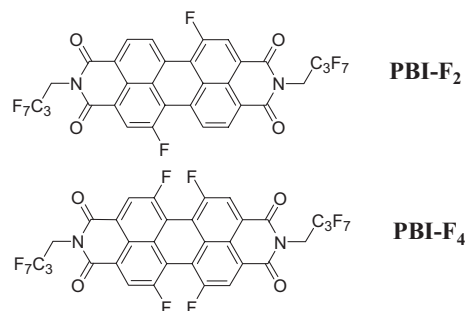


Core-Fluorinated Perylene Bisimide Dyes: Air Stable n-Channel Organic Semiconductors for Thin Film Transistors with Exceptionally High On-to-Off Current Ratios**

By Rüdiger Schmidt, Mang Mang Ling, Joon Hak Oh, Michael Winkler, Martin Könnemann, Zhenan Bao,* and Frank Würthner*

Recent years have witnessed a plethora of research efforts aimed at the rational design of organic semiconductor materials for applications in organic thin film transistors (OTFTs) and related electronic and optoelectronic devices.^[1] Whereas p-type semiconductors have been studied extensively, research on n-channel semiconducting materials still lags behind these developments. The availability of high-performance n-type materials, in which the majority charge carriers are electrons, is desirable for the fabrication of p-n junctions and complementary circuits. Apart from high electron mobilities, practically useful n-type semiconductors should possess a sufficiently high electron affinity to allow for efficient electron injection from common metal electrodes into these materials.^[1d] A major drawback of many compounds described in the literature is the poor stability in devices operated under ambient conditions. The introduction of fluorinated alkyl groups has been shown to lead to improved air-stabilities in various instances, and it has been argued that this stabilization originates in self-segregation of closely-packed fluorocarbon chains that prevents the diffusion of air and moisture into the channel region.^[1a,b] Perylene tetracarboxylic acid bisimides (PBIs) are among the most promising and versatile candidates for (opto)electronic applications, because their electronic and optical properties as well as their solid-state packing can be tuned in a wide range.^[2] The solid state packing and concomitant properties of PBIs can be tailored by introduction of appropriate substituents either in the imide position or by core

substitution in the bay region. Substitution in the 1, 6, 7, and 12 positions of the PBI backbone enforces a considerable twisting of the perylene skeleton out of planarity.^[2] The effect of this structural modification on the electrical and charge transport properties of these semiconductors is not yet well understood, though. Whereas intermolecular coupling might be reduced in core-twisted PBIs, this modification might, on the other hand, help to prevent the formation of dimeric pairs that have been envisaged as potential electron traps.^[3] To elucidate the effect of successive bay substitution, we describe here the synthesis and a comparison of two novel fluoro-substituted PBI derivatives, **PBI-F₂** and **PBI-F₄** (Scheme 1), that combine fluoroalkyl groups in imide position with two or four fluorine atoms in the bay region.^[4]



Scheme 1. Fluorinated PBI derivatives investigated in this work.

Both compounds were prepared by the HALEX procedure from the corresponding dibromo and tetrachloro derivatives, respectively.^[5] The substances were fully characterized by ¹⁹F-, ¹H-NMR, UV/Vis, and fluorescence spectroscopy as well as by high-resolution mass spectrometry. Electrochemical properties of **PBI-F₂** and **PBI-F₄** were investigated by cyclic voltammetry. Solvent-free single-crystals could be obtained and the packing motives were studied by X-ray crystal structure analysis. Field effect characteristics were determined in top-contact organic field effect transistors (OFETs) under various conditions.^[6]

Cyclic voltammetry (CV) measurements were carried out in dry dichloromethane under argon with 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as the supporting electrolyte at a scan rate of 100 mV s⁻¹ (Table 1). The first

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Table 1. Optical absorption and emission wavelengths, quantum yields, half-wave reduction potentials (in V versus Fc/Fc⁺), and LUMO energies of **PBI-F₂** and **PBI-F₄**. Computed electron affinities are given for comparison.

Comp.	λ_{abs} [a] [nm]	λ_{em} [a] [nm]	ϕ_{fl} [b]	E^{red}_1 [V]	E^{red}_2 [V]	$\varepsilon(\text{LUMO})$ [c] [eV]	$\varepsilon(\text{LUMO})$ [d] [eV]	EA_{vert} [d] [eV]	EA_{ad} [d] [eV]
PBI-F₂	509	516	1.00	−0.92	−1.14	−3.88	−4.21	3.00	3.14
PBI-F₄	502	511	0.90	−0.87	−1.12	−3.93	−4.32	3.11	3.26

[a] Measured in CH₂Cl₂ solution. [b] Using *N,N'*-di(2,6-diisopropylphenyl)perylene-3,4:9,10-tetracarboxylic acid bisimide as reference. [c] Determined according to literature methods [7]. [d] Calculated at the B3LYP/6-311+G(d,p)//6-31G(d) level of theory.

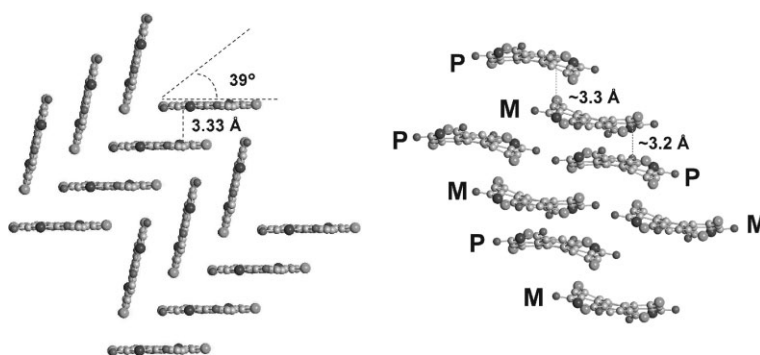
two reduction waves were always reversible, while no oxidation wave could be observed. Compared with *N*-alkyl PBIs lacking core substituents **PBI-F₂** and **PBI-F₄** can be reduced more easily by about 200–250 mV. Thus, the LUMO energies derived from CV data are −3.88 eV and −3.93 eV for **PBI-F₂** and **PBI-F₄**,^[7] respectively, in good agreement with orbital energies calculated at the B3LYP/6-311+G(d,p)//6-31G(d) level of theory.^[8] The calculated electron affinities are also similar for both compounds and fall in the range of 3.0–3.3 eV.^[9]

Single-crystals of **PBI-F₂** and **PBI-F₄** were obtained by recrystallization from toluene and by slow diffusion of methanol into a dichloromethane solution, respectively. The crystal structure of **PBI-F₂** shows a nearly planar π -skeleton (torsion angle 3°), whereas **PBI-F₄** is highly twisted (25° and 19°, the different torsion angles are caused by packing effects), owing to repulsive interactions between the four fluorine atoms in the bay positions (Fig. 1).

The crystal structure of **PBI-F₂** reveals a slip-stacked edge-to-face herringbone arrangement with a smallest intermolecular CC distance of 3.33 Å within the stacks. The slipping angle within the stack is 39°, and the closest distance between neighbouring molecules amounts to 2.49 Å (H-F contacts between perylene hydrogens and fluorine atoms of the perfluoroalkyl group). For **PBI-F₄**, the twisted perylene backbone induces axial chirality giving rise to the presence of two atropisomers (*M* and *P* enantiomers) in the solid state (Fig. 1). In the racemic crystal a dimeric unit is observed consisting of one *M* and one *P* enantiomer that approach each

other at a closest π – π distance of only ~3.2 Å. This dimeric unit exhibits close contacts to several neighbouring molecules which should enable charge carrier transport at least in two dimensions.

To elucidate the potential of the new PBI derivatives for OTFT applications, thin films were deposited onto SiO₂ (300 nm)/n-doped silicon wafers which had been modified using a self-assembled monolayer of octadecyl triethoxysilane (OTS). Subsequently, gold electrodes were deposited through a shadow mask. Out-of-plane X-ray diffraction patterns revealed high crystallinity for both compounds within the films. The measured *I*–*V* characteristics of devices based on both semiconductors are summarized in Table 2. In both cases, well-defined field effect characteristics were obtained in the linear as well as the saturation regime (Fig. 2). As generally

**Figure 1.** Crystal structures of **PBI-F₂** (left) and **PBI-F₄** (right); heptafluorobutyl groups are omitted for clarity.**Table 2.** Charge carrier mobilities, on-to-off current ratios, and threshold voltages of **PBI-F₂** and **PBI-F₄** based top-contact OFETs prepared by vapor-deposition at different substrate temperatures (*T_D*) onto OTS treated SiO₂ wafers. Current-voltage measurements in nitrogen atmosphere were carried out inside a glove-box filled with nitrogen (oxygen level < 1 ppm), whereas the measurements in air were performed under ambient laboratory conditions approximately 1 h after exposing the samples to air.^[a]

Comp.	<i>T_D</i> [°C]	N ₂ atmosphere			Air		
		$\mu[\text{cm}^2\text{V}^{-1}\text{s}^{-1}]$	$I_{\text{on}}/I_{\text{off}}$	V_t [V]	$\mu[\text{cm}^2\text{V}^{-1}\text{s}^{-1}]$	$I_{\text{on}}/I_{\text{off}}$	V_t [V]
PBI-F₂	25	0.063	2.3×10^6	32.2	0.058	6.0×10^5	35.6
	90	0.120	7.8×10^6	11.9	0.110	1.6×10^6	17.5
	125	0.349	3.5×10^7	14.3	0.338	9.2×10^6	19.6
PBI-F₄	25	0.017	3.4×10^5	28.9	0.015	1.1×10^4	29.3
	90	0.025	2.2×10^5	5.56	0.024	1.4×10^5	24.8
	125	0.032	8.1×10^5	1.53	0.031	2.7×10^6	34.3

[a] For **PBI-F₂** measurements in air over a period of three weeks did not reveal significant changes in charge carrier mobilities and on/off ratios. For **PBI-F₄** no measurements in air for a prolonged time have been carried out.

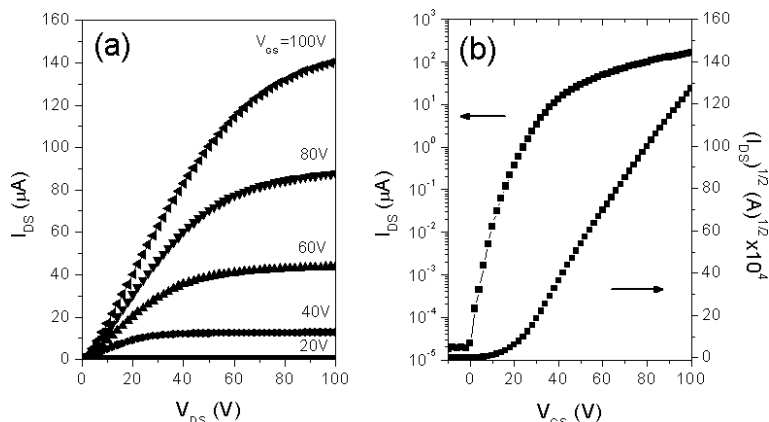


Figure 2. Current–voltage characteristics of **PBI-F₂** OTFT prepared at $T_D = 125^\circ\text{C}$. a) A plot of I_{DS} versus V_{DS} . b) A plot of I_{DS} versus V_{GS} for $V_{DS} = 100$ V. The measurement was carried out under ambient environmental condition.

observed for organic semiconductors,^[1,2e] the charge carrier mobility of both compounds rises with increasing substrate temperature during film deposition, due to increased crystallinity and larger grain sizes. The highest charge carrier mobilities of $0.34\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ (**PBI-F₂**) and $0.03\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ (**PBI-F₄**) were obtained at a deposition temperature of 125°C ; at higher substrate temperatures (150°C) no films could be deposited onto the substrate under the pressure conditions used in our experiments. Remarkably, these excellent charge carrier mobility values and on/off ratios are almost unchanged for devices operated in air (Table 2).

Atomic force microscopy (AFM) measurements revealed rather large grain sizes of approximately $2.5\text{ }\mu\text{m}$ or more for both compounds within the films (Fig. 3). The morphology of the **PBI-F₄** films was found to be less regular with more grain boundaries than that of the **PBI-F₂** films. The lower charge carrier mobility of **PBI-F₄** could thus be attributable to morphological issues or to poorer intermolecular interaction within the grains due to the twisting of the PBI skeleton.^[10]

Although similarly high charge carrier mobilities have previously been reported for PBI derivatives containing cyano groups,^[2c,4,11] a remarkable feature of **PBI-F₂** is the very high on-to-off current ratio of 10^7 —two orders of magnitude high-

er than that usually found for PBI derivatives. This high value extends the range of potential applications for this class of semiconductors significantly. Despite the similar electron affinities, the threshold voltage of **PBI-F₂** in inert atmosphere was always higher (up to about 13 V) than that of **PBI-F₄**, making it harder to switch the device on.

In summary, two fluorine-rich PBI semiconductors were synthesized and characterized. The **PBI-F₂** derivative containing two fluorine atoms in the bay region, adopts a herringbone structure in the solid state, and shows charge carrier mobilities of up to $0.34\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ combined with exceptionally high on-to-off current ratios of 10^7 in vapor-deposited thin film transistors that can be operated under ambient conditions in air. Additional fluorine substitution in **PBI-F₄** enforces a significant twisting of the perylene backbone out of planarity. The measured charge carrier mobility of **PBI-F₄** is one order of magnitude lower as compared to the difluoro derivative. A detailed analysis including a larger number of PBI derivatives will unveil the complex interplay of factors determining the performance of devices based on this versatile class of organic semiconductors and will be the subject of a forthcoming work.

Experimental

Synthesis. Synthetic procedures including complete analytical characterizations and details of the X-ray crystal structure determinations are provided in the Supporting Information section. CCDC 650975 and CCDC 650976 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB21EZ, UK; fax: (+44)-1223-336-033; or deposit@ccdc.cam.ac.uk).

Electrochemistry. Electrochemical data were obtained by cyclic voltammetry (CV) with a standard commercial electrochemical analyzer in a three electrode single-compartment cell under argon. Dichloromethane was used as solvent that was dried over calcium hydride and degassed prior to use. The supporting electrolyte tetrabutylammoniumhexafluorophosphate was recrystallized from ethanol/water and dried in high vacuum. The measurements were carried out at a concentration of 10^{-4} M using ferrocene as an internal standard for calibration purposes. The potentials were obtained from the half-wave reduction potentials.

Device fabrication and characterization. Highly doped n-type (100) Silicon wafers ($<0.004\text{ }\Omega\text{ cm}$) were used as substrates for the organic thin-film transistors (OTFTs). SiO_2 layers (300 nm) were thermally grown as gate dielectric onto Si substrates. Its unit area capacitance (C_i) was 10 nF cm^{-2} . The substrate surface was treated with n-octadecyl triethoxysilane [$\text{C}_{18}\text{H}_{37}\text{Si}(\text{OC}_2\text{H}_5)_3$, OTS]. A few drops of OTS (Aldrich Chemical Co.) were loaded on top of a preheated quartz block ($\sim 100^\circ\text{C}$) inside a vacuum desiccator. The desiccator was immediately evacuated under vacuum ($\sim 25\text{ mmHg}$) for 60 seconds. The SiO_2/Si substrate was treated for at least five hours to give a hydrophobic surface. The wafers were subsequently baked at 110°C for 15 min, and then rinsed with toluene, acetone, and isopropanol with drying under nitrogen after each step. Organic semiconductor thin films (40 nm) were vapor-deposited onto the Si/SiO_2 substrates held at well-defined temperatures between 25 and 150°C with a deposition rate of $1.0\text{ }\text{\AA}\text{ s}^{-1}$ at 10^{-6} Torr, employing a vacuum deposition chamber

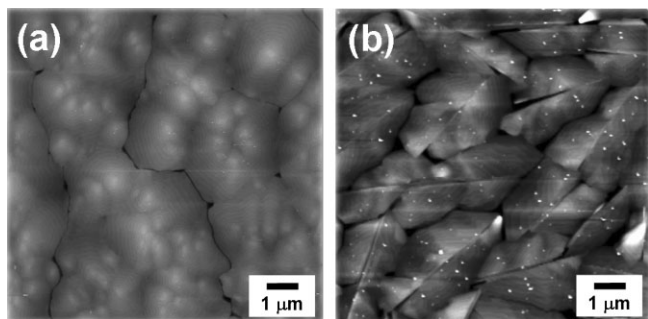


Figure 3. AFM topographies for a) **PBI-F₂** and b) **PBI-F₄** thin films deposited at 125°C onto OTS-treated SiO_2/Si substrates.

(Angstrom Engineering, Inc., Canada). Thin film transistors in top-contact configuration were used to measure the charge mobility of the materials. Gold source and drain electrodes (typical channel length was 100 μm with width/length ratios of about 20) were vapor-deposited through a shadow mask. The current-voltage (I - V) characteristics of the devices were measured using a Keithley 4200-SCS semiconductor parameter analyzer. Key device parameters, such as charge carrier mobility (μ) and on-to-off current ratio ($I_{\text{on}}/I_{\text{off}}$), were extracted from the drain-source current (I_{DS}) versus gate-source voltage (V_{GS}) characteristics employing standard procedures [1]. Out-of-plane X-ray diffraction (XRD) measurements were carried out with a Philips X'Pert PRO system. The beam wavelength was 1.5406 Å operated at 45 keV and 40 mA. The results are shown in the Supporting Information. AFM measurements were performed by using a Multimode Nanoscope III (Digital Instruments/Veeco Metrology Group) AFM instrument in tapping mode.

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