in Schemes 1 and S1 (SI). The methodology used for the selected benzopyrenes is a simple and four-step chemical conversion of anthracene[10] to the target polycyclic aromatic hydrocarbons. The aryl olefins (**4**–**10**) were obtained from dichloro olefin (**3**) and different aryl boronic acids via a Suzuki coupling reaction in excellent yields Schemes 1 and S1. To synthesize the final benzopyrene derivatives (**DBPs**), the aryl olefins were subjected to iodine-mediated (1.2 equiv of iodine) aromatic dehydrogenation reaction by exposing the reaction mixture to UV light for 6–24 h.

The iodine-mediated aromatic coupling exhibited high selectivity for the dehydrogenation reaction with respect to the ring that was annulated, presumably due to the more stable

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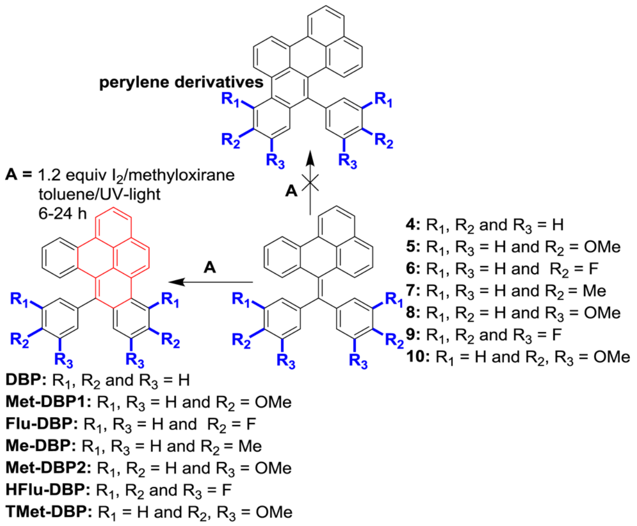
Scheme 1. Synthesis of Benzopyrene (DBP) Derivatives



intermediate involved (Schemes S2 and S3). These coupling reactions are widely used to construct the featured product frameworks in excellent yields with or without the use of methyloxyrane, depending on the reactivity of aryl olefin chosen for the coupling reaction.[11] Besides iodine, a variety of reagents, such as iron chloride, aluminum chloride, DDQ, and others, have also been explored for aromatic dehydrogenation reactions.[12] Except for our report on the Scholl reaction,[10] previous works describing oxidative aromatic coupling protocols focused more on highly symmetrical molecules, while those used for highly selective coupling could not avoid the formation of undesired products.[13] Indeed, the chosen reaction protocol here furnished single-fused benzopyrene products in higher isolated yields, irrespective of the functional group it carried. Nevertheless, a shorter reaction time (6 h) was needed for derivatives carrying electron donors such as methoxy groups with enhanced reaction yields (85−92%). The chemical structures proposed for these benzopyrene derivatives were established by NMR, high-resolution mass, and single-crystal X-ray analyses (Figure S36a−e).

The physical vapor transport (PVT) method was used to grow single crystals that are amenable to X-ray analyses and single-crystal FET device fabrication. Among the compounds, **Met-DBP2** and **TMet-DBP** exhibited typical melting behavior, but their vaporization and crystallization were not successful. The compound **DBP** and others crystallized as yellow, needle-shaped crystals. The X-ray crystal analyses show that the **DBP** molecule exhibits a near-planar polyfused aromatic core, whereas the unfused phenyl group twists away from the central core plane due to steric interactions (Figure 1a, and Figure S37c). The torsional angle for the unfused aryl unit varies in a small range from ∼67° to ∼71° for the **DBP** derivatives, depending on the substituent. All of the **DBP** derivatives show slipped cofacial packing between the fused aromatic blocks with an interplanar distance of ∼3.3−3.7 Å (Figure 1a−j). This packing direction coincides with the long axis of the needle, as indexed from X-ray diffraction (Figure S38). Introducing fluorine and methoxy groups brings about additional van der Waals interactions and helps create stronger packing arrangements in the crystal. In **Flu-DBP** and **HFlu-DBP** molecules, the CH···F interaction results in both electrostatic interactions between fluorinated phenyl rings and a short contact for C···F (2.6 Å) (Figures S36 and 37). The methoxy group has a short contact with the polyaromatic segment of the neighboring molecule at a distance of 2.7 Å due to a shift in the polyfused cores. The small differences in stacking in polyaromatic molecules will also influence their photophysical, electrochemical, and charge-transporting properties.[14]

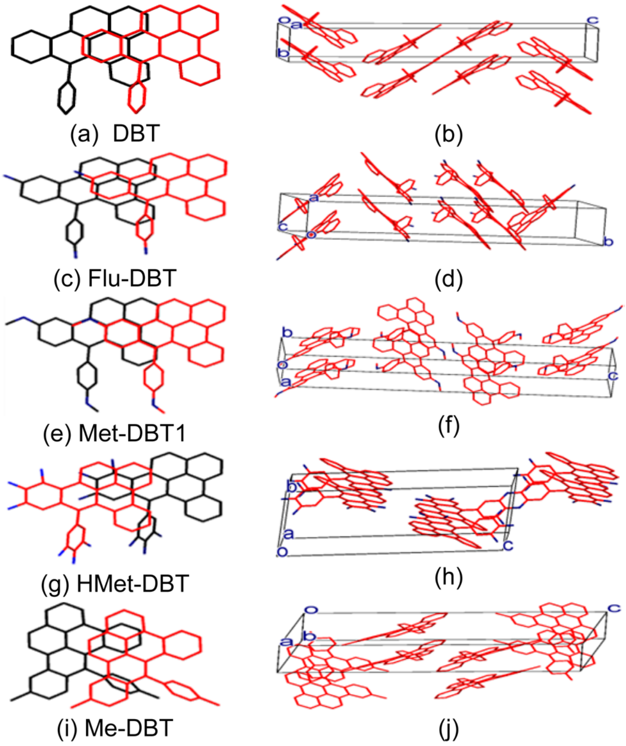


Figure 1. (a−j) Molecular packing showing $\pi-\pi$ stacking distance in **DBP** (3.6 Å), **Flu-DBP** (3.3 Å), **Met-DBP1** (3.6 Å), **TFlu-DBP** (3.7 Å), and **Me-DBP** (3.4 Å).

The benzopyrene derivatives give light yellow to yellow colors in their solid states. They are very soluble in solvents like dichloromethane, chloroform, and benzene, except for **HFlu-DBP**, which is sparingly soluble in these solvents. The absorption spectra of the derivatives as measured in their dilute dichloromethane solutions are given in Figures 2 and S39a with the related data presented in Table S1. The parent derivative **DBP** absorbs light at 385, 366, 307 (max), 296, and 278 nm, respectively. As compared with that of the smaller parent compound pyrene,[15] the two sets of absorption bands in the region of 250−330 and 330−420 nm are assigned as from the excitations occurring in longer and shorter axes of the **DBP**

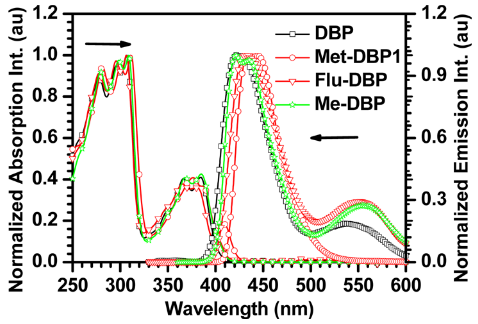


Figure 2. Normalized absorption/emission spectra of benzopyrenes as recorded in dichloromethane.

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molecule (Figure 3a). The HOMO orbitals are primarily localized over benzopyrene, and the absorption pattern of the DBPs is similar to the known benzo[*e*]pyrene framework;[16] thus, the absorption features in these derivatives are likely to originate from the benzo[*e*]pyrene portion. A marginal bathochromic shift in the absorption maxima was observed by embedding electron donors such as methoxy at the dibenzopyrene framework. The derivatives show blue to blue-green emission in their dilute solution. The **DBP** shows two emission bands at 539 and 422 nm, while its completely fused analogue gives only one emission band at 493 nm.[10] These two emission bands are possibly originated from the excited state with a twisted aryl unit attached to the main aromatic core and its relaxed form to a planar and low-energy form. This is a structural and intramolecular feature rather than the intermolecular excimer formation among **DBP** molecules (Figure S40a,b). It is noticed that the methoxy-substituted derivative gives single emission band. We suggest that a good donor restricts the relaxation to the planar excited state. The intramolecular origin of both emission bands in **DBP** was further supported by excitation of **DBP** at 430 and 550 nm wavelengths (Figure S40c), producing an excitation spectrum similar to that of the absorption spectrum. There was a slight bathochromic shift in the emission maxima with methoxy- and fluorine-substituted **DBP**s, possibly due to a polar effect on the excited state involved (Figures 2 and S39b).

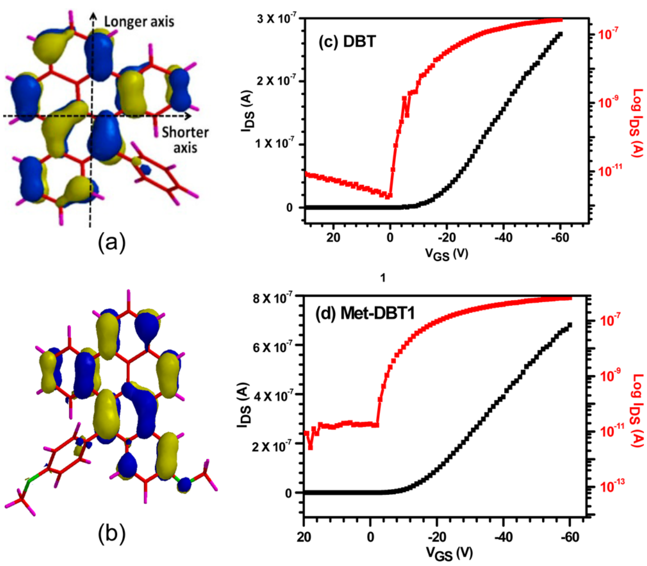

Figure 3. (a, b) HOMO plots of **DBP** and **Met-DBP1**, (c, d) current−voltage ($I_{DS} - V_{GS}$) curves for benzopyrenes.

The oxidation potentials together with HOMO−LUMO energies of these compounds are compiled in Tables 1 and S1, with their oxidation waves sketched in Figure S39c,d. Most compounds displayed single quasi-reversible oxidation waves, whereas **TMet-DBP** having multiple electron donors gave multiple oxidation waves. The oxidation potential values (E_{ox}) for these derivatives range from 0.59 to 1.02 V. The oxidation waves were possibly generated from oxidation of the parent fused core, and E_{ox} values were influenced by both the character and number of substituents at the polyaromatic framework.[12a,17] Thus, the oxidation potential was lowered by introducing electron donors such as methoxy groups in **Met-DBPs** and **TMet-DBP**, while it was raised by changing the substitution from two to six fluorine atoms in **Flu-DBP** and **HFlu-DBP**, respectively. Band gaps of the benzopyrenes were determined from their absorption edges, and the LUMO energies were obtained by subtracting the optical band-gaps from the HOMO values. Low-lying LUMO levels were obtained for **HFlu-DBP** having multiple fluorine atoms attached to the polyaromatic framework. Like redox stability, thermal stability of polyaromatics is also vital for OFET device stability and lifetime.[18] The benzopyrene derivatives displayed good thermal stability, and their thermal decomposition temperatures were >300 °C (Table 1 and Figure S40). Embedding fluorine atoms at the polyfused framework successively enhances the thermal stability of **HFlu-DBP** among the **DBP** series.

Table 1. Electro-optical and Thermal Properties of Benzopyrene Derivatives

compd	$\lambda_{abs}/\lambda_{em}{}^{a}$ (nm)	$E_{HOMO}{}^{c}/E_{LUMO}{}^{b}$ (eV)	$E_g{}^{d}$ (eV)	$T_d{}^{e}$ (°C)
DBP	307/422	5.58/2.46	3.12	378
Flu-DBP	307/416	5.65/2.57	3.08	405
Me-DBP	309/422	5.53/2.45	3.08	395
Met-DBP1	311/445	5.40/2.40	3.00	336
HFlu-DBP	309/431	5.82/2.76	3.06	431

[a]Maxima of absorption and emission. [b]$E_{HOMO} = 4.8 + E_{ox}$ (oxidation potential of compound with respect to ferrocene, $E_{ox} = E_{compound} - E_{Fc}$). [c]$E_{LUMO} = E_{HOMO} - E_g$. [d]Optical bandgap, E_g, was obtained from the intersection of absorption and emission spectra. [e]Thermal decomposition temperature measured at 10% weight loss.

To explore the potential of these benzopyrene-based aromatics as channel material, single-crystal field-effect transistors (SCFETs) were fabricated from these derivatives. Thus, a top-contact, top-gate SCFET was fabricated by laminating the needle-like crystal on a glass substrate. Painted colloidal graphite was used as the source and drain. Parylene film was grown on the crystal as the dielectric, while colloidal graphite on the top was the gate electrode. The channel length, width, and parylene thickness were 1.0−0.5 mm, 0.25−0.20 mm, and 1.8−2.5 μm, respectively. The derivatives demonstrated p-carrier behavior as judged from transfer curves (Figure 3c,d, Figures S42 and S43, and Table S1).

Four to eight devices were fabricated for these molecules. An average mobility of 2.1 cm^2/(V s) with a maximum mobility of 3.2 cm^2/(V s) was observed for **Met-DBP1**-based devices. The **Flu-DBP** gave a lower average mobility of 0.54 cm^2/(V s), with a maximum mobility of 0.7 cm^2/(V s). **HFlu-DBP**, while providing nice crystals, gave no measurable mobility. Even though similar packing motifs were adopted, the derivatives gave widely different mobilities, which may attest to the high sensitivity of the mobility to the perturbation in the packing arrangement and thus electronic coupling.

In conclusion, we have successfully synthesized a new series of unsymmetrical and polyfused aromatics comprising pyrene as the central core. These derivatives were characterized by spectroscopic techniques such as NMR and MALDI-TOF mass techniques, while crystal XRD analyses were obtained for selected samples. The derivatives showed a high p-type SCFET performance of 0.7−3.2 cm^2/(V s) in the single-crystal OFET configuration. The derivative with *para*-linked methoxy groups gave the highest field-effect mobility of 3.2 cm^2/(V s) due to a facile charge injection to the channel material.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02354.

Detailed experimental procedures and complete spectroscopic analyses (PDF)

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Notes

The authors declare no competing financial interest.

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