

Diaryl-Substituted Perylene Bis(imides): Synthesis, Separation, Characterization and Comparison of Electrochemical and Optical Properties of 1,7- and 1,6-Regioisomer

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Keywords: Conducting materials / Semiconductors / Regioisomers / Cross-coupling / Voltammetry / Perylene

A series of diaryl-substituted perylene bis(imides) (PBIs) containing electron-donating and -withdrawing aryl groups in the *bay* region (1-, 6-, 7- and/or 12-positions of the perylene core) were synthesized by Suzuki coupling reaction. The corresponding regioisomers, namely, 1,7- and 1,6-regioisomer, were separated from the mixture by conventional column chromatography without any need of recrystallization. All the individual regioisomers were fully characterized by ¹H NMR and HRMS spectroscopy. The compounds were studied by optical spectroscopy and electrochemical techniques. The

optical and electrochemical properties of 1,7-regioisomer are slightly different from the 1,6-regioisomer of the respective diaryl-PBI. Significant redshift and broadening of the absorption and emission maxima were observed in all synthesized PBIs depending upon the electronic nature of the attached aryl group. This is very first time such large series of 1,6-diarylperylene-tetracarboxydiimides with their corresponding 1,7-regioisomers were synthesized, separated, characterized and studied in detail.

Introduction

Organic photovoltaics based on small molecules received considerable attention in last few decades.^[1] Even though, modern inorganic solar cells dominate most of the commercial market, thin-film based organic semiconductors become attractive alternative owing to their low cost production, ease of fabrication, intergration into devices and large scale manufacturing.^[2] Organic semiconductors have also been applied in e.g. organic light-emitting diodes (OLEDs) in modern electronic devices, memories and field-effect transistors.^[3]

Perylene-3,4,9,10-tetracarboxydiimides [“perylene bis(imides)”, PBIs] are a unique class of molecules with remarkable optical, electronic and physical properties. High molar absorption coefficient, fluorescence quantum yield, high electron affinity and charge carrier mobility, ease of functionalization in addition to excellent chemical, thermal and photo stabilities establish PBIs as one of the most promising *n*-type organic semiconductor.^[4] Potential applications in photovoltaic cells^[5] and OLEDs,^[6] as organic field-effect transistors,^[7] photo-sensitizers,^[8] fluorescent dyes for single molecule spectroscopy^[9] and bio-imaging,^[10]

as xerographic photoreceptors in electro-photography^[11] and as liquid crystalline material,^[12] generated lot of interest in perylene chemistry.

Since, the parent PBA [perylene-tetracarboxylic bis(anhydride)] possess a very narrow absorption band (ca. 520 nm) and is insoluble in all organic solvents, the tuning of optical properties and improving the solubility of PBIs are the two major challenges before organic chemists. The broader absorption range is desirable because it helps to capture more photons for optical devices and higher solubility improves the processability. Tuning of the properties can be achieved by introducing functional groups to the *anhydride* or to the *bay* region of perylene bis(anhydride) (Figure 1). The introduction of substituents in the *anhydride* region improves the solubility of PBIs in common organic solvents but has negligible impact on electronic and optical properties, because the nodes of HOMO–LUMO lie at the long molecular axis; hence, substituents are not expected to induce any electronic interaction between the attached chromophore and the perylene core.^[4b,13] This makes introduction of functional groups in the *bay* region more attractive as it not only modifies the electronic and optical properties but also improves the solubility.

The landmark merging of two concepts was first reported by Böhm et al. in 1997,^[14] as they selectively dibrominated perylene bis(anhydride) and with subsequent imidation, which led to more soluble functional PBIs. This method has been used extensively by other over last decade for synthesizing bis(substituted) PBIs without any suspicion. Würthner et al. in 2004, however, demonstrated that the current bromination method produces two regioiso-

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejoc.201101825>.

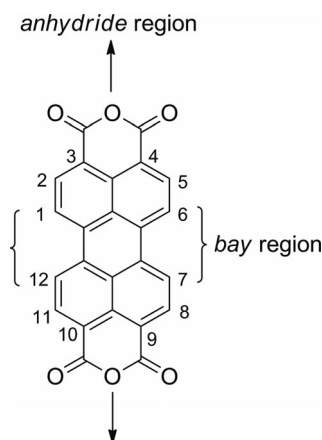


Figure 1. Chemical structure of perylenetetracarboxylic bis(anhydride) and different functional regions of perylene.

mers, namely, 1,7-dibromo-PBA and 1,6-dibromo-PBA in (3:1) ratio. Würthner and co-workers also developed a method (repeated recrystallization) to separate 1,7-regioisomer from the mixture after imidation.^[15] Unfortunately, recrystallization method is cumbersome and protracted (6–10 weeks for pure 1,7-regioisomer). Moreover, it is also not possible to obtain pure 1,6-dibromo-PBI by this method and consequently, the 1,6-bis(substituted) PBIs. On this basis, they postulated that previously reported 1,7-bis(substituted) PBIs might also be contaminated with 1,6-bis(substituted) PBIs. However, even after the clear demonstration, most of the research groups still neglected the presence of 1,6-regioisomer^[16] but there are also some notable exceptions.^[17] Recently, we showed that 1,7- and 1,6-bis(substituted) PBIs can have very different and interesting optical and electrochemical properties depending upon the electronic nature of the substituents attached.^[18]

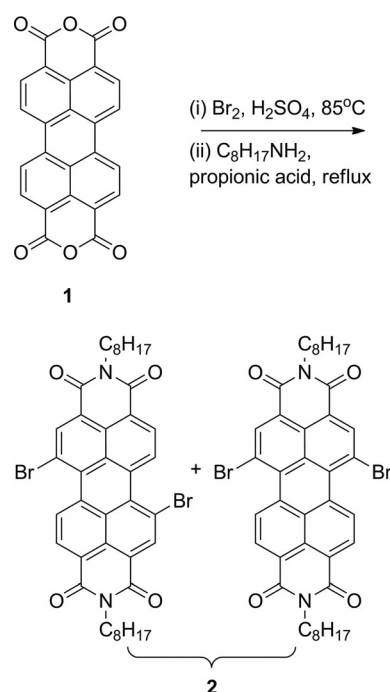
In this paper, we report the detailed synthesis, separation and characterization, as well as some optical and electrochemical properties of a series of bis(substituted) PBIs having electron-donating (ED) and electron-withdrawing (EW) aryl groups attached to the *bay* region of perylene (Figure 2). The Suzuki coupling reaction was employed to attach aryl groups to the perylene core. The introduction of

ED/EW groups is well known strategy to modify the HOMO–LUMO energy levels of the compound and thus, it's the electronic and optical properties,^[4d,19] which were compared for the 1,7- and 1,6-regioisomers of diaryl-PBIs in detail. We were able to isolate the individual regioisomers by conventional chromatographic method without any need of recrystallization. This work is the first time as such wide series of 1,6-diaryl-PBIs were synthesized, separated and their optical and electrochemical properties were compared with their respective 1,7-regioisomer.

Results and Discussion

Synthesis, Separation and Characterization

The syntheses of 1,7- and 1,6-diaryl-PBIs are shown in Schemes 1 and 2. The synthesis of dibromo-PBI **2** was done according to the literature procedure (Scheme 1).^[18,20]



Scheme 1. Synthesis of dibromo-PBI **2**.

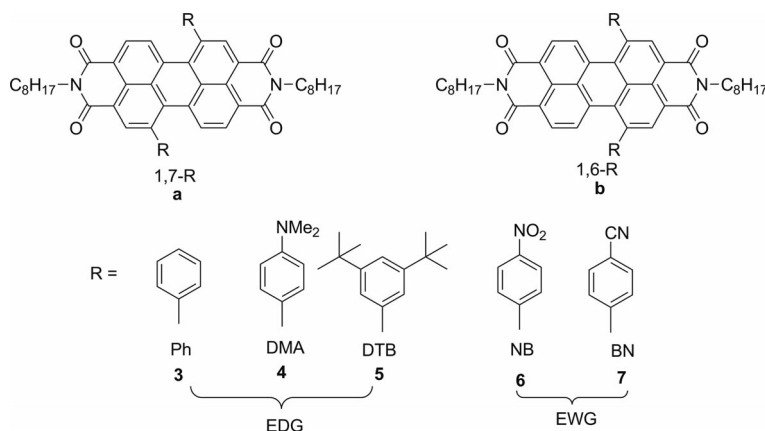
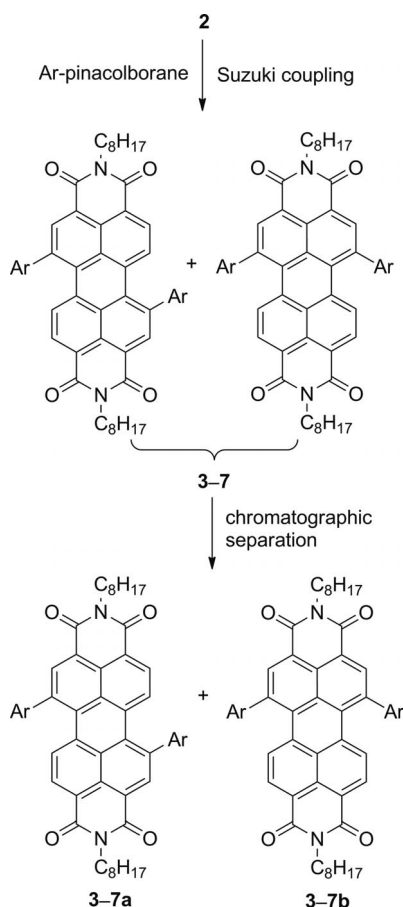


Figure 2. Structures of synthesized 1,7- and 1,6-diaryl-PBIs.

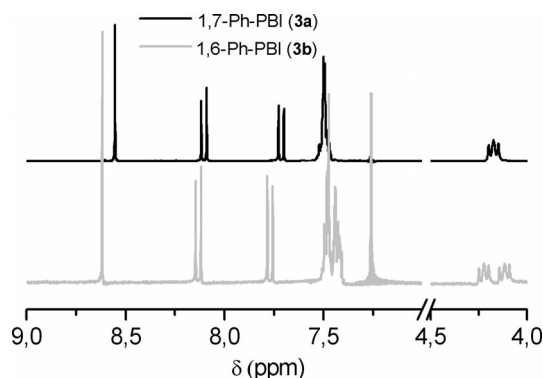


Scheme 2. Syntheses of diaryl-PBIs 3–7.

It should be mentioned that, **2** is a regioisomeric mixture of dibromo-PBI, namely, 1,7- and 1,6-dibromo-PBI in 3:1 ratio. Unfortunately, regioisomers of dibromo-PBI could not be separated using normal phase silica gel chromatography and used without further purification as a mixture of regioisomers. The syntheses of ED/EW diaryl-substituted PBIs **3–7** were done according to Scheme 2. Suzuki coupling reactions were employed between dibromo-PBI **2** and aryl-pinacolborane in a toluene/water biphasic system by using $\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (8 mol-%) catalyst [dppf = 1,1'-bis(diphenylphosphanyl)ferrocene] producing PBI derivatives **3–7**. Aryl-pinacolboranes were synthesized by the similar method reported earlier.^[19a] Even though, presence of steric hindrance in perylene *bay* region is expected, all the Suzuki couplings gave high yields (75–80%). The regioisomers were separated by normal silica gel (very slow running, 2–3 d) column chromatography. Three fractions were generally collected, the first one and the last one contained pure regioisomers and the middle one had a mixture of the two. Detailed separation methods are described in Exp. Section.

The pure regioisomers were consequently fully characterized by 300 MHz ^1H NMR and HRMS spectroscopy. Both 1,7- and 1,6-regioisomers show characteristic one singlet, and two doublets for perylene core protons. Significant difference in the chemical shift values were not observed (<

0.2 ppm). Unequivocal assignments of individual regioisomers were performed on the basis of the signal of methylene protons (in α -position to imide group) which appear ca. 4.2 ppm. For 1,7-regioisomers both the methylene groups are equivalent and appear as one triplet whereas the 1,6-regioisomers produce two distinct triplets for the same two methylene groups (Figure 3). Hence, we can unambiguously characterize 1,7- and 1,6-regioisomers by 300 MHz ^1H NMR spectroscopy. One notable exception is a pair of DMA-PBI (**4a**, **4b**) isomers. Both 1,6- and 1,7- compound showed identical signal of α -imide methylene protons, which made the assignment more difficult. However, the difference in chemical shifts for their perylene core signals is very similar to that of 1,6- and 1,7-Ph-PBI pair. Namely, the perylene proton signals of the faster isomer are evidently shifted to the lower field by 0.05 ppm. Taking into account this difference and the relative mobility of the two DMA-PBI isomers, we identified the faster fraction as 1,6-DMA-PBI, and the slower one as 1,7-DMA-PBI. It should be also mentioned that, on the contrary to the present hypothesis for the need of bulky *bay*-substituents for facile chromatographic separation, we did not use any excessively bulky aryls in the present synthetic work.^[18,21]

Figure 3. ^1H NMR spectra of 1,7- and 1,6-Ph-PBIs.

Albeit, it is possible to separate regioisomers by chromatographic methods, but needs repeated columns and final yield of individual regioisomers were only 20–35%, with large amount of regioisomeric mixtures.

It should be noted that, even though, dibromo-PBI **2** has 1,7- and 1,6-regioisomers in 3:1 ratio, almost all the Suzuki coupling reaction produce 1,7- and 1,6-regioisomer in a ratio of > 2:1 (from ^1H NMR analysis of regioisomeric mixture). This small regio-specificity might be due to less steric interaction between perylene *bay*-hydrogen atoms and aryl moieties for the 1,6-regioisomer than the 1,7-regioisomer.^[22]

Steady-State Absorption Measurements

The spectroscopic parameters of all synthesized PBI derivatives are summarized in Table 1. All the measurements were done in 1–2 μM chloroform solution to prevent strong perylene π - π aggregation.

Table 1. Optical properties, absorption maxima (λ_{max}), molar extinction coefficient (ϵ), emission maxima (λ_{F}), fluorescence quantum yield (Φ_{F}) and fluorescence life times (τ), of 1,7- and 1,6-regioisomers of diaryl-PBIs.

	λ_{max} [nm]	ϵ [mol ⁻¹ cm ⁻¹]	λ_{F} [nm]	Φ_{F}	τ [ns]
dioctyl-PBI	525	78600	535	1	4.32
3a	555	42200	609	0.61	7.25
3b	551	35400	617	0.56	6.82
4a	481, 647	38100, 22000	—	—	—
4b	470, 631	29400, 17300	—	—	—
5a	561	31700	634	0.37	8.26
5b	557	26600	641	0.35	7.53
6a	544	33300	586	0.48	6.32
6b	538	31900	592	0.43	6.14
7a	546	31600	591	0.46	6.21
7b	541	33800	600	0.49	6.53

Depending upon the nature of aryl substituents attached, the solutions of compounds exhibit various colours from dark red (DTB-PBI **5**) to deep green (DMA-PBI **4**). The absorption spectra of all PBIs are dominated by characteristic π - π^* transitions. The strongest absorption can be assigned to S_0 - S_1 electronic transitions while the shoulder band can be assigned to S_0 - S_2 transitions. In comparison to unsubstituted PBI (dioctyl-PBI), the absorption spectra show a significant bathochromic shift of 13–122 nm along with considerable band broadening. These results could be attributed to the inductive effect imposed by the aryl substituents on the perylene core. The negative inductive effect of 4-nitrophenyl or 4-cyanophenyl unit on compound **6**–**7** results in small red shift in their absorption spectra compared to other PBI derivatives.

The absorption spectra of 1,7- and 1,6-regioisomers of Ph-PBIs are shown in Figure 4 and others in the Supporting Information. For both the regioisomers the absorption spectra resemble each other but characteristic S_0 - S_1 electronic transition appear at 555 nm for 1,7-regioisomer **3a** and at 551 nm for 1,6-regioisomer **3b**. It can be clearly noted that, all regioisomeric pair has slightly different absorption spectra. Moreover, molar extinction coefficient is significantly lower for 1,6-regioisomer in comparison to 1,7-regioisomer of Ph-PBI. This trend is universal with notable exception for BN-PBI (**7a**, **7b**) pair (Table 1). It is also interesting to note that, DMA-PBI (**4a**, **4b**) pair shows broad absorption spectrum (see Supporting Information, Figure S1) covering almost whole visible solar spectrum with unusual dual absorption band, one peak at ca. 475 nm and another one at ca. 640 nm. While the first one can be attributed to charge transfer electronic transition from electron-rich dimethylaniline unit to electron-deficient perylene core while the later one usually is a π - π^* transition.^[17a] Small charge-transfer band can also be observed for DTB-PBI (**5a**, **5b**) pair (see Figure S1). From absorption spectra of all PBI derivatives it can be stated that diaryl-PBIs have significantly broader absorption in the visible solar spectrum which is definitely useful for building optical devices involving these derivatives.

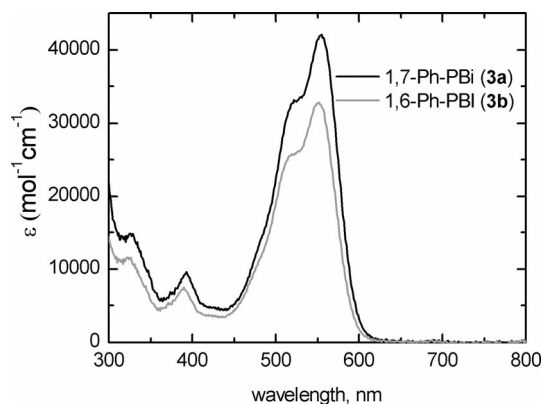


Figure 4. UV/Vis absorption spectra of Ph-PBI pair in chloroform.

Steady-State Emission and Life Time Measurements

All the synthesized compounds except DMA-PBI (**4a**, **4b**) pair are fluorescent and have broad emission in the 550–800 nm range as listed in Table 1. The fluorescence quantum yields Φ_{F} were determined using fluorescein (in 0.1 N NaOH, quantum yield 0.92) as a standard.^[12c] All the PBI derivatives have high fluorescence with quantum yields (0.35–0.61). Strong steric perylene core twisting by di-*t*Bu-phenyl unit results in considerable lower fluorescence quantum yield (0.35 for **5b**) compared to less steric crowding diaryl-PBIs. Fluorescence of Ph-PBI pair in chloroform is shown in Figure 5 and others in Supporting Information. Their emissions are almost mirror image of their S_0 - S_1 absorption bands with Stokes shift of ca. 60 nm. Regioisomeric pair of PBIs all show slight different fluorescence spectra. For 1,7-Ph-PBI the emission maxima is 609 nm and for 1,6-Ph-PBI is 617 nm. The DMA-PBI (**4a**, **4b**) pair does not show any fluorescence which mainly results from more charge-transfer in the excited state of the molecule.

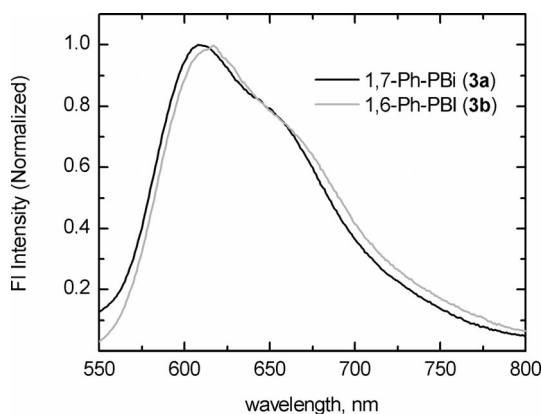


Figure 5. Fluorescence spectra of Ph-PBI pair in chloroform.

For the fluorescence lifetime measurements, the solutions of all the PBIs were excited at 483 nm and emission time profiles were collected at corresponding emission maximum. By fitting the experimental data, it is clear that all PBIs display mainly mono-exponential decay with time constants (τ) in the range of 6–9 ns depending upon the

aryl substituents. The fluorescence life times of all PBIs are summarized in Table 1. Fastest fluorescence decay was observed for PBI with EW aryls (for **6b**, $\tau = 6.14$ ns), whereas PBI with ED aryl showed the slowest decay (for **5a**, $\tau = 8.26$ ns). Hence, it can be said that fluorescence lifetimes are longer for the PBI with larger Stokes shifts. It can be also said that, fluorescence life times of 1,7-regioisomers were longer than 1,6-regioisomer of the respective diaryl-PBI.

Electrochemical Studies

Besides their excellent absorption and high fluorescence quantum yields, PBIs have also have useful electrochemical properties. The electrochemical properties of all diaryl-PBIs were determined by differential pulse voltammetry (DPV) method in benzonitrile containing 0.1 M TBABF₄ as supporting electrolyte. As the PBIs generally considered as *n*-type organic semiconductor, i.e. electron acceptor, hence, only the reduction potentials and calculated HOMO and LUMO energy levels (see the calculation details in the Exp. Section) are shown in Table 2. All the PBIs undergo successive reversible reductions to corresponding radical anions and dianions. The reduction potentials of all the PBI derivatives are comparable to the parent PBI (dioctyl-PBI, $E_{1\text{red}} = -1.02$ V). The reduction potentials can be directly correlated to the electronic nature of the aryl (ED/EW) groups attached to the perylene *bay* region. The reduction potentials of ED diaryl-PBIs are higher ($E_{1\text{red}} = -1.15$ V for **4a**) than EW diaryl-PBIs ($E_{1\text{red}} = -0.91$ V for **6a**), which indicate that upon reduction PBI radical anion is more stable for ED diaryl-PBIs. Their high reduction potentials indicate that they all are essentially strong electron acceptor. It is also evident that all the corresponding regioisomeric pair has slightly different reduction potentials, which suggests that this property can be accentuated when designing materials for optical devices.

Table 2. Reduction potentials (given in V vs. Fc/Fc⁺) and calculated HOMO–LUMO energy levels of 1,7- and 1,6-regioisomers of diaryl-PBIs.

	$E_{1\text{red}}$ [V]	$E_{2\text{red}}$ [V]	HOMO [eV]	LUMO [eV]	E_{opt}^g [eV]
Dioctyl-PBI	−1.02	−1.23	−6.12	−3.78	2.36
3a	−1.08	−1.28	−5.99	−3.72	2.33
3b	−1.11	−1.32	−5.95	−3.69	2.25
4a	−1.15	−1.35	−5.56	−3.65	1.91
4b	−1.13	−1.33	−5.63	−3.67	1.96
5a	−1.12	−1.32	−5.89	−3.68	2.21
5b	−1.14	−1.35	−5.88	−3.66	2.22
6a	−0.91	−1.18	−6.16	−3.89	2.27
6b	−0.94	−1.20	−6.16	−3.86	2.30
7a	−0.94	−1.19	−6.12	−3.86	2.26
7b	−0.96	−1.21	−6.13	−3.84	2.29

The calculated HOMO energy levels are in the range of −6.16 to −5.56 eV and LUMO energy levels are −3.89 to −3.65 eV, which means all the synthesized PBI derivatives are suitable for electron-transport materials in optoelectronic devices.

Conclusions

We have synthesized, separated and characterized an array of 1,7- and 1,6-regioisomers of diaryl-PBIs. The regioisomers are isolated using conventional normal phase silica gel column chromatography. The presented 1,6-diaryl-PBIs had previously been unreported in literature and have interesting optical and electrochemical properties. The described separation method of regioisomers is useful alternative as it does not involve prolonged repetitive recrystallization. The individual regioisomers were unambiguously identified by ¹H NMR spectroscopy by observing the chemical shift of four methylene protons next to imide nitrogens and by the chemical shifts of perylene core protons.

We also compared the photophysical properties of the regioisomers by spectroscopic and electrochemical techniques. Obtained results allow us to conclude that, 1,7- and 1,6-regioisomers of same diaryl-PBI possess slightly different electrochemical and spectroscopic properties which might be important while designing a system for optoelectronic applications. We hope these results will further motivate chemists to build functional PBIs using cross-coupling reactions.

All the synthesized PBI derivatives show broad absorption in visible solar spectrum. Specifically those absorbing in the red-to-NIR region could be useful to convert solar energy to electricity. Solid state properties and solar cell experiments involving these PBIs are also under investigation and the data will be published in due course as a separate manuscript. Moreover, molecular orbital (MO) calculation might be helpful to explain the apparent similar photophysical properties of 1,7- and 1,6-regioisomers and we continue to investigate these in near future.

Experimental Section

General: All the reagents utilized in the synthesis were purchased from Sigma–Aldrich Co. and used as received. The solvents were of HPLC grade and purchased from VWR and used without further purification. The sorbents for column chromatography (Silica 60, Silica 100), TLC plates (aluminium sheets coated with silica gel 60F₂₅₄) were purchased from Merck. NMR spectra were recorded with Varian Mercury 300 MHz spectrometer in CDCl₃ at room temperature. All chemical shifts are quoted relative to TMS ($\delta = 0.0$ ppm); δ values are given in ppm and *J* values in Hz. Mass spectra were measured with Waters LCT Premier XE ESI-TOF benchtop mass spectrometer.

If not otherwise indicated, all the spectroscopic measurements were carried out at room temperature. The absorption spectra were recorded with Shimadzu UV-2501PC spectrophotometer and the fluorescence spectra using a Fluorolog-3 (SPEX Inc.) Fluorimeter. The emission spectra were corrected using a correction function supplied by the manufacturer. Optical densities at excitation wavelengths were maintained at around 0.1 to avoid re-absorption. Fluorescence decays of the samples in the nanosecond and sub-nanosecond time scales were measured using a time-correlated single photon counting (TCSPC) system (PicoQuant GmbH) consisting of PicoHarp 300 controller and PDL 800-B driver. Fluorescence decays were measured at the wave-length of emission maximum. The signals were detected with a micro channel plate photo-

multiplier tube (Hamamatsu R2809U). The time resolution of the TCSPC measurements was 110 ps for 483 nm excitation wavelength (fwhm of the instrument response function).

Differential pulse voltammetry was carried out at room temperature under high-purity nitrogen flow and recorded using a potentiostat (Iviumstat Compactstat IEC 61326 Standard) controlled by an IBM computer with the software Iviumsoft (Version 1.752) in three-electrode single-compartment cell consisting platinum in glass as working electrode, Ag/AgCl as reference electrode and graphite as counter electrode. Benzonitrile containing 0.1 M TBABF₄ was used as solvent. The measurements were done under continuous flow of nitrogen. All potentials were internally referenced to the Fc/Fc⁺ couple. Under these conditions the Fc/Fc⁺ couple potential was determined to be +0.48 V and the data have been recalculated to the reference. The measurements were carried out in both directions: toward the positive and negative potential. The peak reduction and oxidation potentials were calculated as an average of the two scans. HOMO and LUMO energy levels were calculated by using commonly used procedure,^[19b] through the equation as follows:

LUMO = $-(E_{\text{red}} + 4.8)$ eV, in which E_{red} is the reduction potentials referenced against ferrocene.

HOMO = $(\text{LUMO} - E^{\text{opt}}_{\text{g}})$ eV, in which optical band gap, $E^{\text{opt}}_{\text{g}} = 1240/\lambda_{\text{max}}$.

The value for Fc with respect to the zero vacuum level is estimated as -4.8 eV, determined from -4.6 eV for the standard electrode potential E° of normal hydrogen electrode (NHE) on the zero vacuum level, and 0.2 V for Fc vs. NHE.

¹H NMR, ¹³C NMR, UV-visible absorption spectra and emission spectra are included in the Supporting Information.

1,7- and 1,6-Diphenyl-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimides (3): 200 mg (0.26 mmol) of dibromo-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimides **2**, 116 mg (0.57 mmol) of phenylpinacolborane, 15 mg (0.052 mmol) of tetrabutylammonium chloride and 17 mg (0.021 mmol) of PdCl₂(dppf)·CH₂Cl₂ were added to a two-phase mixture of toluene (12 mL) and aqueous 1 M potassium carbonate solution (12 mL). The reaction mixture was intensively stirred under argon atmosphere at 90 °C for 16 h. The organic layer was separated and the aqueous phase was extracted with toluene (3 × 20 mL). The organic layers were combined, washed with water (2 × 20 mL) and dried with anhydrous sodium sulfate and evaporated in vacuo. TLC of the reaction mixture often shows 2–4 spots. Starting material **2**, disubstituted-PBI, very small amount of mono-substituted and debrominated-PBI can be observed. But, the amount of other side products are small in most of the cases and can be easily separated before the isolation of individual regioisomers. The individual regioisomers are generally cannot be distinguished by their R_f values. The crude product was purified on silica 60 using chloroform as eluent. First, the orange band was collected and concentrated by rotary evaporation to afford the product (159 mg, 81%), which was found to be regioisomeric mixture of 1,7- and 1,6-diphenyl-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimides **3** in a 2:1 ratio (according to ¹H NMR analysis).

The regioisomers were separated by slow silica gel (silica 60) column chromatography over 2 d using dichloromethane ($R_f = 0.7$) as eluent. From the ¹H NMR analysis, first fraction was identified as 1,6-regioisomer, second fraction was mixture of regioisomers while the last fraction was 1,7-regioisomer.

1,7-Diphenyl-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimides (3a): Yield 36%. ¹H NMR (CDCl₃, 300 MHz, TMS): $\delta = 8.55$ (s,

2 H), 8.10 (d, $J = 8.6$ Hz, 2 H), 7.71 (d, $J = 8.6$ Hz, 2 H), 7.50 (m, 10 H), 4.18 (t, 4 H), 1.71 (t, 4 H), 1.22–1.35 (m, 20 H), 0.86 (distorted triplet, 6 H) ppm. ¹³C NMR (75 MHz, CDCl₃, TMS): $\delta = 163.6, 163.5, 142.2, 141.2, 135.4, 134.9, 132.6, 130.4, 129.5, 129.3, 129.4, 129.8, 127.7, 122.4, 122, 32, 29.6, 29.45, 28.4, 27.4, 22.9, 14.3$ ppm. HRMS ESI-TOF: m/z for C₅₂H₅₁N₂O₄ [M + H]⁺ calcd. 767.3849; found 767.3848.

1,6-Diphenyl-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimides (3b): Yield 25%. ¹H NMR (CDCl₃, 300 MHz, TMS): $\delta = 8.62$ (s, 2 H), 8.13 (d, $J = 8.6$ Hz, 2 H), 7.77 (d, $J = 8.6$ Hz, 2 H), 7.50 (m, 10 H), 4.23 (t, 2 H), 4.11 (t, 2 H), 1.71 (t, 4 H), 1.22–1.35 (m, 20 H), 0.85 (distorted triplet, 6 H) ppm. ¹³C NMR (75 MHz, CDCl₃, TMS): $\delta = 163.7, 163.4, 141.9, 141.4, 135.4, 134.8, 132.5, 130.3, 129.8, 129.3, 129.6, 129, 127.9, 122.4, 122, 32.4, 29.6, 29.3, 28.3, 27.4, 23, 14.5$ ppm. HRMS ESI-TOF: m/z for C₅₂H₅₁N₂O₄ [M + H]⁺ calcd. 767.3849; found 767.3874.

The synthesis and crude product separation of product **4–7** were done by the same method described for product **3**.

1,7- and 1,6-Bis[4-(dimethylamino)phenyl]-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimides (4): Reaction time 24 h. Yield 76%. The regioisomers were separated by slow silica gel (silica 60) column chromatography over 3 d using dichloromethane/ethanol, 200:1 ($R_f = 0.6$) as eluent. From the ¹H NMR analysis, first fraction was identified as 1,6-regioisomer, second fraction was mixture of regioisomers while the last fraction was 1,7-regioisomer.

1,7-Bis[4-(dimethylamino)phenyl]-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimide (4a): Yield 28%. ¹H NMR (CDCl₃, 300 MHz, TMS): $\delta = 8.58$ (s, 2 H), 8.13 (d, $J = 8.1$ Hz, 2 H), 7.94 (d, $J = 7.95$ Hz, 2 H), 7.39 (d, $J = 7.4$ Hz, 4 H), 6.76 (d, $J = 6.8$ Hz, 4 H), 4.18 (t, 4 H), 3.06 (s, 6 H), 1.72 (t, 4 H), 1.22–1.35 (m, 20 H), 0.87 (distorted triplet, 6 H) ppm. ¹³C NMR (75 MHz, CDCl₃, TMS): $\delta = 162.9, 162.8, 147.1, 146.5, 145.1, 140.4, 135.3, 134.6, 132.4, 130.1, 129.7, 129.5, 129.4, 129.2, 129.1, 128.8, 128.0, 124.7, 123.7, 123.6, 123.3, 121.8, 121.4, 29.5, 24.4, 24.3, 14.3$ ppm. HRMS ESI-TOF: m/z for C₅₂H₅₁N₂O₄ [M + H]⁺ calcd. 853.4693; found 853.4689.

1,6-Bis[4-(dimethylamino)phenyl]-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimide (4b): Yield 16%. ¹H NMR (CDCl₃, 300 MHz, TMS): $\delta = 8.63$ (s, 2 H), 8.15 (d, $J = 8.14$ Hz, 2 H), 7.99 (d, $J = 8$ Hz, 2 H), 7.41 (d, $J = 7.4$ Hz, 4 H), 6.76 (d, $J = 6.8$ Hz, 4 H), 4.17 (t, 4 H), 3.07 (s, 6 H), 1.73 (t, 4 H), 1.22–1.35 (m, 20 H), 0.87 (distorted triplet, 6 H) ppm. ¹³C NMR (75 MHz, CDCl₃, TMS): $\delta = 163.1, 162.9, 148, 146.6, 145.5, 140.5, 135.3, 134.6, 132.4, 130.2, 129.7, 129.5, 129.4, 129.2, 129, 128.9, 128.0, 124.5, 123.4, 123.6, 123.3, 121.9, 121.4, 29.6, 24.5, 24.2, 14.1$ ppm. HRMS ESI-TOF: m/z for C₅₂H₅₁N₂O₄ [M + H]⁺ calcd. 853.4693; found 853.4697.

1,7- and 1,6-Bis(3,5-di-*tert*-butylphenyl)-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimides (5): Reaction time 22 h. Yield 76%. The regioisomers were separated by slow silica gel (silica 60) column chromatography over 2 d using dichloromethane/hexane, 5:3 ($R_f = 0.55$) as eluent. From the ¹H NMR analysis, first fraction was identified as 1,6-regioisomer, second fraction was mixture of regioisomers, while the last fraction was 1,7-regioisomer.

1,7-Bis(3,5-di-*tert*-butylphenyl)-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimide (5a): Yield 32%. ¹H NMR (CDCl₃, 300 MHz, TMS): $\delta = 8.67$ (s, 2 H), 8.09 (d, $J = 8.2$ Hz, 2 H), 7.75 (d, $J = 8.2$ Hz, 2 H), 7.55 (t, 2 H), 7.37 (d, $J = 1.8$ Hz, 4 H), 4.17 (t, 4 H), 1.73 (t, 4 H), 1.38 (s, 36 H), 1.22–1.33 (m, 20 H), 0.87 (distorted triplet, 6 H) ppm. ¹³C NMR (75 MHz, CDCl₃, TMS): $\delta = 163.3, 163.2, 145.4, 141.8, 141.3, 135.6, 135.4, 133.1, 130.5, 130.4, 130.3, 130.1, 129.5, 129.4, 128.8, 128.7, 128.3, 124.1, 122, 121.9, 29.3,$

24.2, 24.1 14.1 ppm. HRMS ESI-TOF: m/z for $C_{52}H_{51}N_2O_4$ [$M + H$]⁺ calcd. 991.6353; found 991.6374.

1,6-Bis(3,5-di-*tert*-butylphenyl)-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimide (5b): Yield 17%. ¹H NMR ($CDCl_3$, 300 MHz, TMS): δ = 8.65 (s, 2 H), 8.08 (d, J = 8.2 Hz, 2 H), 7.70 (d, J = 8.2 Hz, 2 H), 7.52 (t, 2 H), 7.24 (d, J = 1.8 Hz, 4 H), 4.23 (t, 2 H), 4.11 (t, 2 H), 1.73 (t, 4 H), 1.38 (s, 36 H), 1.22–1.33 (m, 20 H), 0.87 (distorted triplet, 6 H) ppm. ¹³C NMR (75 MHz, $CDCl_3$, TMS): δ = 163.4, 163.2, 146, 141.9, 141.3, 135.6, 135.4, 133, 130.6, 130.4, 130.3, 130.2, 129.6, 129.4, 128.8, 128.7, 128.3, 124.4, 122.2, 121.9, 29.3, 24.3, 24.2 14.2 ppm. HRMS ESI-TOF: m/z for $C_{52}H_{51}N_2O_4$ [$M + H$]⁺ calcd. 991.6353; found 991.6381.

1,7- and 1,6-Bis(4-nitrophenyl)-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimides (6): Reaction time 3 h. Yield 80%. The regioisomers were separated by slow silica gel (silica 60) column chromatography over 3 d using chloroform/hexane, 6:1 (R_f = 0.5) as eluent. From the ¹H NMR analysis, first fraction was identified as 1,6-regioisomer, second fraction was mixture of regioisomers, while the last fraction was 1,7-regioisomer.

1,7-Bis(4-nitrophenyl)-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimide (6a): Yield 33%. ¹H NMR ($CDCl_3$, 300 MHz, TMS): δ = 8.61 (s, 2 H), 8.40 (d, J = 8.4 Hz, 2 H), 8.24 (d, J = 8.25 Hz, 4 H), 7.75 (m, 6 H), 4.18 (t, 4 H), 1.72 (t, 4 H), 1.38 (s, 36 H), 1.22–1.33 (m, 20 H), 0.87 (distorted triplet, 6 H) ppm. ¹³C NMR (75 MHz, $CDCl_3$, TMS): δ = 163.5, 163.4, 159, 141.4, 138, 136.6, 134.8, 130.1, 130, 129.5, 128.2, 127.3, 123, 121.6, 119.6, 106.6, 31.9, 29.6, 29.5, 29.4, 29.2, 28.5, 27.1, 22.6, 14.2 ppm. HRMS ESI-TOF: m/z for $C_{52}H_{51}N_2O_4$ (M)⁺ calcd. 856.3472; found 856.3530.

1,6-Bis(4-nitrophenyl)-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimide (6b): Yield 17%. ¹H NMR ($CDCl_3$, 300 MHz, TMS): δ = 8.62 (s, 2 H), 8.40 (d, J = 8.4 Hz, 2 H), 8.24 (d, J = 8.25 Hz, 4 H), 7.75 (m, 6 H), 4.20 (distorted triplet, 4 H), 1.73 (t, 4 H), 1.38 (s, 36 H), 1.22–1.33 (m, 20 H), 0.87 (distorted triplet, 6 H) ppm. ¹³C NMR (75 MHz, $CDCl_3$, TMS): δ = 163.5, 163.4, 159.1, 141.2, 138.1, 136.8, 135, 130.3, 129.9, 129.3, 128.1, 127.4, 123.2, 121.5, 119.7, 106.5, 31.8, 29.6, 29.5, 29.4, 29.3, 28.6, 27, 22.4, 14.2 ppm. HRMS ESI-TOF: m/z for $C_{52}H_{51}N_2O_4$ [$M + H$]⁺ calcd. 857.3550; found 857.3560.

1,7- and 1,6-Bis(4-cyanophenyl)-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimides (7): Reaction time 3 h. Yield 76%. The regioisomers were separated by HPTLC plate using chloroform/ethanol, 100:1 (R_f = 0.5) as eluent. From the ¹H NMR analysis, first fraction was identified as 1,7-regioisomer, while the second fraction was 1,6-regioisomer.

1,7-Bis(4-cyanophenyl)-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimide (7a): Yield 35%. ¹H NMR ($CDCl_3$, 300 MHz, TMS): δ = 8.58 (s, 2 H), 8.23 (d, J = 8.2 Hz, 2 H), 7.83 (d, J = 7.8 Hz, 4 H), 7.70 (m, 6 H), 6.76 (d, J = 6.8 Hz, 4 H), 4.18 (t, 4 H), 1.72 (t, 4 H), 1.22–1.35 (m, 20 H), 0.87 (distorted triplet, 6 H) ppm. ¹³C NMR (75 MHz, $CDCl_3$, TMS): δ = 163.3, 163.1, 146.4, 138.9, 134.5, 134.1, 132.4, 130.7, 130.2, 129.9, 129.2, 128, 122.6, 122.6, 118.1, 112.7, 77.4, 76.8, 76.5, 31.8, 29.5, 29.6, 29.4, 29.2, 29, 27.2, 22.6, 14.2 ppm. HRMS ESI-TOF: m/z for $C_{52}H_{51}N_2O_4$ [$M + H$]⁺ calcd. 817.3754; found 817.3759.

1,6-Bis(4-cyanophenyl)-*N,N'*-dioctyl-3:4,9:10-perylenetetracarboxydiimide (7b): Yield 19%. ¹H NMR ($CDCl_3$, 300 MHz, TMS): δ = 8.58 (s, 2 H), 8.21 (d, J = 8.2 Hz, 2 H), 7.81 (m, 4 H), 7.70 (m, 4 H), 7.59 (d, J = 7.6 Hz, 2 H), 4.17 (distorted triplet, 4 H), 1.71 (t, 4 H), 1.22–1.35 (m, 20 H), 0.86 (distorted triplet, 6 H) ppm. ¹³C NMR (75 MHz, $CDCl_3$, TMS): δ = 163.1, 162.9, 146.3, 138.9, 134.5, 134.2, 132.4, 130.6, 130.2, 130, 129.3, 128, 122.6, 122.4, 118,

112.7, 77.4, 76.8, 76.4, 31.8, 29.5, 29.6, 29.4, 29.3, 29.1, 27.2, 22.6, 14 ppm. HRMS ESI-TOF: m/z for $C_{52}H_{51}N_2O_4$ [$M + H$]⁺ calcd. 817.3754; found 817.3748.

Supporting Information (see footnote on the first page of this article): Absorption spectra of compounds 4–7, emission spectra of compounds 5–7, ¹H and ¹³C NMR spectra of compounds 3–7.

Acknowledgments

Financial support of Academy of Finland is greatly acknowledged.

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Received: December 20, 2011
Published Online: March 13, 2012