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Air-Stable n-Type Semiconductor: Core-Perfluoroalkylated Perylene Bisimides

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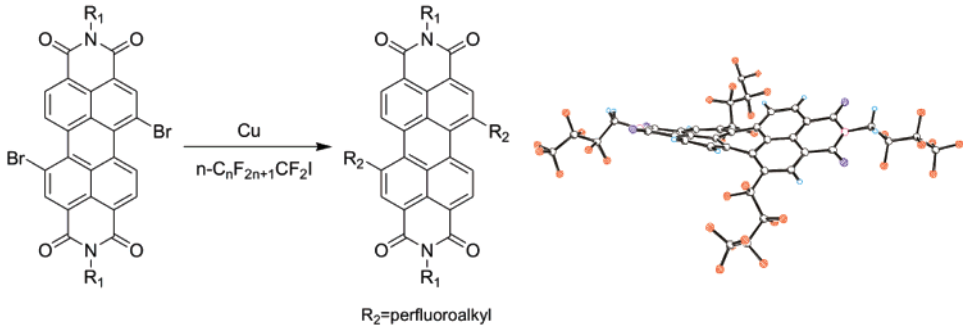
ABSTRACT



A series of core-perfluoroalkylated perylene bisimides (PBIs) have been efficiently synthesized by copper-mediated perfluoroalkylation of dibrominated PBIs. Their aromatic cores are highly twisted due to the steric encumbrance in the bay regions as revealed by single-crystal X-ray analysis. The organic field-effect transistors (OFETs) incorporating these new n-type semiconductors show remarkable air-stability and good field effect mobility.

Over the past decade, organic semiconducting materials have attracted much attention due to their potential use in organic thin film transistors (OTFTs), light-emitting diodes (LEDs), photovoltaic cells, and sensors.[1,2] Organic semiconducting materials are commonly classified as either p-type (hole-conducting) or n-type (electron-conducting) depending on which type of charge carrier is more efficiently transported through the material. To this end, stable organic p-type semiconductors have fulfilled many of the requirements for use in diverse applications.[3] However, n-type semiconductor materials, which are essential for the fabrication of organic complementary circuits, are far less developed, reflecting low mobilities, instability in air, and difficulties in synthesis.[4,5]

Of the n-type materials, derivatives of perylene-3,4:9,10-tetracarboxylic acid bisimides (PBIs) are of increasing interest, due to their exceptional optical and electronic properties,[6,7] and have already been used in a variety of device architectures.[8−10]

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One of the design principles for air-stable n-type PBIs-based semiconductor materials is to incorporate strong electron-withdrawing groups. Core-cyanated and *N*-fluoroalkylated PBI derivatives were reported to exhibit air-stable high n-type mobilities.[11] Meanwhile, the core-fluorinated perylene bisimides have been synthesized and achieved promising n-type semiconducting properties.[12]

We are particularly interested in bay region functionalization of PBIs. Recently, we reported the palladium-catalyzed cross-coupling reaction of tetrachloro-PBI with $Bu_3SnSSnBu_3$ and facile one-pot synthesis of novel triply linked diperylene bisimides.[13,14] Stimulated by these results, we decided to synthesize bay-perfluoroalkylated perylene bisimides, which are expected to possess substantially improved n-type semiconducting properties.

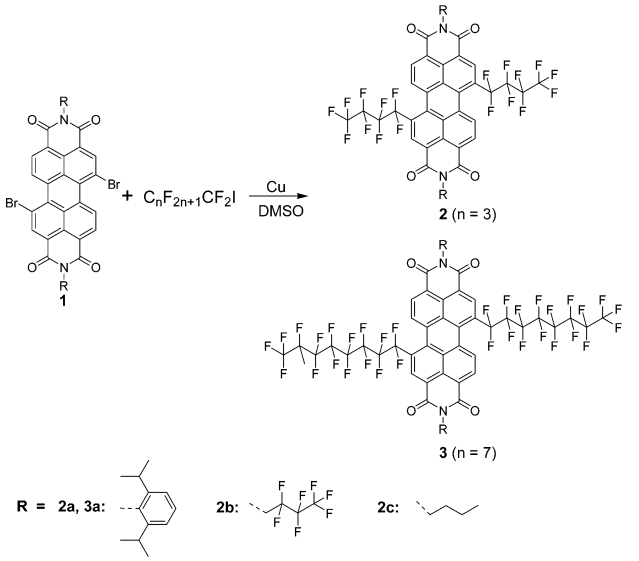
To our knowledge, perfluoroalkylation of halogenated PBIs via perfluoroalkyl-copper intermediates have not been reported to date, although the copper-mediated cross-coupling reaction between aryl halides and perfluoroalkyl iodides has been successfully used to synthesize perfluoroalkylated aryl compounds.[15] Herein we present a convenient synthesis of core-perfluoroalkylated PBIs. We also elucidate the molecular packing arrangement in single crystals, and preliminary results reveal good n-channel transistor performance and air-stability for field-effect transistors (FETs).

Perfluoroalkylation via copper coupling of 1,7-dibromo perylene bisimides with perfluoroalkyl iodides gives excellent yields of core-perfluoroalkylated PBIs (Scheme 1). Three different substituents (**a**, **b**, and **c**) and different-length perfluoroalkyl chain are used to explore the general scope of this method. All the desired products (**2a**, **3a**, **2b**, and **2c)** were characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry, and elemental analyses (see Supporting Information).

To assess the effect of the bay substituents on molecular order in the solid state, attempts were devoted to single-crystal growth. Ultimately, crystals suitable for single-crystal X-ray analysis were obtained by slow evaporation of chloroform solutions of **2b** and **2c**, respectively. The molecular structure and crystal packing of **2b** and **2c** are depicted in Figure 1.

Two molecules of **2b** and **2c** were found in the unit cell. As can be seen from Figure 1a and 1b, owing to the steric encumbrance effect of perfluoroalkyl substituents, the perylene cores are highly twisted as expected. However, the twisting of the central six-membered ring is surprisingly unsymmetrical with dihedral angles of 26.4° and 29.6° for **2b** and 25.0° and 28.9° for **2c**, which are similar to the tetrafluoro-

Scheme 1. Synthesis of Core-Perfluoroalkyl-Substituted Perylene Bisimides



substituted perylene bisimide with unsymmetrical twisting of ~18° and ~28°,[12] while the tetrachloro-substituted

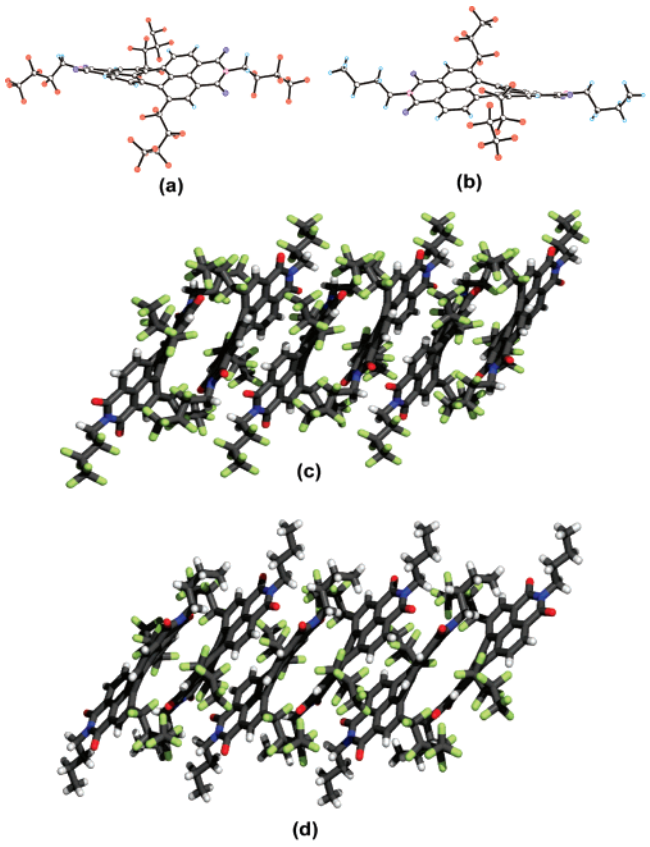


Figure 1. Molecular structure of **2b** (a) and **2c** (b). Crystal packing of **2b** (c) and **2c** (d).

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perylene bisimide has a torsional angle of 37°.[16] The unsymmetrical twisting of **2b** and **2c** is probably due to different conformations of perfluoroalkyl chains and packing effects in the crystal lattice.

The crystal packing arrangements of **2b** and **2c** are shown in Figure 1c and 1d, which reveal that the molecules are arranged in stacks along the α-axis of the unit cell. The stacked molecules share more than 50% of their core surface, between which the interplanar separation corresponds approximately to a distance of 3.69 Å for **2b** and 3.52 Å for **2c**. The closest intermolecular contact is of 3.51 Å for **2b** and 3.35 Å for **2c** (Figures S1−S4, Supporting Information).

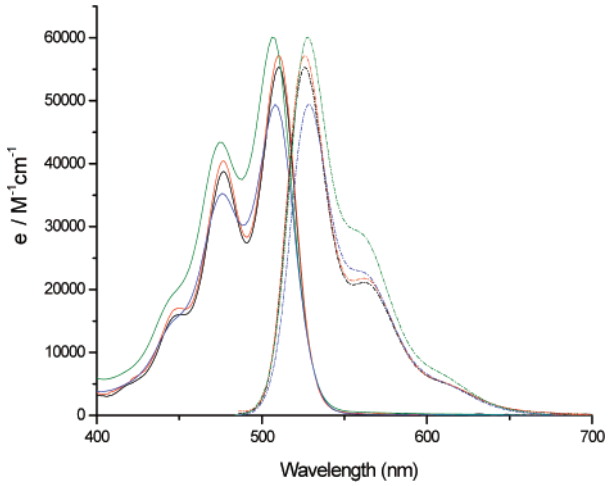

Figure 2. UV−vis absorption (solid line) and fluorescence emission (dash−dot line) spectra of **2a** (black line), **3a** (red line), **2b** (olive line), and **2c** (blue line) in chloroform.

The absorption and fluorescence spectra of core-perfluoroalkylated PBIs **2a**, **3a**, **2b**, and **2c** are shown in Figure 2, and the summarized optical data are given in Table 1.

Table 1. UV−vis Absorption and Fluorescence Emission Properties of Core-Perfluoroalkyl-Substituted Perylene Bisimides **2a**, **3a**, **2b**, and **2c** in Chloroform

	λ_{abs} (nm)	ϵ (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_{fl}[a,b]
2a	510	55337	526	0.92
3a	510	57220	526	0.91
2b	506	60079	528	0.94
2c	508	49425	528	0.97

[a] Average deviation for Φ_{fl}, ±0.04. [b] Determined with *N,N′*-di(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic acid bisimide as reference.

The absorption spectra of core-perfluoroalkylated compounds show a well-defined vibronic fine structure of the S_0-S_1 transition with a maximum at 510 nm for **2a** and **3a**, 506 nm for **2b**, and 508 nm for **2c**, hypsochromically shifted by 16, 20, and 18 nm, respectively, in comparison with parent PBI derivatives.[17] The absorption and emission spectra of **2a** and **3a** are not significantly influenced by the number of fluorine substituents when the fluorinated alkyl chains contain four or more carbon atoms. It should be also noted that the absorption and emission maxima of **2b** and **2c** are only slightly hypsochromically and bathochromically shifted in comparison with **2a**, which suggests that introduction of perfluoroalkyl chains directly to the aromatic core has a more substantial influence on the optical properties than *N*-perfluoroalkylation. The core-perfluoroalkylated PBIs presented here possess small Stokes shifts (16−22 nm) and exhibit very high fluorescence quantum yields (0.91−0.97).

The electronic consequences of core-perfluoroalkylation of PBIs were also investigated by cyclic voltammetry. Voltammograms of **2a**−**2c** and **3a** exhibit two reversible reduction waves (Table 2), whereas within the accessible scanning range in dichloromethane no oxidation waves could be detected.

Table 2. Half-Wave Reduction Potentials (in V vs Fc/Fc^+) of Core-Perfluoroalkyl-Substituted Perylene Bisimides **2a**, **3a**, **2b**, and **2c**[a]

	E (PBI^-/PBI^{2-})	E (PBI/PBI^-)
2a	−0.99	−0.67
3a	−0.99	−0.67
2b	−0.88	−0.60
2c	−0.98	−0.72

[a] Measured in 0.1 M solution of Bu_4NPF_6 in dichloromethane with a scan rate of 50 mV/s.

The first reduction waves for **2a**, **3a** were observed at −0.67 V vs Fc/Fc^+, whereas the second reduction waves appeared at −0.99 V. Both first and second reduction waves appeared at higher potentials with comparison to those of PBIs and tetrafluorinated PBIs, indicating that core-perfluoroalkylation induces strong electron-accepting ability. Due to the additional electron affinity of fluoroalkyl chains at the *N*-substituents, the reduction potentials of **2b** are less negative than those of **2a** and **2c**.

Electron-withdrawing fluorinated substituents are expected to both benefit the ambient stability of n-type organic semiconductors because of the stabilization of charge carriers and lead to closer packing through fluorocarbon self-segregation. Accordingly, preliminary studies on FET devices made of **2b** and **2c** were carried out. The devices were made in a "top contact" geometry; 60 nm thick organic active layers were evaporated onto a octadecyltrichlorosilane (OTS)-treated SiO_2 (400 nm, C_i = 9 nF/cm²)/n-doped Si substrate. Gold film (22 nm) was evaporated on the organic semiconductors as the source/drain electrodes. Figure 3 shows the transfer characteristics of the fabricated OTFTs

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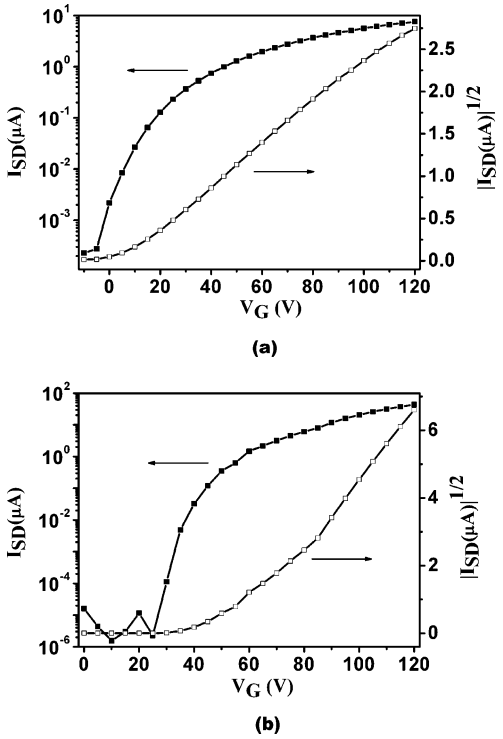

Figure 3. (a) Transfer characteristics of **2b** in ambient atmosphere. (b) Transfer characteristics of **2c** in ambient atmosphere.

of **2b** and **2c**. The measured $I-V$ characteristics of devices based on both semiconductors are summarized in Table 3. As a representative, the FET mobility of **2b** in ambient air was 0.003 $cm^2\ V^{-1}\ s^{-1}$, the on/off ratio was 4×10^3, and the threshold voltage was 4.7 V. Comparatively, the mobility of compound **2c** in ambient air was as high as 0.052 $cm^2\ V^{-1}\ s^{-1}$, the on/off ratio was 8×10^6, and the threshold voltage was 57 V. It should be noted the good charge carrier mobility value and on/off ratio of compound **2c** are almost unchanged for devices operated in air. The better performance of **2c** is probably due to its slightly more compressed packing arrangement.

Table 3. Summary of Field Effect Mobilities (μ), On/Off Ratios (I_{on}/I_{off}), and Threshold Voltages (V_t) for **2b** and **2c** Prepared on OTS-Treated Substrates at Room Temperature (25 °C)

	μ ($cm^2\ V^{-1}\ s^{-1}$)	I_{on}/I_{off}	V_t (V)
2b (in ambient air)	0.003	4.0×10^3	4.7
2c (in ambient air)	0.052	8.0×10^6	57
2c[a] (in vacuum)	0.053	3.4×10^7	27
2c[b] (in vacuum)	0.014	2.9×10^6	30
2c[b] (in ambient air)	0.009	4.7×10^6	45

[a] The values were obtained by TTP-6 Probe Station Desert Cryogenics, LLC. [b] The values were obtained from the TFT of compound **2c** which were stored in ambient air for 6 months.

In conclusion, we report a highly efficient synthetic methodology toward the core-perfluoroalkylated perylene bisimides from readily available dibrominated PBIs. The introduction of electron-deficient perfluoroalkyl chains directly on the core has substantial influence on the optical and electronic properties of PBIs. The OFETs incorporating this new n-type semiconductor shows remarkable air-stability and good charge carrier mobility. Further optimization of the fabrication process to improve its performance is currently underway.

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Supporting Information Available: Experimental procedure and characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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