Synthesis and Characterization of Pentafluorophenyl-Substituted Perylenebis(dicarboximides)

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Dedicated to Professor *Jean-Claude Bünzli* on the occasion of his 65th birthday

A series of 1,7-bis(perfluorophenyl)substituted perylenebis(dicarboximides) were synthesized by Cu-mediated *Ullmann* coupling of bromopentafluorobenzene with 1,7-dibromoperylenebis(dicarboximides) (*Scheme*). The photophysical and electrochemical properties of these dyes were investigated with regard to their potential use as building blocks in organic photovoltaics (OPV) or organic field-effect transistors (OFET).

Introduction. – In recent years, molecular semiconductors for electronics have approached the same level of importance as the traditionally used inorganic materials. There are some key advantages of the former approach as small molecules or conjugated polymers are inherently inexpensive and easily processible [1–4]. These features offer the potential of achieving the long-term goal of developing organic electronics that are inexpensive, flexible, and suitable for large-area applications, such as organic field-effect transistors (OFET) [1], organic photovoltaics (OPV) [5], and organic light-emitting diodes (OLED) [6–8].

In the field of organic semiconductors, p-type (hole-conducting) materials have been investigated extensively, and some have fulfilled many of the needs of industrial applications due to their high charge-carrier mobilities and easily scalable, high-speed printing processibility [9]. However, n-type (electron conducting) materials remain less investigated. In general, crucial issues in the development of n-type semiconductors include mobilities, air-stability, and solubility. In addition to these aspects, a functional n-type material should also exhibit high electron affinity to provide efficient electron injection to the interface of common metal electrodes.

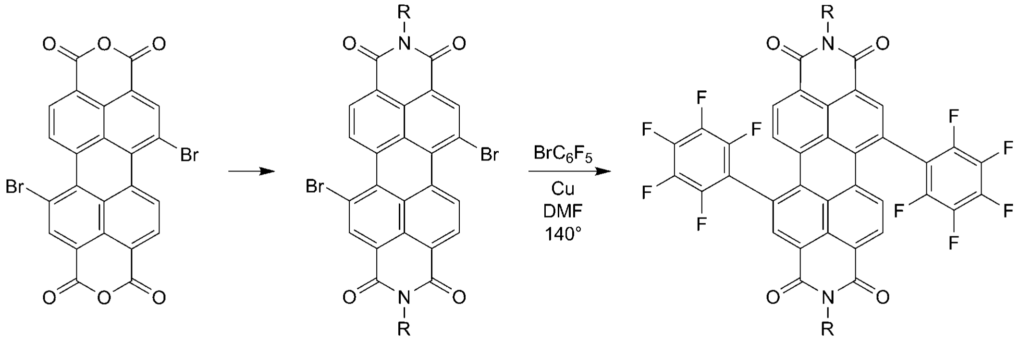
Perylenebis(dicarboximides) (= perylene diimides = PDIs) have been intensively investigated since the beginning of the last century. Their remarkable chemical stability and the variety of possible chemical functionalization, as well as their outstanding optical and electronic properties make PDIs outstanding and versatile candidates for applications in organic electronic devices, biochemistry, sensors, and single-molecule spectroscopy [10–12]. With two imide groups, PDIs present themselves as promising organic n-type materials [13]. Furthermore, the introduction of strong electron-withdrawing groups into the PDI scaffold has been developed as a strategy to improve the performance of PDI derivatives in n-channel FETs. Meanwhile, core-cyanated [14], core-fluorinated [15][16] and core-perfluoroalkylated [17] PDIs have been synthesized and exhibit excellent stability in air. Furthermore, it has been demonstrated that electron-withdrawing groups at the imide groups afford promising substituents for n-type arylene-based OFET materials (*e.g.*, naphthalenes [18] and perylenes [19]). Fluoroalkyl and fluorophenyl-functionalized imide groups are particularly noteworthy because of their strong influence on the LUMO level and the solid-state packing of PDI molecules [16][20].

The synthesis of core-phenyl-substituted PDI was up to now only accomplished by Pd-catalyzed *Suzuki* coupling of phenylboronic acids with 1,7-dibromo-PDIs [21][22]. The disadvantage of this route lies in the use of potentially difficult to synthesize molecules (*i.e.*, boronic acids or esters) and expensive Pd catalysts.

Herein, we report the first synthesis of core-phenyl-substituted PDI by the Cu-catalyzed *Ullmann* reaction. With the use of simple aryl halides and Cu bronze, *Ullmann* coupling offers a promising alternative to 'classical' *Suzuki* coupling towards core-phenyl-substituted PDIs. By employing bromopentafluorobenzene as a coupling reagent, we were able to synthesize PDIs with two strong electron-withdrawing groups in the 1,7-positions of the perylene. The PDIs **3a**–**3c** were synthesized in high yields. The chemical structures of the new perylene compounds were established by ^{1}H-, ^{13}C-, and ^{19}F-NMR, IR and mass spectroscopy. Their optical properties were investigated by UV/VIS and fluorescence spectroscopy. The electrochemical properties of the PDIs were characterized by cyclic voltammetry.

Results and Discussion. – *Synthesis.* The 1,7-dibromo-PDIs have already been established as very useful intermediates for the synthesis of a broad range of 1,7-substituted PDIs [21][23–25]. The imidisation of perylene-3,4,9,10-tetracarboxylic acid dianhydride (PDA; **1**) with octan-1-amine or 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctan-1-amine to form the bis-imide **2a** and **2b**, respectively, followed the published standard conditions and was performed in AcOH in good yields (75 and 78%, resp.) [20][26] (*Scheme*). Due to the very low nucleophilicity of pentafluoroaniline, the reaction to form **2c** required 1-methylpyrrolidin-2-one (NMP) as a solvent and

Scheme. *Synthesis of* **3a**–**3c**



1

2a R = octyl
2b R = $C_7F_{15}CH_2$
2c R = C_6F_5

3a R = octyl 65%
3b R = $C_7F_{15}CH_2$ 68%
3c R = C_6F_5 60%

a large excess of pentafluoroaniline (yield 22%) [27]. The purifications of **2a** – **2c** were carried out by column chromatography (silica gel, CH_2Cl_2).

The subsequent conversion into the 1,7-bis(pentafluorophenyl)perylenebis(dicarboximides) **3a** – **3c** was performed under *Ullmann* conditions [28] with Cu-bronze as catalyst. The Cu-bronze was activated, as others have noted that the activation of the Cu-bronze is crucial for the yield in *Ullmann* couplings [29] [30]. The PDIs **2a** – **2c** were suspended together with an excess of bromopentafluorobenzene (10 equiv.) and activated Cu-bronze in dry DMF (*Scheme*). After flushing with Ar for 15 min, the reaction mixtures were heated overnight at 140° in a sealed microwave tube. In this way, the PDIs **3a** – **3c** were obtained in good yields (60 – 68%) as red-orange solids.

Optical Properties. Fig. 1 shows the UV/VIS absorption spectra of PDIs **3a** – **3c** in $CHCl_3$. The bathochromic shifts of the absorbance of the pentafluorophenyl-substituted PDIs **3a** – **3c** are, compared to the parent PDIs **2a** – **2c**, remarkably small (2 nm, for details see *Table 1*). This can be explained by the steric restrictions of the bulky pentafluorophenyl substituents. These 1,7-substituents are forced into an orthogonal orientation with respect to the perylene core, minimizing the π-conjugative interaction (as can be seen in the molecular model in *Fig. 2*; structure produced with PM3 by Hyperchem 6) [22].

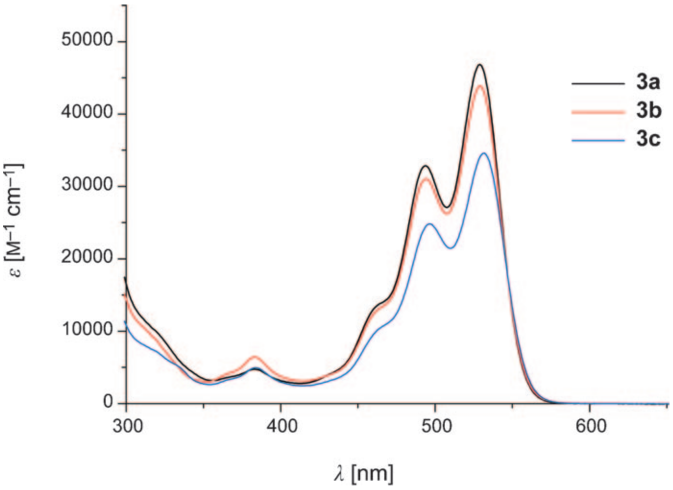


Fig. 1. *UV/VIS Spectra of* **3a** – **3c** *in* $CHCl_3$

Table 1. *Photophysical Properies of PDIs* **2a** – **2c** *and* **3a** – **3c** *in* $CHCl_3$

	λ_{max} (abs.) [nm]	ε [kM^{-1} cm^{-1}]	λ_{max} (fl.) [nm]	Φ_f [%]
2a	527	47.8	554	0.77
2b	527	46.1	552	0.80
2c	530	49.2	554	0.88
3a	529	46.8	555	0.93
3b	529	43.8	556	0.92
3c	532	34.6	559	0.95

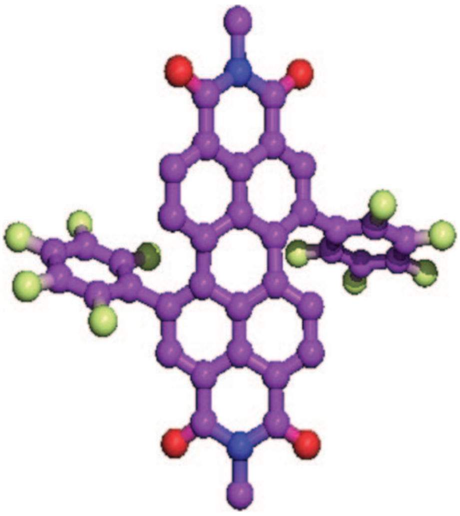


Fig. 2. *3D-Model of 1,7-bis(pentafluorophenyl)-substituted PDI*

The absorption maxima of the dyes **3a** – **3c** are quite similar as the effect of the imide substituent R on the absorption wavelength is minor. A significant spectral broadening of the absorption is observed when comparing the spectra of unsubstituted PDIs with **3a** – **3c**. This phenomenon can be explained by loss of the vibronic fine structure. This is caused by the strong twist of the perylene cores due to the space-demanding pentafluorophenyl substituents.

The PDIs **3a** – **3c** are also highly fluorescent. Their emission maximum lies in the range of 555 – 559 nm with remarkably high fluorescence quantum yields from 0.92 – 0.95 (for details see *Table 1*). The fluorescence of **3a** is, in comparison with the parent compound **2a**, only slightly red-shifted (1 nm), whereas the bathochromic shift is stronger in case of the PDIs **3b** and **3c** (4 and 5 nm). This might be explained by the additional electron-withdrawing effect of the fluorinated imide substituents.

Electrochemical Properties. Cyclic voltammetry (CV) was performed to investigate the energy levels of the frontier orbitals. In CV, the dyes **3a** – **3c** showed two reversible reduction waves, a typical pattern for PDIs [31]. Due to the limited potential range of the solvent (CH_2Cl_2), no oxidation wave was observed. The band gaps (E_g) were estimated from the onset of the absorption in the UV/VIS spectra (for results, see *Table 2*). The energy levels for the LUMO and HOMO of 1,7-unsubstituted PDIs lie near – 3.8 and – 5.8 eV, respectively. As our results show, the introduction of the 1,7-bis(pentafluorophenyl) substituents causes a significant decrease of the HOMO and LUMO levels (see *Table 2*). This is highly important for the use in OFETs. It should be noted that the imide substituents have also a profound influence on the energy levels. The LUMO level is also lowered by 0.10 eV for the *N*-(pentafluorophenyl)-substituted PDI **3c** in comparison with the *N*-alkyl-substituted PDI **3a**. The extremely low LUMO levels of **3a** – **3c** (– 4.21 to – 4.33) compared with other PDIs render these dyes promising candidates for use in OPV and OFETs. The low LUMO levels improve the charge driving force in OPV and also stabilize the FET device.

Table 2. *Half-Wave Reduction Potentials* E (*vs.* Fc/Fc$^+$) *of* **3a**–**3c** *Measured in* CH_2Cl_2

	E (PDI$^-$/PDI^{2-}) [V]	*E* (PDI/PDI$^-$) [V]	E_g [eV]	LUMO [eV]	HOMO [eV]
3a	– 0.77	– 0.57	2.23	– 4.23	– 6.40
3b	– 0.83	– 0.59	2.23	– 4.21	– 6.44
3c	– 0.66	– 0.47	2.20	– 4.33	– 6.25

Conclusion. – We established a convenient synthetic route for the synthesis of 1,7-bis(pentafluorophenyl)-substituted PDIs by *Ullmann* coupling. The PDIs **3a**–**3c** were obtained in high yields. Due to their significant lower LUMO level, as compared to unsubstituted PDI, these chromophores are promising n-type molecular semiconductors for use in either organic photovoltaic or organic field-effect transistors. OPV and OFET measurements are currently in progress.

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Experimental Part

General. The 1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid 3,4 : 9,10-dianhydride was provided by *BASF AG.* All other starting materials were purchased from *Aldrich*, *Acros*, *ABCR*, or *Lancaster*, and used as received. Cyclic voltammetry (CV) data were obtained with a standard commercial electrochemical analyzer in a three-electrode single cell. CV Measurements were carried out in dry CH_2Cl_2 under Ar with $Bu_4N(PF_6)$ as a supporting electrolyte. The experimental setup was calibrated with ferrocene. Potentials were obtained from the half-wave reduction potentials. UV/VIS Spectra: *Perkin-Elmer-Lambda-900* spectrophotometer; at r.t.; λ_{max} (log ε) in nm. Fluorescence spectra: *T&D TIDAS* diode-array spectrometer. IR Spectra: *Nicolet-730*-FT-IR spectrometer with a *Endurance* diamant ATR unit; $\tilde{\nu}$ in cm^{-1}. ^{1}H-, ^{13}C- and ^{19}F-NMR Spectra: *Bruker-Avance-300* and *Bruker-Avance-700* in CD_2Cl_2, with the residual H-atom resonance or the C-atom signal of the solvent as the internal standard; δ in ppm, *J* in Hz. FD-MS: *VG Instruments ZAB 2-SE-FPD*; in *m*/*z* (rel. %).

1,7-Dibromoperylene-3,4 : 9,10-bis(dicarboximides) (*=5,12-Dibromoanthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H,9H*)-tetrones*) **2a**–**2c**, were synthesized according to standard literature procedures.

Ullmann *Coupling of 1,7-Dibromoperylene-3,4 : 9,10-bis(dicarboximides) with Bromopentafluorobenzene: General Procedure.* The 1,7-dibromo-PDI (100 mg), bromopentafluorobenzene (10 equiv.), and activated Cu-bronze (150 mg) were suspended in dry DMF (0.7 ml). The mixture was flushed with Ar and stirred for 16 h at 140° in a sealed tube. After cooling at r.t., H_2O (15 ml) was added, and the reaction mixture was filtered and washed thoroughly with H_2O (50 ml). The filter cake was dried and washed out with CH_2Cl_2 (100 ml) to extract the crude product. The org. phase was filtered, and the solvent was evaporated *in vacuo.* The crude product was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether 1 : 1). Compound **3c** was additionally purified by prep. TLC (CH_2Cl_2/petroleum ether 1 : 1).

N,N′*-Bis(octyl)-1,7-bis(2,3,4,5,6-pentafluorophenyl)perylene-3,4 : 9,10-bis(dicarboximide)* (*=2,9-Dioctyl-5,12-bis(2,3,4,5,6-pentafluorophenyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H,9H*)-tetrone*; **3a**). Yield 65%. Orange-red solid. M.p. 205°. IR: 2955, 2925, 2856, 1703, 1663, 1601, 1590, 1522, 1496, 1462, 1434, 1412, 1401, 1350, 1331, 1246, 1089, 990, 813. ^{1}H-NMR (300 MHz, CD_2Cl_2): 8.55 (*s*, 2 H); 8.34 (*d*, *J* = 8.1, 2 H); 7.83 (*d*, *J* = 8.1, 2 H); 4.25–4.09 (*m*, 4 H); 1.79–1.64 (*m*, 4 H); 1.49–1.21 (*m*, 24 H); 0.87 (*t*, *J* = 6.6, 6 H). ^{13}C-NMR (75 MHz, CD_2Cl_2): 163.09; 162.98; 135.41; 134.95; 134.45; 131.16; 128.92; 128.41; 127.61; 124.24; 123.77; 123.73; 41.04; 32.21; 29.70; 29.60; 28.39; 27.48; 23.03; 14.24. ^{19}F-NMR

(471 MHz, CD_2Cl_2): -142.16 (*d*, $J=16.1$); -153.69 (*t*, $J=20.5$); -160.67 (*t*, $J=17.9$). FD-MS: 943.4 (100, $[M-3]^+$, $C_{52}H_{37}F_{10}N_2O_4^+$; calc. 943.3).

N,N′-*Bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-1,7-bis(2,3,4,5,6-pentafluorophenyl)perylene-3,4 : 9,10-bis(dicarboximide)* (*=2,9-Bis(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-5,12-bis(2,3,4,5,6-pentafluorophenyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H,9*H*)-tetrone*; **3b**). Yield 68%. Orange-red solid. M.p. 236°. IR: 2920, 2850, 1730, 1718, 1682, 1524, 1499, 1463, 1418, 1351, 1335, 1240, 1207, 1148, 1087, 1022, 991, 815. ^{1}H-NMR (300 MHz, CD_2Cl_2): 8.69 (*s*, 2 H); 8.51 (*d*, $J=8.1$, 2 H); 7.99 (*d*, $J=8.1$, 2 H); 5.06 (*t*, $J=15.7$, 4 H). ^{13}C-NMR (75 MHz, CD_2Cl_2): 162.87; 162.80; 136.25; 135.66; 135.13; 132.08; 129.15; 128.68; 128.02; 124.79; 123.01 (2 C); 30.08. ^{19}F-NMR (471 MHz, CD_2Cl_2): -81.09 (*d*, $J=9.1$); -115.20 (*s*); -121.77 (*s*); -122.15 (*s*); -122.86 (*s*); -123.64 (*s*); -126.29 (*s*); -140.82 (*d*, $J=16.3$); -151.93 (*t*, $J=20.5$); -159.18 (*t*, $J=17.9$). FD-MS: 1485.7 (75, M^+, $C_{52}H_{10}F_{40}N_2O_4^+$; calc. 1486.0), 1466.0 (100, $[M-F]^+$), 1446.3 (65, $[M-2F]^+$), 1427.4 (10, $[M-3F]^+$).

N,N′-*1,7-Tetrakis(2,3,4,5,6-pentafluorophenyl)perylene-3,4 : 9,10-bis(dicarboximide)* (*=2,5,9,12-Tetrakis(2,3,4,5,6-pentafluorophenyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H,9*H*)-tetrone*; **3c**). Yield 60%. Orange-red solid. M.p. >300°. IR: 2930, 1724, 1688, 1516, 1496, 1398, 1337, 1310, 1243, 1188, 1122, 1105, 1022, 989, 811, 801, 723, 698. ^{1}H-NMR (300 MHz, CD_2Cl_2): 8.70 (*s*, 2 H); 8.52 (*d*, $J=8.1$, 2 H); 8.03 (*d*, $J=8.1$, 2 H). ^{13}C-NMR (75 MHz, CD_2Cl_2): 161.14; 161.09; 136.08; 135.61; 135.07; 131.93; 129.20; 128.51; 127.82; 124.66; 122.63 (2 C). ^{19}F-NMR (471 MHz, CD_2Cl_2): -141.88 (*d*, $J=15.9$); -144.79 (*d*, $J=18.0$); -152.77 (*t*, $J=20.5$); -153.57 (*t*, $J=21.0$); -160.14 (*t*, $J=17.8$); -163.30 (*t*, $J=19.2$). FD-MS: 1054.4 (100, M^+, $C_{48}H_6F_{20}N_2O_4^+$; calc. 1054.5).

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