Synthesis and Optical and Electrochemical Properties of Core-Fluorinated Perylene Bisimides
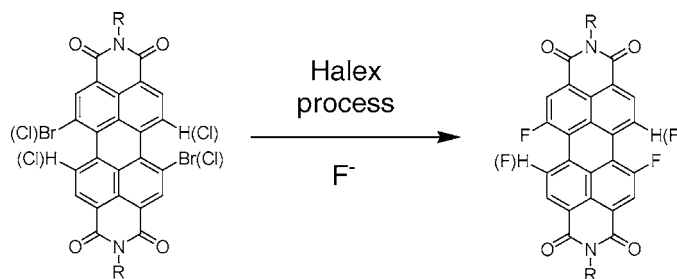
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Received June 1, 2006

ABSTRACT

A series of bay position difluoro- or tetrafluoro-substituted perylene bisimides have been synthesized by nucleophilic halogen exchange reaction of the corresponding dibromo- and tetrachloro-substituted perylene bisimides, respectively, with potassium fluoride. Compared to the parent unsubstituted perylene bisimides, these compounds display hypsochromically shifted absorption and fluorescence spectra with fluorescence quantum yields up to unity enabling bright yellow emission. Their electrochemical properties and crystal structures of two perylene bisimides are also reported.

Organic semiconducting materials have gained great attention as a result of their promising application in organic field effect transistors (OFETs), light-emitting diodes, and solar cells.[1] Although several classes of organic compounds with high p-type charge carrier mobility have been known for many years,[2] their n-type counterparts have become available only recently. According to this work the most general approach toward n-type semiconducting materials seems to be given by attachment of fluorine substituents at electron-

poor π-conjugated cores, e.g., naphthalene bisimides[3] and thiazols,[4] or even at originally electron-rich π-conjugated systems, e.g., oligothiophenes,[5] anthracenes,[6] and phthalo-cyanines.[7] A particularly promising class of dyes for n-type semiconducting materials are perylene bisimides (PBIs). Besides fullerenes, unsubstituted perylene bisanhydrides and PBIs, bearing only hydrogen atoms at the bay position (1, 6, 7, 12-positions), are considered to be the archetype n-type semiconducting materials, and their application in solar cell

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(1) For recent reviews on organic semiconducting materials, see: (a) Reese, C.; Bao, Z. *J. Mater. Chem.* **2006**, *16*, 329. (b) Würthner, F.; Schmidt, R. *ChemPhysChem* **2006**, *7*, 793. (c) Newman, C. R.; da Silva Filho, D. A.; Brédas, J.-L.; Ewbank, P. C.; Mann, K. R.; Frisbie, C. D. *Chem. Mater.* **2004**, *16*, 4436. (d) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.
(2) Garnier, F. In *Electronic Materials: The Oligomer Approach*, Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998.

(3) Katz, H. E.; Johnson, J.; Lovinger, A. J.; Li, W. *J. Am. Soc. Chem.* **2000**, *122*, 7787.
(4) Ando, S.; Muratami, R.; Nishida, J.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *J. Am. Chem. Soc.* **2005**, *127*, 14996.
(5) (a) Facchetti, A.; Yoon, M.-h.; Stern, C. L.; Hutchinson, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13480. (b) Yoon, M.-h.; Facchetti, A.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 5792.
(6) Sun, M. *Chem. Phys.* **2006**, *320*, 155.
(7) Bao, Z.; Lovinger, A. J.; Brown, J. *J. Am. Chem. Soc.* **1998**, *120*, 207.

devices, xerographic photoreceptors, and OFETs has been demonstrated.[8] Recently, high charge carrier mobilities up to 0.6 cm^2 V^{-1} s^{-1} have been reported for a dioctyl perylene bisimide derivative in vapor-deposited films under vacuum as well as for liquid-crystalline derivatives cast from solution.[9]

PBIs bearing four chlorine atoms at the bay position have also been investigated for application in thin film transistors, and charge carrier mobilities up to 0.14 cm^2 V^{-1} s^{-1} were determined for vapor-deposited films.[10] Furthermore, the introduction of two strongly electron-withdrawing cyano groups into the bay area has significantly improved the applicability of PBI dyes with charge carrier mobilites of 0.10−0.64 cm^2 V^{-1} s^{-1} under *ambient conditions*.[11] Very recently, a comparative investigation on application of different bay-substituted perylene bisimide derivatives in solar cell devices has been reported[12] and new tetrabrominated PBIs have been synthesized.[13]

As the introduction of electron-withdrawing and, in particular, fluorine groups leads to an improvement of the n-type semiconducting properties, we have decided to synthesize PBIs bearing two or four fluorine atoms at the bay position. To our knowledge, such core-fluorinated perylene bisimides are not reported to date. Nucleophilic substitution is commonly used for the introduction of substituents in the bay area of PBIs.[14] Thus, nucleophilic displacement of bromine or chlorine by fluoride ions appeared to be a promising strategy for the synthesis of core-fluorinated perylene bisimides. Indeed, fluorine atoms could be introduced into the bay position of perylene bisimides by nucleophilic substitution of brominated or chlorinated PBIs with potassium fluoride (KF) in tetrahydrothiophene-1,1-dioxide (sulfolane) as solvent in the presence of either (*N*,*N*-dimethylimidazolidino)-tetramethylguanidinium chloride (CNC$^+$) (recently used as an efficient catalyst for such Halex reactions)[15] or 18-crown-6 as catalyst (Scheme 1). Three different substituents (**a**−**c**) were used to explore the general scope of this method. Thus, the difluoro-perylene bisimides **2a**−**c** were obtained from the corresponding

Scheme 1. Synthesis of Core-Fluorinated Perylene Bisimides
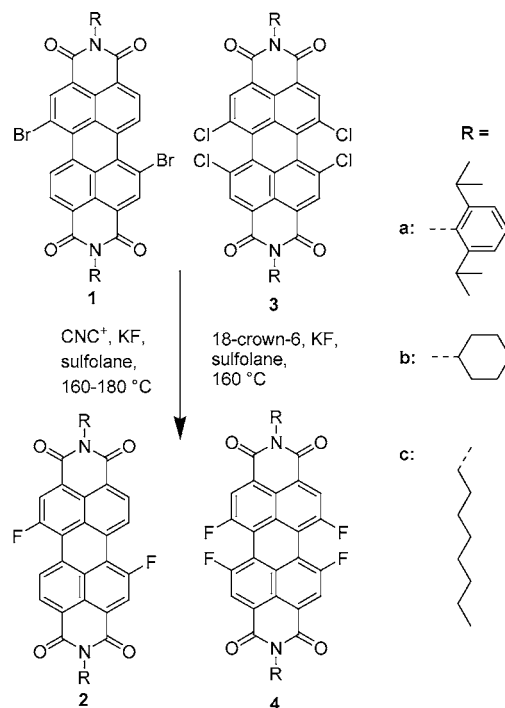
	isolated yield (%)	
Compound	CNC$^+$	18-crown-6
2a	7	63
2b	46	5
2c	28	59
4a	25	4
4b	no conv.	no conv.
4c	3	1

dibromoperylene bisimides **1a**−**c** by nucleophilic halogen exchange reaction with 10−14 equiv of KF and 20−30 mol % of CNC$^+$ or with 6 equiv of KF and 20 mol % of 18-crown-6 in moderate to good yields (Scheme 1).

Some tetrafluoroperylene bisimides **4a,c** were also accessible by nucleophilic halogen exchange reaction of the corresponding tetrachloroperylene bisimides **3a,c** under similar conditions as applied for difluorinated compounds **2**. In comparison to difluoro-substituted compounds, lower yields were obtained for the tetrasubstituted perylene bisimides, which might be due to the sterical congestion imparted by the four chlorine atoms compared to two bromine atoms. On the other hand, the overall yield of a four-step reaction sequence in the chlorine case must be lower than the overall yield of a two-step sequence in the bromine case even if the single exchange reactions had the same yield. Also the yields of **4a** and **4c** reached with the CNC$^+$ catalyst were much higher than those obtained with 18-crown-6. The CNC$^+$ catalyst is especially designed for the chlorine-fluoride exchange,[15] whereas the crown ether is "only" a common phase transfer catalyst.

To our surprise, PBI **3b** did not show any conversion under the similar reaction conditions applied for other tetrachloro derivatives **3a**,**c**. This might be ascribed to the very poor

(8) (a) Tang, C. W. *Appl. Phys. Lett.* **1986**, *48*, 183. (b) Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449. (c) Forrest, R. F. *Chem. Rev.* **1997**, *97*, 1793.

(9) (a) Chesterfield, R. J.; McKeen, J. C.; Newman, C. R.; Ewbank, P. C.; da Silva Filho, D. A.; Brédas, J.-L.; Miller, L. L.; Mann, K. R.; Frisbie, C. D. *J. Phys. Chem. B* **2004**, *108*, 19281. (b) Struijk, C. W.; Sieval, A. B.; Dakhorst, J. E. J.; Dijk, M.; Kimkes, P.; Koehorst, R. B. M.; Donker, H.; Schaafsma, T. J.; Picken, S. J.; van de Craats, A. M.; Warman, J. M.; Zuilhof, H.; Sudholter, E. J. R. *J. Am. Chem. Soc.* **2000**, *122*, 11057. (c) An, Z.; Yu, J.; Jones, S. C.; Barlow, S.; Yoo, S.; Domercq, B.; Prins, P.; Siebbeles, L. D. A.; Kippelen, B.; Marder, S. R. *Adv. Mater.* **2005**, *17*, 2580.

(10) (a) Graf, H.; Michaelis, W.; Schnurpfeil, G.; Jaeger, N.; Schlettwein, D. *Org. Electron.* **2004**, *5*, 237. (b) Chen, Z.; Debije, M. G.; Debaerdemaeker, T.; Osswald, P.; Würthner, F. *ChemPhysChem* **2004**, *5*, 137.

(11) Jones, B. A.; Ahrens, M. J.; Yoon, M.-h.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6363.

(12) Shin, W. S.; Jeong, H.-H.; Kim, M.-K.; Jin, S.-H.; Kim, M.-R.; Lee, J.-K.; Gal, Y.-S. *J. Mater. Chem.* **2006**, *16*, 384.

(13) (a) Fan, L.; Xu, Y.; Tian, H. *Tetrahedron Lett.* **2005**, *46*, 4443. (b) Qiu, W.; Chen, S.; Liu, Y.; Zhu, D. *Org. Lett.* **2006**, *8*, 867.

(14) (a) Iden, R.; Seybold, G.; BASF AG; Ger. Pat. Appl. DE 3434059 A1, 1985; *Chem. Abstr.* **1985**, *103*, 38696q. (b) Seybold, G.; Wagenblast, G. *Dyes Pigm.* **1989**, *11*, 303. (c) Zhao, Y.; Wasielewski, M. R. *Tetrahedron Lett.* **1999**, *40*, 7047.

(15) Pleschke, A.; Marhold, A.; Schneider, M.; Kolomeitsev, A.; Röschenthaler, G.-V. *J. Fluorine Chem.* **2004**, *125*, 1031.

solubility of **3b** in sulfolane. The difluoro and tetrafluoro PBIs synthesized here were characterized by ^{1}H NMR, ^{19}F NMR, and mass spectrometry, and two derivatives **2a** and **4c** have been analyzed by X-ray crystallography.

Single crystals of **2a** and **4c** suitable for single-crystal X-ray analysis could be obtained by cooling a toluene solution of **2a** to −30 °C and by slow evaporation of a dichloromethane solution of **4c**. The molecular structures of **2a** and **4c** are depicted in Figure 1.
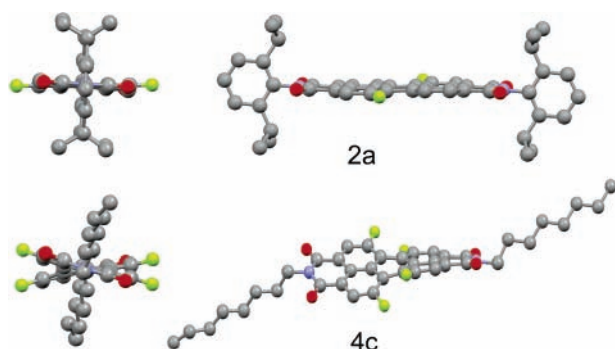
Figure 1. Molecular structures of **2a** and **4c** in the crystal. View along the *N,N*-axis of the perylene bisimide (left) and the side view of the molecule (right).

The crystal structure of **2a** comprises of two crystallographically independent molecules of **2a** and four toluene molecules. As can be seen from Figure 1, the molecular structure of the difluorinated perylene bisimide **2a** was found to be close to planar with dihedral angles of ∼4.0° for both of the two crystallographically independent molecules of **2a**. The cocrystallized toluene molecules are situated between the **2a** molecules, preventing close contact of the perylene cores. There are, however, clear $\pi\cdots\pi$ interactions between the toluene and perylene molecules (closest intermolecular toluene to perylene C to C distances being ∼3.1 Å). The crystal packing is depicted in Figure S2 (Supporting Information).

For **4c** bearing four fluorines at the bay position, the twisting of the perylene core was surprisingly unsymmetrical but, as expected, significantly larger than for **2a**: thus, the dihedral angle on the one bay area is ∼18°, the other being ∼28°. The extended twist angle for **4c** can mainly be attributed to the repulsive interactions of the strongly electronegative fluorine atoms at the bay area. The unsymmetrical twisting is most probably induced by packing effects and intermolecular interactions in the crystal lattice. The fluorine atoms possess a van der Waals radius of 135 pm, which is between that of oxygen atom (140 pm) and hydrogen atom (120 pm). The unsubstituted PBIs exhibit a planar perylene core[16] and tetraphenoxy-substituted PBIs possess a torsion angle of ∼26° in the solid state.[17] The crystal packing of **4c** is shown in Figure S4 (Supporting

(16) Graser, F.; Hädicke, E. *Liebigs Ann. Chem.* **1980**, 1994.

Table 1. UV−vis Absorption and Fluorescence Emission Properties of Fluoro-Substituted Perylene Bisimides **2** and **4** in Dichloromethane

	λ_{abs} (nm)	ϵ (M^{-1} cm^{-1})	λ_{em} (nm)	$\phi_{fl}{}^{a,b}$	τ_{fl} (ns)^a
2a	511	94600	516	1.00	3.4
2b	508	88000	513	0.98	3.6
2c	508	84000	514	1.00	3.7
4a	503	77200	512	0.94	3.4
4c	500	66000	509	0.88	3.6

^{a} Average deviation for ϕ_{fl}, ±0.08; for τ_{fl}, ±0.3 ns. ^{b} Determined with *N,N'*-di(2,6-diisopropylphenyl)-perylene-3,4:9,10-tetracarboxylic acid bisimide as reference.

Information), which reveals that the dyes are arranged in stacks along the *a*-axis of the unit cell. It must be noted that the stacked molecule share less than 50% of their perylene core surface. Despite the offset arrangement and twisting of the molecules there are clear $\pi\cdots\pi$ interactions between the chromophores; the closest intermolecular C-to-C distances between two stacked perylene core carbons are in the range of 3.6 Å.

The absorption and fluorescence spectra of difluorinated PBI **2b** and tetrafluorinated derivative **4a** are shown as representative examples in Figure 2, and the optical data for
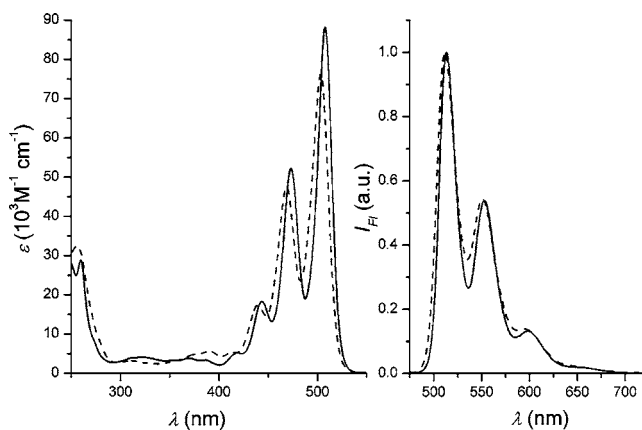
Figure 2. UV−vis absorption (left) and fluorescence emission (right) spectra of **2b** (solid line) and **4a** (dashed line) in dichloromethane.

all compounds are given in Table 1. The absorption spectra of difluorinated compounds show a well-defined vibronic fine structure of the S_0-S_1 transition with a maximum at 511 nm for **2a** and 508 nm for **2b** and **2c**. The absorption and emission maxima of difluoro derivatives are hypsochromically shifted by 15 and 18 nm, respectively, in comparison with those of the related unsubstituted PBI derivatives. Such hypsochromic shifts are unprecedented for PBI

(17) (a) Würthner, F.; Sautter, A.; Schilling, J. *J. Org. Chem.* **2002**, *67*, 3037. (b) Osswald, P.; Leuser, D.; Stalke, D.; Würthner, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 250.

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dyes and enable for the first time bright yellow fluorescence color for this class of fluorophores.[18] The similar absorption coefficients and vibronic progressions in the spectra of difluorinated and unsubstituted perylene bisimides are in agreement with a flat rather than a twisted perylene core as demonstrated for **2a** by X-ray analysis. The absorption maxima for tetrafluoro-substituted PBIs **4** are even further shifted to shorter wavelength (503 nm for **4a** and 500 nm for **4c**). The absorption coefficients of tetrafluorinated PBIs **4** are considerably decreased compared with those of difluorinated derivatives **2**, which can be attributed to the twist of the perylene core in former compounds as demonstrated for **4c** by X-ray analysis. The fluorescence spectra of all core-fluorinated PBIs fulfill the mirror image condition as exemplified for compounds **2b** and **4a** in Figure 2. The core-fluorinated PBIs presented here possess only very small Stokes shifts (5−9 nm) indicating rigid structure of the molecules. They all exhibit very high fluorescence quantum yields (88−100%) and fluorescence lifetimes in the range of 3.4−3.7 ns, which correspond very well with the values reported for unsubstituted PBI derivatives (3.4 ns).[19]

The electrochemical properties of core-fluorinated PBIs **2** and **4** were investigated by cyclovoltammetry, and their reduction potentials are given in Table 2. Exemplified cyclovoltammograms for **2b** and **4a** are shown in Figure S5 (Supporting Information). The fluorinated PBIs exhibit two reversible reduction waves, whereas within the accessible scanning range in dichloromethane no oxidation waves could be detected. The first reduction waves for **2a−c** were observed at −0.99 to −1.08 V vs Fc/Fc$^+$, whereas the second reduction waves appeared at −1.26 to −1.29 V. Both first and second reduction waves of tetrafluorinated PBIs **4a,c** were observed at slightly higher potentials (−0.92 and −1.22 V vs Fc/Fc$^+$), indicating that the tetrafluorinated perylene

Table 2. Half-Wave Reduction Potentials (in V vs Fc/Fc$^+$) of Core-Fluorinated Perylene Bisimides **2** and **4**[a]

	E (PBI$^-$/PBI^{2-})	E (PBI/PBI$^-$)
2a	−1.26	−0.99
2b	−1.29	−1.08
2c	−1.26	−1.04
4a	−1.22	−0.92
4c	−1.22[b]	−0.98

[a] Measured in 0.1 M solution of Bu$_4$NPF$_6$ in dichloromethane with a scan rate of 100 mV/s. [b] Quasi-reversible.

bisimides are somewhat easier to reduce than the corresponding difluorinated derivatives, as expected.

In summary, the hitherto unknown core-fluorinated perylene bisimides can be synthesized by Halex process from the corresponding brominated or chlorinated derivatives. The optical and electrochemical properties of the present fluorinated PBIs are promising for many applications, e.g., as fluorescent dyes and materials for organic field effect transistors and organic light-emitting devices. Thus, our future interests include detailed investigations of the solid-state properties of these compounds as well as the characterization of their n-type semiconducting properties.

Supporting Information Available: Synthesis and characterization and ^{1}H and ^{19}F NMR spectra of compounds **2a−c** and **4a,c** and cyclovoltammograms for **2b** and **4a**; crystal structures of **2a** and **4c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) The position of the absorption maxima of PBIs is mainly dependent on the electronic properties of the substituents at the bay area, whilst the imide substituents can have some effect on absorption coefficients. See Table 1 in: Würthner, F. *Chem. Commun.* **2004**, 1564.

(19) You, C.-C.; Dobrawa, R.; Saha-Möller, C. R.; Würthner, F. *Top. Curr. Chem.* **2005**, *258*, 39.