Synthetic Routes to Core-fluorinated Perylene Bisimide Dyes and their Properties

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Z. Naturforsch. **2009**, *64b,* 735 – 746; received March 26, 2009

Dedicated to Professor Gerhard Maas on the occasion of his 60th birthday

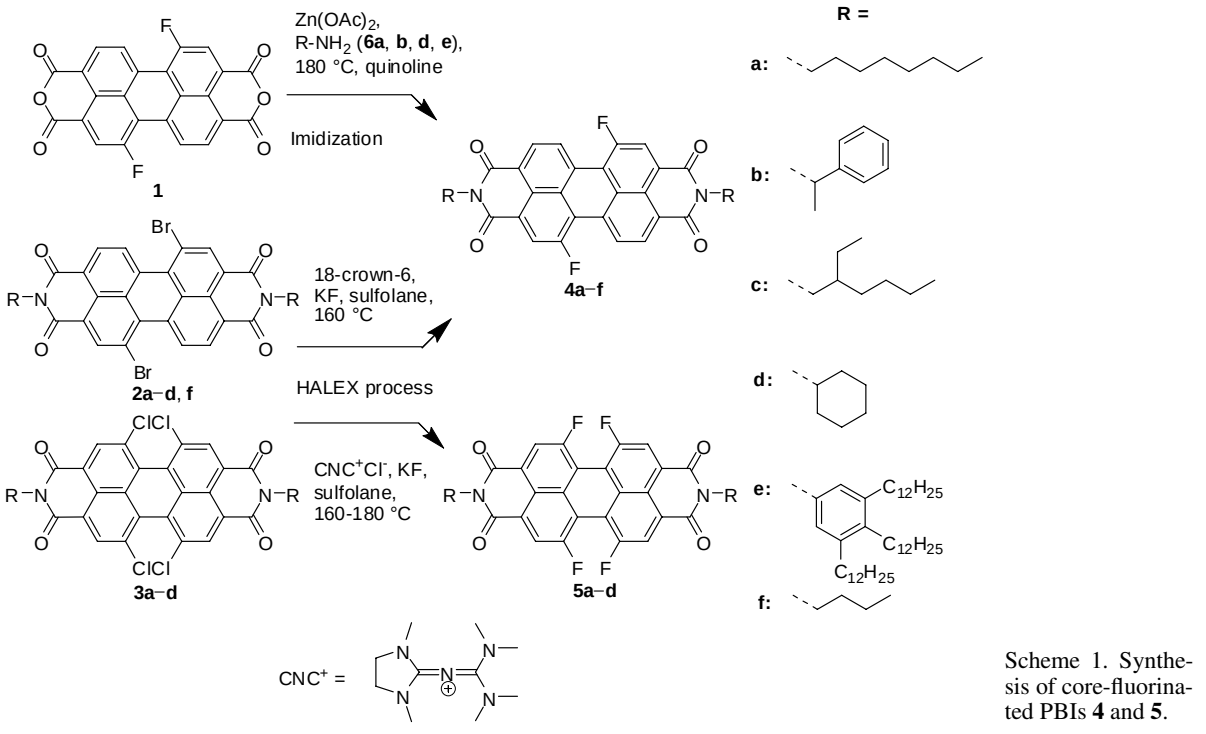
Numerous core-fluorinated perylene bisimide (PBI) dyes with various substituents at the imide positions have been synthesized by different methods. Core-difluorinated PBIs **4a–f** are obtained by imidization of difluoro-substituted perylene bisanhydride **1** with appropriate primary amines or, alternatively, by nucleophilic halogen exchange reactions (Halex process) of the corresponding dibromo-substituted PBIs **2a–d**,**f** with potassium fluoride. Core-tetrafluorinated PBIs **5a–c** could also be synthesized by halogen exchange reactions of the respective tetrachlorinated PBIs **3a–c**. In particular, core-fluorinated perylene bisimide pigments **4h**, **5h** containing hydrogen atoms in the imide positions could be obtained for the first time by deprotection of α-methylbenzyl-substituted precursors. Compared with core-unsubstituted perylene bisimides, these fluorinated dyes display hypsochromically shifted absorption and fluorescence spectra, and they exhibit fluorescence quantum yields up to unity, enabling bright yellow emission. The electrochemical properties of these electron-poor perylene bisimides have been studied. Furthermore, the packing features of a tetrafluorinated PBI derivative in the solid state have been discussed.

Key words: Dyes and Pigments, Fluorination, n-Type Semiconductors, Perylene Bisimides

Introduction

Electronic materials based on organic semiconducting molecules are becoming increasingly important due to their widespread applications in organic field effect transistors (OFETs) [1], light emitting diodes (OLEDs) [2], and solar cells [3]. Whilst several classes of organic materials with high p-type charge carrier mobility have been known for a long time, their n-type counterparts have become available only recently. One general approach toward n-type semiconducting materials is the introduction of perfluorinated substituents or other electron-withdrawing groups to electron-poor extended aromatic π systems, *e. g.*, naphthalene bisimides [4] and thiazols [5], or even at originally electron-rich π-conjugated systems, *e. g.*, oligothiophenes [6], acenes [7], and phthalocyanines [8]. Among organic n-type semiconductors, perylene bisimide (PBI) dyes are very auspicious candidates since core-unsubstituted perylene bisanhydride and PBIs are considered to be the archetype n-type semiconducting materials [9]. Their application in solar cell devices and OFETs has been demonstrated [10]. Recently, high charge carrier mobilities up to 2.1 cm^2 V^{-1} s^{-1} were determined for vapor-deposited films [10c]. PBIs bearing four chlorine atoms in the bay area (1,6,7,12-positions) have also been investigated for applications in thin film transistors, and charge carrier mobilities up to 0.18 cm^2 V^{-1} s^{-1} were determined for vapor-deposited films [11]. Furthermore, the introduction of two strongly electron-withdrawing cyano groups in the bay area has significantly improved the applicability of PBI dyes with air-stable charge carrier mobilities up to 0.64 cm^2 V^{-1} s^{-1} [12].

As the incorporation of electron-withdrawing, in particular, fluorine groups afforded significant improvements of the n-type semiconducting properties for several classes of organic semiconductors [8a, 12], we have recently introduced the first examples of core-fluorinated perylene bisimides [13], and demonstrated very recently that such fluorinated PBIs indeed afford air-stable n-channel semiconductors [14]. Thus, core-fluorinated PBIs are highly promising for OFETs, and hence further derivatives with varied imide sub-



Scheme 1. Synthesis of core-fluorinated PBIs **4** and **5**.

stituents are in demand. Here we report the synthesis of a broad spectrum of core-fluorinated PBI derivatives by different routes and discuss their optical and electronic properties. Moreover, core-fluorinated perylene bisimides without imide substituents are also of interest as the corresponding parent compound itself is an n-type semiconductor, and incorporation of fluorine atoms into the bay area should enhance its electron-accepting properties. However, such core-fluorinated PBIs are so far not known and are considered to be difficult to purify owing to their extremely low solubility. Here we present for the first time di- and tetrafluoriantes PBIs with N-H imide functionality that are made accessible by a novel deprotection procedure developed in our group [15].

Results and Discussion

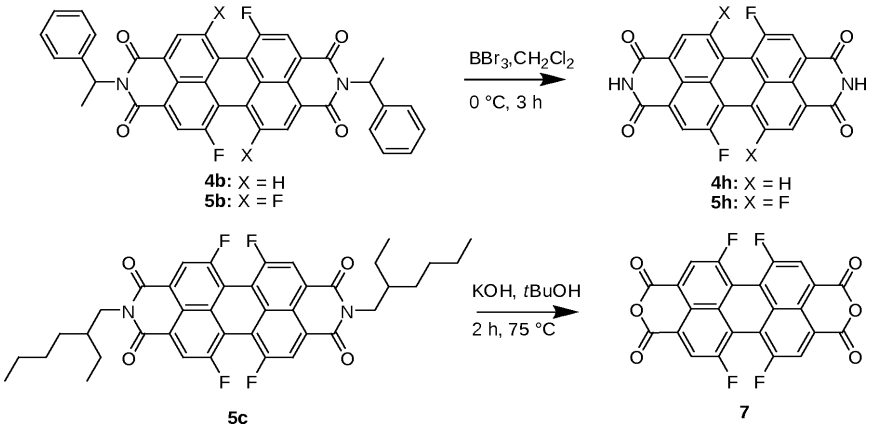
Synthesis

The core-fluorinated perylene bisimides **4** and **5** (Scheme 1) were synthesized by a sequence of halogen exchange and imidization reactions and both routes, *i. e.*, halogen exchange of perylene bisanhydrides and subsequent imidization, or first imidization and subsequent halogen exchange, were explored. The difluorinated perylene bisanhydride **1** was obtained by the reaction of dibrominated perylene bisanhydride with potassium fluoride at 160 °C in anhydrous sulfolane containing 18-crown-6 [16], while the dibrominated and tetrachlorinated precursor PBIs **2** and **3** were synthesized according to literature methods [17]. Imidization of difluorinated perylene bisanhydride **1** with amines **6a**, **b**, **d** or **e** afforded the corresponding difluorinated perylene bisimides **4a**, **b**, **d** and **e** in relatively lower yields (see Table 1). The reasons for these unsatisfactory yields might be, on the one hand, the insufficient purity of the starting material **1** [16] and, on the other hand, facile nucleophilic exchange

Table 1. Yields (%) of difluorinated PBIs **4a–f** by imidization of perylene bisanhydride **1** and Halex reaction of PBIs **2a–d**, **f**.

	— Method —	
PBI	Imidization	Halex reaction[a]
4a	13	59[b]
4b	27	60
4c	[c]	46
4d	10	46[b]
4e	12	[c]
4f	[c]	25

[a] Catalyst: 18-crown-6; [b] previously communicated [13]; [c] not performed.



Scheme 2. Synthesis of PBIs **4h**, **5h** and bisanhydride **7**.

of fluorine atoms by aliphatic amines. Indeed, for the reaction of perylene bisanhydride **1** with an excess amount of the more nucleophilic primary amine *n*-octylamine high quantities of a green byproduct with an NH-octyl substituent in bay position were obtained. Thus, the alternative route, namely, halogen exchange reaction (Halex process) [18] of dibrominated perylene bisimides **2a**–**d** and **f** was chosen. This reaction was carried out in sulfolane with potassium fluoride and catalytic amounts of 18-crown-6, and indeed significantly higher yields (between 25 % and 60 %, see Table 1) were achieved. Notably, the use of the *N*,*N*-dimethylimidazolidino-tetramethylguanidinium chloride (CNC^+) catalyst, which was previously applied for Halex reactions [18], was less successful for the fluorination of dibrominated PBIs [13].

The Halex reaction of tetrachlorinated perylene bisimides **3a**–**c** afforded the corresponding tetrafluorinated PBIs **5a**–**c** in lower yields (Table 2), while for PBI **3d** no conversion was observed. The deficient yields of these reactions can be explained by the sterical congestion imparted by four halogen atoms and the four step reaction sequence required for complete halogen exchange. For this Halex reaction, the CNC^+ catalyst was used, as this catalyst was developed particularly for the chloride-fluoride exchange [18], while 18-crown-6 is a quite general phase transfer catalyst. The solubility of PBIs in sulfolane has a strong influence on the yield, and thus for the almost insoluble PBI **3d** no conversion could be observed, and the yield of the poorly soluble dye **5a** (3 %) was significantly lower than those for the better soluble compounds **5b** and **5c** (20 % and 18 %, respectively). Replacement of the CNC^+ with 18-crown-6 catalyst led to even lower yields.

Table 2. Yields of tetrafluorinated PBIs **5a**–**c** by the Halex process of chlorinated PBIs **3a**–**c**.

PBI	**5a**	**5b**	**5c**
Yield (%)	3	20[a]	18[a]

[a] These yields are based on the conversion of the PBIs **3b** and **3c**, respectively, as about 50 % of the starting materials was recovered (see Experimental Section).

Notably, the core-fluorinated PBIs with NH imide groups **4h** and **5h** could be synthesized for the first time by the cleavage of the α-methylbenzyl imide substituents of PBIs **4b** and **5b**, respectively, with boron tribromide in dichloromethane in nearly quantitative yield (Scheme 2). These fluorinated PBIs are insoluble pigments, and thus could be characterized only by mass spectrometry. It is noteworthy that the above-mentioned deprotection method is applicable not only to PBI derivatives bearing electron-withdrawing bay substituents, but also to those containing electron-donating core substituents such as amino [15a] and aryloxy groups [15b]. Thus, boron tribromide-mediated deprotection of α-methylbenzyl imide substituents is a quite general method with broad scope for the synthesis of core-substituted perylene bisimides with NH imide groups.

By saponification of **5c** the tetrafluorinated perylene bisanhydride **7** was obtained in a yield of 94 %. Mass spectrometry revealed a trifluoro-hydroxy-substituted perylene as an impurity, which obviously originates from the nucleophilic substitution of one fluorine atom by potassium hydroxide. The saponification of **4c** led also to an insoluble compound, but the desired difluorinated bisanhydride could neither be isolated nor identified.

All the di- and tetrafluorinated PBIs were characterized by ^1H and ^{19}F NMR spectroscopy and high-

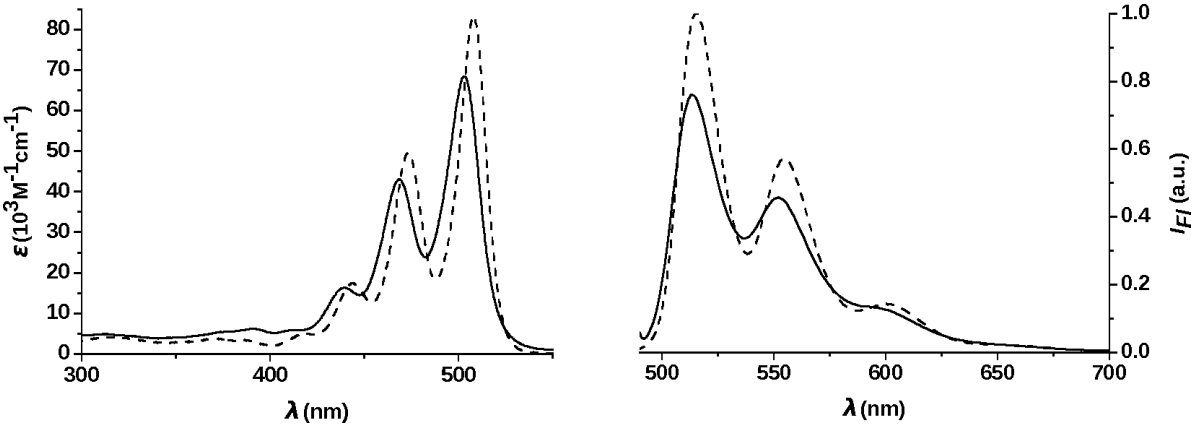


Fig. 1. UV/Vis absorption spectra (left) and fluorescence emission (right) spectra of **4f** (dashed lines) and **5b** (solid lines) in dichloromethane.

Table 3. UV/Vis absorption and fluorescence emission properties of core-fluorinated perylene bisimide dyes **4** and **5** in dichloromethane.

PBI	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_{fl}[a]
4a[b]	508	81300	514	1.00
4b	510	80900	518	0.98
4c	508	76600	516	1.00
4d[b]	508	89000	513	0.98
4e	511	96900	518	0.35
4f	508	83300	515	1.00
5a[b]	500	66000	509	0.88
5b	503	68400	514	0.85
5c	501	71900	513	1.00

[a] Average deviation ±0.03; the quantum yields were determined at three different wavelenghts with *N,N′*-di(2,6-diisopropylphenyl)-perylene-3,4 : 9,10-tetracarboxylic acid bisimide (Φ_{fl} = 1.00 in chloroform) as reference (for details see Experimental Section); [b] taken from ref. [13] and shown for completeness.

resolution mass spectrometry (see Experimental Section).

Optical properties

The optical properties of the perylene bisimide dyes **4** and **5** were investigated by UV/Vis and fluorescence spectroscopy. Absorption and fluorescence spectra of the difluorinated PBI **4f** and its tetrafluorinated derivative **5b** are shown as representative examples in Fig. 1, and the optical data for these compounds are collected in Table 3. The absorption spectra of the difluorinated compounds **4a–f** show a well-defined vibronic fine structure of the S_0–S_1 transition with maxima between 508 and 511 nm, depending on the imide substituent. The absorption and emission maxima of difluorinated derivatives are hypsochromically shifted by 16 and 17 nm, respectively, in comparison with those of the related unsubstituted PBI derivatives. Such hypsochromic shifts are unprecedented for PBI dyes and lead for the first time to a bright yellow fluorescence for this class of fluorophores [13]. 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 has been demonstrated by single crystal X-ray analysis of a difluorinated PBI derivative [13].

The absorption maxima for tetrafluorinated PBIs **5a–c** are even further shifted to shorter wavelengths (503 to 500 nm). Their absorption coefficients are decreased considerably as compared to those of difluorinated derivatives **4a–f**, which can be attributed to the population of conformations with a twisted perylene core as demonstrated for **5a** by X-ray analysis (see below). The fluorescence spectra of all core-fluorinated PBIs fulfill the mirror image condition as exemplified for compounds **4f** and **5b** in Fig. 1. The core-fluorinated PBIs presented here show rather small Stokes shifts (5 – 12 nm), indicating a quite rigid structure of the molecules. Nearly all of the dyes exhibit very high fluorescence quantum yields (85 – 100 %) which correspond very well with the values reported for unsubstituted PBI derivatives. The only exception is dye **4e**, which has a lower fluorescence quantum yield of 35 %. This value is in good accordance with the low quantum yield of the parent chromophore (without core fluorination) bearing identical imide substituents [19], where the fluorescence quenching could be attributed to a photoinduced electron transfer process from the electron-rich imide substituents to the electron-poor PBI core.

Table 4. First and second half-wave reduction potentials (in V *vs.* Fc/Fc^+) of core-fluorinated perylene bisimides **4** and **5**.

PBI	E (PBI/PBI^-)(V)[a]	E (PBI^-/PBI^{2-})(V)[a]	ε LUMO (eV)[b]
4a[c]	−1.04	−1.26	−3.76
4b	−1.04	−1.25	−3.76
4c	−1.07	−1.28	−3.73
4d[c]	−1.08	−1.29	−3.72
4e	−1.02	−1.26	−3.78
4f	−1.04	−1.25	−3.76
5a[c]	−0.98	−1.22	−3.82
5b	−0.98	−1.21	−3.82
5c	−0.98	−1.21	−3.82

[a] Measured in 0.1 M solution of Bu_4NPF_6 in dichloromethane with a scan rate of 100 mV s^{-1}; ferrocene served as internal standard; [b] calculated according to the literature method by using the equation: εLUMO = −4.8 eV − E(PBI/PBI^-) [21]; [c] taken from ref. [13] and shown for completeness.

Electrochemical properties

The electrochemical properties of core-fluorinated PBIs **4** and **5** were investigated by cyclic voltammetry, and their reduction potentials are given in Table 4. Exemplified cyclic voltammograms for **4b** and **5c** are shown in Fig. 2. 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

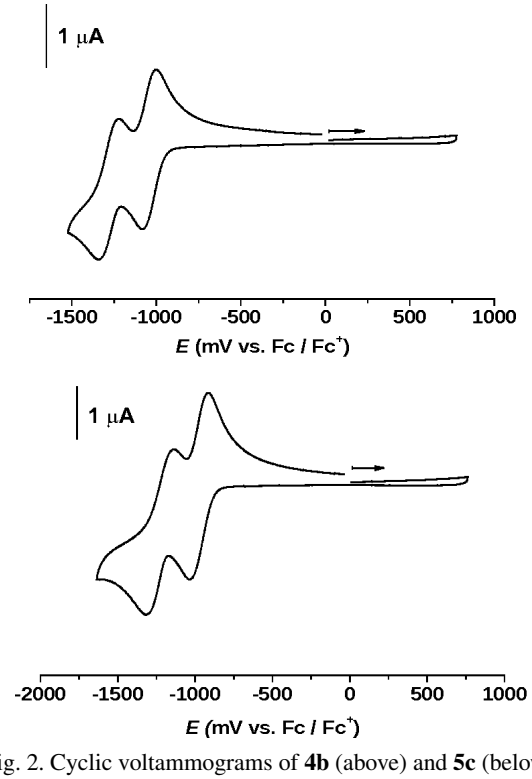


Fig. 2. Cyclic voltammograms of **4b** (above) and **5c** (below).

difluorinated PBIs **4a–f** were observed between −1.02 and −1.08 V *vs.* Fc/Fc^+, while the second reduction waves appeared in the range of −1.26 to −1.29 V. Both first and second reduction waves of tetrafluorinated PBIs **5a–c** were observed at slightly higher potentials (−0.98 and −1.21 V *vs.* Fc/Fc^+), indicating that the tetrafluorinated perylene bisimides are easier to reduce than the corresponding difluorinated derivatives. In regard to the effect of imide substituents on the redox properties of these PBIs, it is to note that the aromatic substituent in **4e** led to a 20–60 mV higher reduction potential compared to aliphatic substituents.

Interestingly, the influence of fluorine core substituents on the redox potential of PBIs is very small. The core-unsubstituted reference compound *N,N′*-di(cyclohexyl)-perylene-3,4:9,10-tetracarboxylic acid bisimide shows under identical conditions a first reduction potential of −1.10 V, which is only 20 mV lower than the potential of the difluorinated compound **4d**. In contrast, significantly larger effects are observed for core-chlorinated or core-brominated PBIs [20].

Properties in the solid state

We have presented the crystal structure of the tetrafluorinated PBI **5a** in our recently published letter [13]. However, the highly interesting packing properties of this PBI in the solid state that are related to the conformational chirality of core-substituted PBIs, imparted by a dihedral twist of the perylene core [22], were not discussed there. We now turn to this aspect in this full paper. The molecular structure of PBI **5a** is depicted in Fig. 3. For this derivative, bearing four fluorines at the bay position, the twisting of the perylene core was surprisingly unsymmetrical but, as expected, significantly larger than for difluorinated perylene bisimide dyes [13]. Thus, the dihedral angle of the one bay area is ∼17° (carbon atoms C16–C4–C3–C22), the other being ∼28° (carbon atoms C24–C5–C7–C15). The extended twist angle for **5a** can mainly be attributed to the repulsive interactions of the strongly electronegative fluorine atoms at the bay area.

The unsymmetrical distortion is most probably induced by packing effects and intermolecular interactions in the crystal lattice, allowing a denser arrangement in the solid state. The fluorine atoms possess a van-der-Waals radius of 135 pm, which is in between that of oxygen (140 pm) and hydrogen (120 pm). Due to the small size of the fluorine atom the difluorinated PBIs exhibit a nearly planar perylene core quite sim-

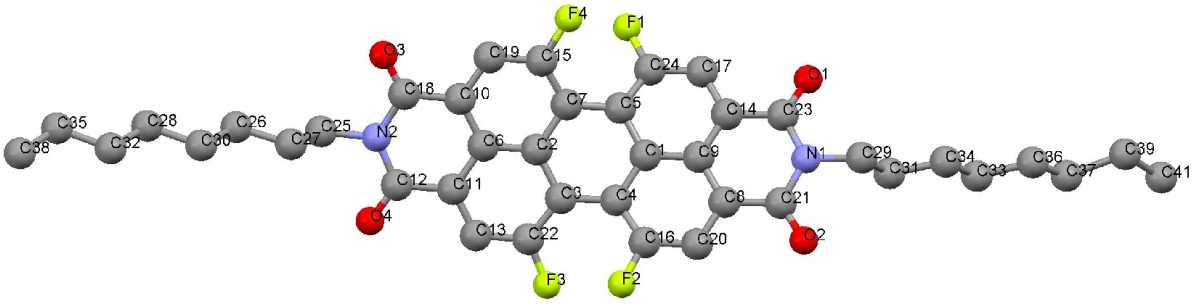


Fig. 3. Ball and stick representation of the molecular structure of PBI **5a** in the crystal.

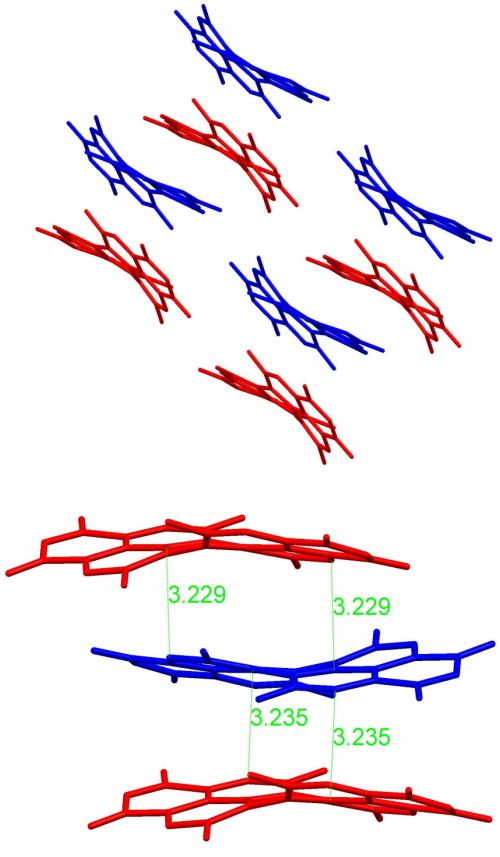


Fig. 4. Molecular packing in crystals of **5a**. The *P*-enantiomers are shown in blue and the *M*-enantiomers in red. Distances between naphthalene subunits of the two neighboring molecules are given in Å. Imide substituents are omitted for clarity, (color online).

ilar to that of the unsubstituted PBIs [13, 23], while tetrachloro- and tetraphenoxy-substituted PBIs possess a torsion angle of 25 – 37° in the solid state [24]. Accordingly, the dihedral angles of 17° and 28° observed for **5a** are in the expected range.

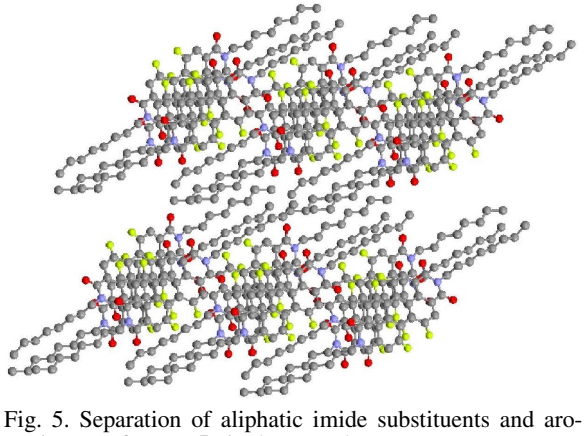


Fig. 5. Separation of aliphatic imide substituents and aromatic cores for PBI **5a** in the crystal.

The crystal packing of **5a** is shown in Fig. 4. The dye molecules are arranged in stacks along the *a* axis of the unit cell, but share less than 50 % of their perylene core surface. Two molecules of **5a** with opposite chirality are found in one unit cell (blue: *P*-enantiomer, red: *M*-enantiomer). Furthermore, no solvent molecules are embedded in the crystal lattice, which is quite unusual for a perylene molecule of this size, and only the outer areas of the octyl substituents are partly disordered.

The closest intermolecular contacts of about 2.4 Å, which can be assigned to CH···O contacts, are found between hydrogen atoms of the perylene core and oxygen atoms of imide groups. The closest π-π interactions are found between neighboring molecules of opposite chirality (*P*- and *M*-enantiomer) in one stack and are in the range of 3.2 – 3.3 Å, which is smaller than the interplane spacing (3.37 Å) of graphite [25]. The intermolecular distances between the π surfaces of naphthalene units in a stack are identical, although the contacts to the upper and lower neighboring molecules are slightly different along a given stack. Furthermore, as

shown in Fig. 5, the lipophilic octyl chains and the aromatic perylene cores are well separated in the crystal. This packing should enable a two-dimensional charge carrier transport along the PBI stacks, hence this PBI might be suitable for application in OFETs.

Conclusion

A series of di- and tetrafluorinated perylene bisimide dyes were synthesized by employing the Halex reaction. Owing to the high sensibility of the fluorinated bisanhydrides towards nucleophilic amines leading to undesired side reactions, only low yields were obtained for the imidization of fluorinated perylene bisanhydrides. Therefore, for the synthesis of core-fluorinated perylene bisimides the sequence of first imidization and subsequent Halex reaction is the better choice.

The physical attributes of the difluorinated derivatives are, apart from the hypsochromic shift of the optical absorption and emission, quite similar to those of the corresponding unsubstituted dyes. Like core-unsubstituted PBIs, the difluorinated derivatives can build up strong π-π interactions in the solid state due to their negligible torsion angle in the bay area [13]. Nevertheless, the quadrupole moments of the dyes are changed by the two bay substituents, which induces a modified packing of these dyes in the solid state. The structural attributes of tetrafluorinated derivatives are very similar to those of other tetrasubstituted PBI dyes (*e. g.*, tetrachloro). For one example (**5a**), the packing in the solid state revealed close π-π distances between the naphthalene units of conformationally twisted chromophores, and an alternate arrangement of *P*- and *M*-enantiomers as in the case of a core-tetrachlorinated PBI [24c].

Since π-π interactions are indispensable for high charge carrier mobilities, the present core-fluorinated PBI derivatives are promising n-type semiconductors for organic electronic applications.

Experimental Section

General information

Dibrominated PBIs **2a**, **c**, **d**, **f** and tetrachlorinated PBIs **3a**, **c**, **d** were synthesized according to the literature [17]. For the former compounds, mixtures of the 1,7- and 1,6-regioisomers in a ratio of about 9 : 1 were used. Potassium fluoride, zinc acetate, propionic acid, cyclohexylamine, 1-*n*-octylamine, 2-ethylhexylamine, 1-*n*-butylamine, 1-phenylethylamine, sulfolane, 18-crown-6, and silica gel (Si 60, 40 – 63 μm) were purchased from commercial sources, while 3,4,5-tridodecylaniline was synthesized according to the literature [26]. Potassium fluoride was dried in vacuum (60 °C/10^{-3} mbar), sulfolane was fractionally distilled under vacuum prior to use. All other chemicals and solvents were used as received. The catalyst (*N,N′*-dimethyl-imidazolidino)-tetramethylguanidinium chloride (CNC^+) was synthesized according to literature procedures [18]. ^{1}H NMR spectra (400 MHz) were recorded on a Bruker Advance 400 spectrometer; chemical shifts in $CDCl_3$ are given relative to $CHCl_3$ (δ = 7.26 ppm). ^{19}F NMR spectra (376.5 MHz) were recorded on a Bruker Avance 400 spectrometer, chemical shifts in $CDCl_3$ are given relative to $CClF_3$ (δ = 0.0 ppm). UV/Vis spectra were measured in quartz glass cuvettes under ambient conditions, unless otherwise stated. The measurements were performed with a PE 950 spectrometer (Perkin Elmer GmbH, Rodgau, Germany). Fluorescence emission and excitation spectra were recorded on a PTI QM4-2003 fluorescence spectrometer and corrected against photomultiplier and lamp intensity. The fluorescence quantum yields were determined by the optical dilution method [27] (A $<$ 0.05) using *N,N′*-di(2,6-diisopropylphenyl)-perylene-3,4 : 9,10-tetracarboxylic acid bisimide (Φ_{fl} = 1.00 in chloroform) [28] as reference. Cyclic voltammetry (CV) was performed with a standard commercial electrochemical analyzer in a three-electrode single-compartment cell under argon atmosphere. Dichloromethane (HPLC grade) was used as solvent and was dried over calcium hydride and degassed prior to measurement. The supporting electrolyte tetrabutylammonium hexafluorophosphate was recrystallized from ethanol/water and dried in high vacuum. The measurements were carried out at a concentration of 10^{-4} M with ferrocene as internal standard for the calibration of potential. Working electrode: Pt disc; reference electrode: Ag/AgCl; auxiliary electrode: Pt wire.

*Crystal structure determination of **5a***

Single crystals of **5a** were obtained by recrystallization from dichloromethane and methanol. The X-ray diffraction data for **5a** were collected on a Bruker X8 APEX diffractometer with a CCD area detector, using graphite-monochromatized MoK_α radiation. The structure was solved with Direct Methods, and expanded by means of Fourier techniques with the SHELX software package [29]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and included in structure factor calculations.

Crystal and structure determination data: $C_{40}H_{38}F_4N_2O_4$, orange needles, triclinic, space group $P\bar{1}$, a = 7.8097(4), b = 12.1717(7), c = 18.2517(11) Å, α = 75.605(1)°, β = 80.791(1)°, γ = 80.2050(1)°, V = 1643.3(2) Å^3, Z = 2, T = 193(2) K, ρ_{calc} = 1.388 g cm^{-3}, μ = 0.105 mm^{-1}, $F(000)$ =

720 e, *R1* = 0.1024, *wR2* = 0.1829, 5792 independent reflections [$2\theta \leq 50.0°$] and 467 parameters.

The CIF file of **5a** is available as supporting information in ref. [13].

Synthesis

*1,7-Difluoro-3,4:9,10-tetracarboxylic acid bisanhydride (**1**)*

A mixture of 11.4 g (43.2 mmol) of 18-crown-6 and 6.30 g (108.8 mmol) of potassium fluoride in 75 mL anhydrous sulfolane was heated to 160 °C, and at this temperature a suspension of 3.0 g (5.4 mmol) of 1,7-dibromoperylene bisanhydride that contained about 15 % of the 1,6-regioisomer in 75 mL anhydrous sulfolane was added within 30 min. The reaction mixture was stirred at 160 °C for 1 h and then cooled to 80 °C. Subsequently, 250 mL of water was added dropwise, and stirring was continued for additional 1 h at 80 °C. After cooling down to room temperature (r. t.), the precipitate was separated by vacuum filtration, washed several times with water, and dried under vacuum at 80 °C to give 2.47 g (quantitative) of a red solid.

^{1}H NMR spectroscopic analysis in D_2SO_4 revealed that this product consists of a mixture of 1,7- and 1,6-regioisomers (about 85 : 15). Because of signal overlapping, the ratio of the isomers could not be determined accurately. The crude product could not be purified since it is insoluble in organic solvents, and was used as such for further reactions. – ^{1}H NMR (500 MHz, D_2SO_4, TMS): δ = 9.0 (m, 2 H), 8.5 (m, 2 H), 8.3 (m, 2 H). (Values for the center of multiplets are given). – ^{13}C NMR (125 MHz, D_2SO_4, TMS): δ = 165.5 (s, CO), 164.4 (s, CO), 162.2 (d, CF, ^1J(C,F) = 266 Hz), 136.6 (d), 132.5 (d), 129.9 (s), 129.4 (s), 127.2 (d), 125.6 (s), 120.0 (s), 119,9 (s), 118.2(s). – MALDI-MS (neg. mode, DHB): *m*/*z* = 427.7 (calcd. 428.01 for $C_{24}H_6F_2O_6$, $[M]^-$).

*N,N′-Bis(α-methylbenzyl)-1,7-dibromo-3,4:9,10-tetracarboxylic acid bisimide (rac) (**2b**)*

A mixture of 2.00 g (3.63 mmol) 1,7-dibromo-3,4 : 9,10-tetracarboxylic acid bisanhydride, 0.5 mL α-methylbenzylamine (*rac*) and 10 mg $Zn(OAc)_2$ was stirred in 12 mL quinoline for 3 h at 130 °C. After cooling to r. t. the mixture was poured into 200 mL 2 N HCl, and the precipitate was filtered off and dried in vacuum. After column chromatography (CH_2Cl_2) 1.31 g (1.74 mmol, 48 %) of a dark red solid was obtained. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.46 (d, 2 H, ^3J(H,H) = 8.2 Hz), 8.90 (s, 2 H), 8.67 (d, 2 H, ^3J(H,H) = 8.1 Hz), 7.51 (m, 4 H), 7.34 (m, 4 H), 7.2 – 7.3 (m, 2 H), 6.54 (q, 2 H, ^3J(H,H) = 7.2 Hz), 2.02 (d, 6 H, ^3J(H,H) = 7.2 Hz). – HRMS (apci (pos. mode, chloroform)): *m*/*z* = 755.0178 (calcd. 755.0176 for $C_{40}H_{24}Br_2N_2O_4$, $[M+H]^+$).

*N,N′-Bis(α-methylbenzyl)-1,6,7,12-tetrachloro-3,4:9,10-tetracarboxylic acid bisimide (rac) (**3b**)*

A mixture of 3.00 g (5.66 mmol) 1,6,7,12-tetrachloro-3,4:9,10-tetracarboxylic acid bisanhydride, 7.5 mL (65.2 mmol) α-methylbenzylamine (*rac*) and 1.00 g $Zn(OAc)_2$ were stirred in 65 mL quinoline at 180 °C for 4 h. After cooling to r. t. the mixture was poured into 300 mL 2 N HCl, and the precipitate was filtered off and dried in vacuum. After column chromatography (CH_2Cl_2) 3.70 g (5.03 mmol, 88 %) of a dark red solid was obtained. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (s, 4 H), 7.51 (m, 4 H), 7.34 (m, 4 H), 7.2 – 7.3 (m, 2 H), 6.54 (q, 2 H, ^3J(H,H) = 7.2 Hz), 2.01 (d, 6 H, ^3J(H,H) = 7.2 Hz). – HRMS (apci (pos. mode, chloroform)): *m*/*z* = 735.0414 (calcd. 735.0406 for $C_{40}H_{23}Cl_4N_2O_4$, $[M]^-$).

General procedure A (imidization)

A mixture of difluorinated perylene bisanhydride **1** [16], the respective amine and zinc acetate in quinoline was stirred at 180 °C under argon for 2 h. After cooling to r. t., the reaction mixture was poured into 2 N HCl and extracted with CH_2Cl_2. The organic layer was washed with 2 N HCl, and the solvent was removed in vacuum. The crude products were first purified by silica gel column chromatography and subsequently precipitated from CH_2Cl_2/methanol to give red-orange solids.

General procedure B (Halex process)

A mixture of dibrominated perylene bisimide **2** or tetrachlorinated perylene bisimide **3**, KF and 18-crown-6 (for **2**) or (*N,N′*-dimethylimidazolidino)-tetramethylguanidinium chloride (CNC^+) (for **3**) in sulfolane was stirred at 160 – 180 °C for 6.5 – 27 h under argon. The reaction was terminated by cooling and addition of 10 mL of water. The precipitate was separated by filtration, washed several times with water, and dissolved in CH_2Cl_2. The solution was dried over $MgSO_4$, and the product was purified by silica gel column chromatography. After removing the solvent under reduced pressure, the obtained solid material was re-dissolved in dichloromethane, precipitated by addition of methanol and dried in vacuum (60 °C, 10^{-3} mbar, 1 day).

*N,N′-Di(n-octyl)-1,7-difluoroperylene-3,4:9,10-tetracarboxylic acid bisimide (**4a**)*

According to general procedure A, the reaction of 44.0 mg (103 μmol) 1,7-difluoroperylene-3,4:9,10-tetracarboxylic acid bisanhydride (**1**), 78.1 mg (604 μmol) 1-*n*-octylamine and 20.0 mg $Zn(OAc)_2$ in 5 mL quinoline afforded after column chromatography ($CHCl_3$: *n*-hexane = 4 : 1, and 7 : 3) 9 mg (14 μmol, 13 %) of **2a** as an orange solid.

Details according to general procedure B were reported previously [13]. – M. p. 335 – 338 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.13 (m, 2 H), 8.74 (m, 2 H), 8.51 (m, 2 H), 4.21 (m, 4 H), 1.77 (m, 4 H), 1.49 – 1.21 (m, 20 H), 0.88 (t, 6 H, ^3J(H,H) = 6.8 Hz). – ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −102.99 (m). – HRMS (apci (pos. mode, chloroform)): *m/z* = 650.2947 (calcd. 650.2962 for $C_{40}H_{40}F_2N_2O_4$, $[M]^-$). – UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}, $M^{-1}cm^{-1}$) = 508 nm (81300), 474 (48400), 444 (17300). – Fluorescence (CH_2Cl_2): λ_{max} = 514 nm, fluorescence quantum yield Φ_{fl} = 1.00. – CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/ Fc^+): $E_{1/2}$ (PBI/PBI^-) = −1.04 V, $E_{1/2}$ (PBI^-/PBI^{2-}) = −1.26 V.

*N,N′-Bis(α-methylbenzyl)-1,7-difluoro-3,4:9,10-tetracarboxylic acid bisimide (rac) (**4b**)*

a) According to general procedure A, the reaction of 100 mg (0.233 mmol) 1,7-difluoroperylene-3,4 : 9,10-tetracarboxylic acid bisanhydride (**1**), 200 mg (1.65 mmol) 1-phenylethylamine and 50.0 mg $Zn(OAc)_2$ in 12 mL quinoline afforded after column chromatography (CH_2Cl_2 : pentane = 4 : 1) 40.0 mg (63.0 μmol, 27 %) of **4b** as an orange solid.

b) According to general procedure B, the reaction of 651 mg (1.36 mmol) *N,N′*-di(1-phenylethyl)-1,7-dibromo-3,4:9,10-tetracarboxylic acid bisimide (**2b**), 650 mg KF and 200 mg 18-crown-6 in 13 mL sulfolane afforded after column chromatography (CH_2Cl_2) 330 mg (0.52 mmol, 60 %) of a red solid. – Melting range: 311 – 322 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.04 (m, 2 H), 8.63 (d, 2 H, ^3J(H,H) = 7.8 Hz), 8.46 (d, 2 H, ^3J(H,H) = 13.7 Hz), 7.51 (m, 4 H), 7.34 (m, 4 H), 7.2 – 7.3 (m, 2 H), 6.54 (q, 2 H, ^3J(H,H) = 7.2 Hz), 2.04 (d, 6 H, ^3J(H,H) = 7.2 Hz). – ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −103.07. – HRMS (apci (pos. mode, chloroform)): *m/z* = 635.1776 (calcd. 635.1777 for $C_{40}H_{25}F_2N_2O_4$, $[M+H]^+$). – UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}, $M^{-1}cm^{-1}$) = 510 nm (80900), 475 (47400), 445 (16600). – Fluorescence (CH_2Cl_2): λ_{max} = 518 nm, fluorescence quantum yield Φ_{fl} = 0.98. – CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/ Fc^+): $E_{1/2}$ (PBI/PBI^-) = −1.04 V, $E_{1/2}$ (PBI^-/PBI^{2-}) = −1.25 V.

*N,N′-Di(2-ethylhexyl)-1,7-difluoro-3,4:9,10-tetracarboxylic acid bisimide (rac) (**4c**)*

According to general procedure B, the reaction of 590 mg (1.36 mmol) *N,N′*-di(2-ethylhexyl)-1,7-dibromo-3,4:9,10-tetracarboxylic acid bisimide (**2c**), 590 mg KF and 295 mg 18-crown-6 in 20 mL sulfolane afforded after column chromatography (CH_2Cl_2) 270 mg (0.43 mmol, 46 %) of **4c** as a red solid. – M. p. 311 – 315 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.12 (m, 2 H), 8.68 (d, 2 H, ^3J(H,H) = 8.0 Hz), 8.49 (d, 2 H, ^3J(H,H) = 13.6 Hz), 4.15 (m, 4 H), 1.97 (m, 2 H), 1.2 – 1.5 (m, 16 H), 0.96 (m, 6 H), 0.90 (m, 6 H). – ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −102.90. – HRMS (apci (pos. mode, chloroform)): *m/z* = 650.2945 (calcd. 650.2951 for $C_{40}H_{40}F_2N_2O_4$, $[M]^-$). – UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}, $M^{-1}cm^{-1}$) = 508 nm (76600), 474 (45200), 444 (16000). – Fluorescence (CH_2Cl_2): λ_{max} = 516 nm, fluorescence quantum yield Φ_{fl} = 1.00. – CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/ Fc^+): $E_{1/2}$ (PBI/PBI^-) = −1.07 V, $E_{1/2}$ (PBI^-/PBI^{2-}) = −1.28 V.

*N,N′-Di(cyclohexyl)-1,7-difluoroperylene-3,4:9,10-tetracarboxylic acid bisimide (**4d**)*

According to general procedure A, the reaction of 40.0 mg (93.4 μmol) 1,7-difluoroperylene-3,4:9,10-tetracarboxylic acid bisanhydride (**1**), 86.7 mg (874 μmol) cyclohexylamine and 20.0 mg $Zn(OAc)_2$ in 5 mL quinoline yielded after column chromatography (CH_2Cl_2 : *n*-pentane = 4 : 1 and 3 : 2) 5.0 mg (8.47 μmol, 10 %) of **4d** as an orange solid.

For details according to general procedure B, see ref. [13]. – M. p. > 440 °C (decomposition). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.14 (dd, 2 H, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 5.2 Hz), 8.69 (d, 2 H, ^3J(H,H) = 7.7 Hz), 8.50 (d, 2 H, ^3J(H,F) = 13.8 Hz), 5.04 (m, 2 H), 2.56 (m, 4 H), 1.20 – 2.00 (m, 16 H). – ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −103.22 (m). – HRMS (ESI, CH_2Cl_2, acetonitrile 1 : 1): *m/z* = 590.2015 (calcd. 590.2023 for $C_{36}H_{28}N_2O_4F_2$, $[M]^-$). – UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}, $M^{-1}cm^{-1}$) = 508 nm (89000), 473 (52100), 444 (18300). – Fluorescence (CH_2Cl_2): λ_{max} = 513 nm, fluorescence quantum yield Φ_{fl} = 0.98. – CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/Fc^+): $E_{1/2}$ (PBI/PBI^-) = −1.08 V, $E_{1/2}$ (PBI^-/PBI^{2-}) = −1.29 V.

*N,N′-Di(3,4,5-tridodecylphenyl)-1,7-difluoroperylene-3,4:9,10-tetracarboxylic acid bisimide (**4e**)*

According to general procedure A, the reaction of 100 mg (233 μmol) 1,7-difluoroperylene-3,4:9,10-tetracarboxylic acid bisanhydride (**1**), 550 mg (920 μmol) 3,4,5-tridodecylaniline and 51.0 mg $Zn(OAc)_2$ in 13 mL quinoline yielded after column chromatography (CH_2Cl_2 : *n*-pentane = 1 : 1, 1 : 3 and 2 : 3) 45.0 mg (28.0 μmol, 12 %) of **4e** as an orange sticky solid. According to optical polarizing microscopy and powder X-ray analysis a soft crystalline phase is present at r.t. – M. p. 321 °C (ΔH_m = 22.4 kJ mol^{-1} according to DSC). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.22 (m, 2 H), 8.78 (d, 2 H, ^3J(H,H) = 7.8 Hz), 8.58 (d, 2 H, ^3J(H,F) = 13.5 Hz), 6.97 (s, 4 H), 2.66 (t, 12 H), 1.19 – 1.64 (m, 120 H), 0.88 (m, 18 H). – ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −102.83 (m). – HRMS (apci (neg. mode, chloroform)): 1587.2344 (calcd. 1587.2352 for $C_{108}H_{160}F_2N_2O_4$, $[M]^-$). – UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}, $M^{-1}cm^{-1}$) = 511 nm (96900), 476 (57300), 446 (20500). – Fluorescence (CH_2Cl_2): λ_{max} = 518 nm, fluorescence quantum yield Φ_{fl} = 0.35. – CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.*

Fc/Fc$^+$): $E_{1/2}$ (PBI/PBI$^-$) = −1.02 V, $E_{1/2}$ (PBI$^-$/PBI^{2-}) = −1.26 V.

*N,N′-Di(n-butyl)-1,7-difluoroperylene-3,4:9,10-tetracarboxylic acid bisimide (**4f**)*

According to general procedure B, the reaction of 100 mg (151 μmol) *N,N′*-di(*n*-butyl)-1,7-dibromo-3,4:9,10-tetracarboxylic acid bisimide (**2f**), 100 mg KF and 35 mg 18-crown-6 in 5 mL sulfolane afforded after column chromatography (CH_2Cl_2) 20 mg (37.2 μmol, 25 %) of **4f** as a red solid. – M. p. 375 – 377 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.19 (m, 2 H), 8.73 (d, 2 H, ^3J(H,H) = 7.8 Hz), 8.54 (d, 2 H, ^3J(H,F) = 13.5 Hz), 4.22 (m, 4 H), 1.70 – 1.80 (m, 4 H), 1.4 – 1.6 (m, 4 H), 0.90 – 1.20 (t, 6 H). – ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −103.12 (m). – HRMS (apci (pos. mode, acetonitrile, chloroform)): *m/z* = 538.1709 (calcd. 538.1710 for $C_{32}H_{24}F_2N_2O_4$, [M+H]$^+$). – UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}, M^{-1}cm^{-1}) = 508 nm (83300), 473 (49500), 444 (17400). – Fluorescence (CH_2Cl_2): λ_{max} = 515 nm, fluorescence quantum yield Φ_{fl} = 1.00. – CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/Fc$^+$): $E_{1/2}$ (PBI/PBI$^-$) = −1.04 V, $E_{1/2}$ (PBI$^-$/PBI^{2-}) = −1.25 V.

*1,7-Difluoro-3,4:9,10-tetracarboxylic acid bisimide (**4h**)*

612 mg (0.96 mmol) *N,N′*-di(1-phenylethyl)-1,7-difluoro-3,4:9,10- tetracarboxylic acid bisimide (**4b**) was dissolved in 450 mL dry CH_2Cl_2 and cooled to 0 °C. Then 2.5 mL boron tribromide was added, and the solution was stirred for 3 h at r. t. Afterwards CH_2Cl_2 was removed in vacuum, and the residue was poured into in a mixture of water and methanol. After treatment in an ultrasonic bath for 30 min the precipitate was filtered off and washed with water and CH_2Cl_2 to give 390 mg (0.92 mmol, 96 %) of a dark powder. – M. p. > 450 °C (subl.). – ^{1}H NMR (400 MHz, $CDCl_3$): insoluble compound. – MS (EI (pos. mode)): *m/z* = 426.0445 (calcd. 426.0447 for $C_{24}H_6F_4N_2O_4$, [M]$^+$).

*N,N′-Di(n-octyl)-1,6,7,12-tetrafluoroperylene-3,4:9,10-tetracarboxylic acid bisimide (**5a**)*

According to general procedure B, the reaction of 200 mg (270 μmol) *N,N′*-di(*n*-octyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid bisimide (**3a**), 154 mg KF and 17 mg CNC$^+$ in 6.5 mL sulfolane at 170 °C for 28 h afforded after column chromatography (CH_2Cl_2 : *n*-pentane = 3 : 2 and chloroform : *n*-pentane = 7 : 3) 5.2 mg (8.00 μmol, 3 %) of **5a** as an orange solid. – M. p. 237 – 242 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (t, 4 H, ^3J(H,F) = 5.2 Hz), 4.21 (t, 4 H, ^3J(H,H) = 7.2 Hz), 1.76 (m, 4 H), 1.47 – 1.24 (m, 20 H), 0.88 (t, 6 H, ^3J(H,H) = 6.9 Hz). – ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −94.27 (t, ^3J = 5.31 Hz). – HRMS (ESI (neg. mode, CH_2Cl_2, acetonitrile)): *m/z* = 686.2762 (calcd. 686.2768 for $C_{40}H_{38}F_4N_2O_4$, [M]$^-$). – UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}, M^{-1}cm^{-1}) = 500 nm (66000), 466 (41300), 438 (15000). – Fluorescence (CH_2Cl_2): λ_{max} = 509 nm, fluorescence quantum yield Φ_{fl} = 0.88. – CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/Fc$^+$): $E_{1/2}$ (PBI/PBI$^-$) = −0.98 V, $E_{1/2}$ (PBI$^-$/PBI^{2-}) = −1.22 V.

*N,N′-Bis(α-methylbenzyl)-1,6,7,12-tetrafluoroperylene-3,4:9,10-tetracarboxylic acid bisimide (**5b**)*

According to general procedure B, the reaction of 1.00 g (1.36 mmol) *N,N′*-bis(α-methylbenzyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid bisimide (**3b**), 1.25 g KF and 100 mg CNC$^+$ in 8 mL sulfolane at 160 °C for 5 h afforded after column chromatography (CH_2Cl_2 : *n*-pentane = 2 : 1) 80.0 mg (43.0 μmol, 9 %) of **5b** as an orange solid. Since 550 mg of starting material was re-isolated, the yield referring to the converted amounts of starting material **3b** is about 20 %. – M. p. 275 – 279 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (t, 4 H, ^3J(H,F) = 5.3 Hz), 7.34 (m, 4 H), 7.51 (m, 4 H), 7.26 (m, 2 H), 6.54 (q, 2 H, ^3J(H,H) = 7.3 Hz), 2.01 (d, 6 H, ^3J(H,H) = 7.0 Hz). – ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −94.29 (t, ^3J(H,F) = 5.3 Hz). – HRMS (apci (neg. mode, chloroform)): *m/z* = 670.1532 (calcd. 670.1521 for $C_{40}H_{22}F_4N_2O_4$, [M]$^-$). – UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}, M^{-1}cm^{-1}) = 503 nm (68400), 468 (43000), 440 (16300). – Fluorescence (CH_2Cl_2): λ_{max} = 514 nm, fluorescence quantum yield Φ_{fl} = 0.85. – CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/Fc$^+$): $E_{1/2}$ (PBI/PBI$^-$) = −0.98 V, $E_{1/2}$ (PBI$^-$/PBI^{2-}) = −1.21 V.

*N,N′-Di(2-ethylhexyl)-1,6,7,12-tetrafluoroperylene-3,4:9,10-tetracarboxylic acid bisimide (**5c**)*

According to general procedure B, the reaction of 300 mg (400 μmol) *N,N′*-di(2-ethylhexyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid bisimide (**3c**), 250 mg KF and 100 mg CNC$^+$ in 2.4 mL sulfolane at 160 °C for 2 h afforded after column chromatography (CH_2Cl_2 and CH_2Cl_2 : *n*-hexane = 7 : 3) 30.0 mg (43.0 μmol, 9 %) of **5c** as an orange solid. Since 150 mg of starting material **3c** was re-isolated, the yield referring to the converted amounts of starting material **3c** is about 18 %. – M. p. 222 °C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (t, 4 H, ^3J(H,F) = 5.2), 4.16 (m, 4 H), 1.95 (m, 2 H), 1.43 – 1.25 (m, 16 H), 0.97 – 0.88 (m, 12 H). – ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −94.27 (t, ^3J(H,F) = 5.3 Hz). – HRMS ((apci (neg. mode, chloroform)): *m/z* = 686.2783 (calcd. 686.2773 for $C_{40}H_{38}F_4N_2O_4$, [M]$^-$). – UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}, M^{-1}cm^{-1}) = 501 nm (71900), 466 (44900), 437 (16400). – Fluorescence (CH_2Cl_2): λ_{max} = 513 nm, fluorescence quantum yield Φ_{fl} = 1.00. – CV (CH_2Cl_2, 0.1 M TBAHFP, *vs.* Fc/Fc$^+$): $E_{1/2}$ (PBI/PBI$^-$) = −0.98 V, $E_{1/2}$ (PBI$^-$/PBI^{2-}) = −1.21 V.

*1,6,7,12-Tetrafluoro-3,4:9,10-tetracarboxylic acid bisimide (**5h**)*

A portion of 70.0 mg (104 μmol) of *N,N′*-di(1-phenylethyl)-1,6,7,12-tetrafluoro-3,4:9,10-tetracarboxylic acid bisimide (**5b**) was dissolved in 15 mL dry CH_2Cl_2 under argon and cooled to 0 °C. Then 200 μL boron tribromide was added and the solution was stirred for 3 h at r. t. CH_2Cl_2 was removed in vacuum, and the residue was poured into a mixture of water and methanol. After treatment in an ultrasonic bath for 30 min the precipitate was filtered off and washed with water and CH_2Cl_2 to obtain 45.0 mg (97.0 μmol, 93 %) of a red powder. – M. p. > 495 °C (decomp.). – This compound is not soluble in common solvents, thus no ^{1}H NMR spectrum could be measured. – HRMS (EI (pos. mode, chloroform)): *m/z* = 462.0255 (calcd. 462.0260 for $C_{24}H_6F_4N_2O_4$, $[M]^+$).

*1,6,7,12-Tetrafluoro-3,4:9,10-tetracarboxylic acid bisanhydride (**7**)*

A mixture of 55.0 mg (80.0 μmol) *N,N′*-di(2-ethylhexyl)-1,6,7,12-tetrafluoro-3,4:9,10- tetracarboxylic acid bisimide (**5c**), 300 mg KOH, 200 μL water and 10 mL butanol was stirred at 75 °C for 2 h. Then the mixture was poured into 200 mL acetic acid and stirred for 5 h at 100 °C. The mixture was diluted with water and the product precipitated over night. The precipitate was filtered off and dried in vacuum to obtain 34.0 mg (75.0 μmol, 94 %) of a dark powder. – M. p. > 450 °C (decomp.). – MS (EI (pos. mode)): *m/z* = 464.1 (calcd. 464.0 for $C_{24}H_4F_4O_6$, $[M]^+$).

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