

# **1,7-** And **1,6-Regioisomers of Diphenoxy and Dipyrrolidinyl Substituted** Perylene Diimides: Synthesis, Separation, Characterization, and Comparison of Electrochemical and Optical Properties<sup>†</sup>

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1,7- And 1,6-regioisomers of N,N'-dioctyl-di(2,4-di-*tert*-butylphenoxy) perylene diimide (1,7-5 and 1,6-5) and N,N'-dioctyl-dipyrrolidinylperylene diimide (1,7-8 and 1,6-8) dyes are prepared. These 1,7and 1,6-regioisomers are successfully isolated from the regioisomeric mixture using conventional methods of separation and subsequently characterized, unambiguously, by 300 MHz <sup>1</sup>H NMR spectroscopy. This is the very first time when 1,6-regioisomers of diphenoxy and dipyrrolidinyl substituted perylene diimides are obtained in pure form. Optical and redox properties of these 1,6-regioisomers are examined extensively and compared with respective 1,7-regioisomers. The optical and electrochemical characteristics of diphenoxy substituted isomers, 1,7-5 and 1,6-5, were found to be virtually the same. However, quite unexpectedly, crucial differences were observed in the properties of regioisomers of dipyrrolidinyl substituted PDIs, 1,7-8 and 1,6-8. Differential pulse voltammetry revealed that 1,7-8 has better electron-donating ability compare to that of 1,6-8. Pronounced differences were observed in the optical properties too. In addition to the lowest energy absorption band at around 700 nm, 1,6-8 exhibits another strong absorption band at ca. 560 nm, and consequently, covers larger part of the visible region relative to that of 1,7-8. Steady-state emission and fluorescence lifetime studies, carried out in solvents of different polarities, revealed that regioisomer 1,6-8 has inherently lower fluorescence quantum yields and lifetimes compared to that of 1,7-8. This fundamental information on the redox and optical properties of 1,6- and 1,7regioisomers of diphenoxy and dipyrrolidinyl substituted PDIs will be of value especially for material chemists to develop more efficient systems and devices from bay-functionalized perylene diimides.

## Introduction

Perylene diimides (PDIs) represent a classical example of an inherently robust and outstandingly versatile family of organic compounds that have been extensively utilized for a wide range of high technology applications including field effect transistors,<sup>1</sup> logic gates,<sup>2</sup> organic light-emitting diodes,<sup>3</sup> organic solar cells,<sup>4</sup> optical switches,<sup>5</sup> photosensitizers,<sup>6</sup> sensors,<sup>7</sup> and so forth. These compounds have also been utilized as building blocks to construct light-harvesting

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arrays and artificial photosynthetic systems.<sup>8</sup> In light of their diverse and fascinating properties, such as easy fictionalization, excellent electron acceptor ability, high molar extinction coefficient in the visible region, and high fluorescence quantum yields, PDI dyes can also be considered as potential building blocks for many new applications.<sup>9</sup>

In the early nineties, there were two major challenges in front of material chemists working with imide-substituted PDIs (Figure 1). First, to increase the solubility of these dyes, which was low because of the planar structure of the perylenediimide core that facilitates the formation of  $\pi - \pi$  aggregates. Second, to tune the photophysical and redox properties, which are not affected by the chemical modification at the imide position because the frontier orbitals of these compounds have nodes at the imide nitrogen atoms.9a

For these reasons, the discovery of Böhm et al. (1997) that perylene-3,4,9,10-tetracarboxylic dianhyride (PTCDA) can be selectively dibrominated to yield regioisomerically pure

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Figure 1. Chemical structure of imide-substituted perylene diimide (PDI)

1,7-dibromoperylene-3,4,9,10-tetracarboxylic dianhyride and subsequently, after imidization, bromine atoms can also be exchanged by phenoxy and alkyne groups, established a landmark in the developed field of PDI compounds.<sup>10</sup> This synthetic work not only helped to improve the solubility of PDI-based systems but also opened an efficient way to tune their electrochemical, optical, and electronic properties through functionalization of the perylene core with electron donor or acceptor groups. Later on, these particular dibromination and imidization procedures were repeated in several laboratories for many years, without any skepticism, to prepare bay-functionalized PDIs with interesting properties.<sup>2,11</sup>

A comprehensive study was carried out by Würthner et al., in the year 2004, on the procedure used by Böhm et al. for the dibromination of PTCDA and subsequent imidization.<sup>12</sup> This study clearly revealed that dibromination reaction is not regioselective, rather, yields a regioisomeric mixture of 1,7- and 1,6-dibromoperylene dianhydride. Consequently, the subsequent imidization with cyclohexyl amine also yields regioisomeric mixture of 1,7- and 1,6-dibromoperylene diimides which can be observed only by 600 MHz <sup>1</sup>H NMR. They successfully separated, and also unequivocally characterized, regioisomerically pure N,N'-dicyclohexyl-1,7-dibromoperylene diimide from the regioisomeric mixture using repetitive recrystallization. This repetitive recrystallization method is the only existing method, until date, to obtain regioisomerically pure 1,7-dibromoperylene diimide. The method is cumbersome and it is not possible to obtain 1,6-dibromoperylene diimide in pure form. As a consequence, regioisomerically pure 1,6-difunctionalized PDIs could not be prepared. On the basis of their study, Würthner et al. also predicted that the previously reported 1,7-difunctionalized PDIs were contaminated with 1,6-regioisomer. However, even after this clear demonstration, a mixed response has been observed on this issue among the research groups.

Some of them took this issue into consideration,<sup>13</sup> whereas the majority of chemists still neglected the presence of 1,6-regioisomer.<sup>14</sup> To our biggest surprise, the presence of 1,6-regioisomer is completely ignored even in very recent reports.15

Among all substituents, linked to the PDI core until date by substitution of bromine atoms, phenoxy and pyrrolidinyl groups are of special interest. Basically, nonbay-substituted PDIs are excellent n-semiconductors but exhibit poor solubility because of  $\pi - \pi$  stacking when employed in complex systems. The phenoxy groups were attached at the bay region aiming to improve solubility of the system in common organic solvents while retaining the basic electron acceptor and optical characteristics.<sup>14c,16,13a</sup> On the other hand, attachment of electron-donating pyrrolidinyl groups makes the dye a good electron donor.<sup>11a</sup> Moreover, the lowest energy electronic transition moves to substantially longer wavelengths and acquires significant charge-transfer character.<sup>17</sup> Later on, these 1,7dipyrrolidinyl-substituted PDIs (green PDIs) have been used, extensively, as building blocks to prepare light harvesting and photosynthetic systems.<sup>18</sup> In addition, the green PDI has also been applied in dye-sensitized solar cells<sup>13b</sup> and photochromic systems.<sup>19</sup> Recently, prepared dyads of these chromophores with good electron acceptors, e.g., fullerene, which exhibited efficient photoinduced electron transfer from PDI excited singlet state to fullerene, are also a candidate for the photovoltaic devices.<sup>14e,17</sup> In view of their different absorption range in the visible region, these 1.7-diphenoxy and 1.7-dipyrrolidinyl-functionalized PDIs were also linked together to construct complex systems which exhibited better lightharvesting and charge-separation properties.<sup>18b,17</sup> In most of the cases, both 1,7-diphenoxy and 1,7-dipyrrolidinyl PDI derivatives were prepared from a regioisomeric mixture of 1,7- and 1,6-dibromoperylene diimide that was synthesized according to the same, above-mentioned, dibromination and imidization reactions described by

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Böhm et al., but dibromoperylene diimide and product were both claimed to be pure 1,7-regioisomer.<sup>11a,17,18b,18c</sup>

We report herein the synthesis, separation, and unambiguous characterization of the novel 1,6- and 1,7-regioisomers of diphenoxy and dipyrrolidinyl substituted PDI dyes. This article also includes a detailed comparative study of optical and electrochemical properties of both sets of regioisomers (1,7-5 & 1,6-5 and 1,7-8 & 1,6-8) in different solvents. Electrochemical characteristics of these isomers were investigated using differential pulse voltammetry, whereas optical properties were examined by steady-state UV-vis absorption and fluorescence spectroscopy. In addition, fluorescence lifetime measurements were also undertaken. This is the very first time when 1,6-regioisomer of either diphenoxy or dipyrrolidinyl-functionalized perylenediimide is obtained in pure form and investigated in detail.

# **Experimental Section**

**Materials.** All the reagents utilized in the synthesis were purchased from Sigma-Aldrich Co. and used as received. Dibromoperylene-3,4,9,10-tetracarboxylic dianhydride **2** was synthesized according to the literature procedure. <sup>12</sup> The solvents were of HPLC grade and purchased from VWR and used without further purification. Thin-layer chromatography (TLC) was done on aluminum sheets precoated with Silica 60 F<sub>254</sub>. The purification and isolation of the products were performed by column chromatography on silica gel 60, mesh size 40–63  $\mu$ m or silica gel 100, mesh size 63–200  $\mu$ m. The sorbents for column chromatography and TLC plates were purchased from Merck.

Instrumentation and Characterization. The proton and carbon NMR spectra were recorded with Varian Mercury 300 MHz spectrometer in CDCl<sub>3</sub> at room temperature. All chemical shifts are quoted relative to TMS ( $\delta = 0.0$  ppm);  $\delta$  values are given in ppm and J values in Hz. High-resolution mass spectra were measured with Waters LCT Premier XE ESI-TOF benchtop mass spectrometer. To obtain accurate mass value, we simultaneously infused the solution of the reference compound (leucine enkephaline) with analyte, and processed the experimental spectra according to the routine of accurate mass measurements (peak centering and lock-mass TOF correction). Differential pulse voltammetry was performed with Faraday MP, Obbligato Objectives Inc., in three-electrode single-compartment cell consisting of platinum in glass as working electrode, Ag/AgCl as reference electrode and a graphite rod as counter electrode. During the measurements, the values of pulse height, pulse width, and step voltage were set to 20 mV, 20 ms, and 2.5 mV, respectively. Benzonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate was used as solvent. The measurements were done under continuous flow of nitrogen. A  $Fc/Fc^+$  couple was used as an internal standard. The measurements were carried out in both directions: toward the positive and negative potential. The reduction and oxidation potentials were calculated as an average of the two scans.

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. Fluorescence quantum yields were determined relative to fluorescein ( $\Phi_f = 0.92$  in 0.1 N NaOH aqueous solution) and cresyl violet ( $\Phi_f = 0.54$  in methanol).<sup>20</sup> The given quantum yields are averaged from values measured at three different excitation wavelengths. Optical densities at excitation wavelengths were maintained at around 0.1 to avoid reabsorption.

Fluorescence decays of the samples in the nanosecond and subnanosecond 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. The diphenoxy substituted PDIs (1,7-5 and 1,6-5) were excited with the pulsed diode laser head LDH-P-C-485 at 483 nm, whereas, dipyrrolidinyl substituted PDIs (1,7-8 and 1,6-8) were excited with the pulsed diode laser head LDH-P-C-650 at 648 nm. Fluorescence decays were measured at the wavelength of emission maximum. The signals were detected with a micro channel plate photomultiplier tube (Hamamatsu R2809U). The time resolution of the TCSPC measurements was 110 ps for 483 nm excitation wavelength and 80 ps for 648 nm excitation wavelength (fwhm of the instrument response function).

Synthesis of N,N'-Dioctyl-dibromoperylene-3,4,9,10-tetracarboxy diimide (3). Crude dibromoperylene-3,4,9,10-tetracarboxylic dianhydride 2 (2.5 g, 4.54 mmol), obtained by the dibromination of PTCDA 1, was suspended in propionic acid (250 mL) and subsequently *n*-octylamine (11.7 g, 90.76 mmol) was added. The reaction mixture was refluxed under stirring for 48 h, cooled to room temperature and poured into water (200 mL). The precipitate was filtered off, thoroughly washed with several portions of water, and dried to give the crude product. The crude product was chromatographed on silica 60 with CH<sub>2</sub>Cl<sub>2</sub> to yield regioisomeric mixture of N,N'-dioctyl-1,7- and 1,6-dibromoperylene diimides 3 (2.7 g, 77%) as major product and N,N'-dioctyl-1,6,7-tribromoperylene diimide 4 (0.037 g, 1%) as a minor product.

*N*,*N***-Dioctyl-1,7- and 1,6-Dibromoperylene Diimides (3).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 9.36$  (d, J = 8.2 Hz, 2H), 8.80 (s, 2H), 8.59 (d, J = 8.2 Hz, 2H), 4.17 (t, J = 7.6 Hz, 4H), 1.72 (m, 4H), 1.49–1.18 (m, 20H), 0.88 (t, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 163.0$ , 162.5, 138.2, 133.1, 132.9, 130.2, 129.3, 128.6, 127.1, 123.3, 122.9, 121.0, 41.1, 32.0, 29.6, 29.5, 28.3, 27.4, 22.9, 14.4. MS (ESI-TOF): [M]<sup>+</sup> calcd for C<sub>40</sub>H<sub>40</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>4</sub>, 772.1339; found, 772.1321.

*N*,*N*'-Dioctyl-1,6,7-tribromoperylene Diimide (4). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 9.38$  (d, J = 8.1 Hz, 1H), 8.87 (s, 1H), 8.78 (s, 2H), 8.65 (d, J = 8.1 Hz, 1H), 4.19 (m, 4H), 1.74 (m, 4H), 1.49–1.20 (m, 20H), 0.88 (t, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 162.8$ , 162.5, 162.1, 162.0, 137.4, 136.6, 136.5, 133.3, 133.2, 131.4, 131.2, 130.7, 129.9, 129.4, 127.9, 125.9, 125.1, 124.5, 124.0, 123.3, 122.9, 122.8, 122.5, 121.6, 41.2, 41.0, 29.6, 29.5, 28.3, 28.2, 27.3, 23.0, 14.3. MS (ESI-TOF): [M]<sup>-</sup> calcd for C<sub>40</sub>H<sub>39</sub>Br<sub>3</sub>N<sub>2</sub>O<sub>4</sub>, 852.0428; found, 852.0475.

Synthesis of N,N-Dioctyl-1,7- and 1,6-Di(2,4-di-*tert*-butylphenoxy)perylene-3,4,9,10-tetracarboxy Diimide (1,7-5 and 1,6-5). A mixture of 2,4-di-*tert*-butylphenol (80.0 mg, 0.38 mmol), K<sub>2</sub>CO<sub>3</sub> (107 mg, 0.78 mmol) and 18-Crown-6 (401 mg, 1.55 mmol), in dry toluene (30 mL), was stirred for 20 min under argon and subsequently N,N'-dioctyl-dibromoperylene-3,4,9,10-tetra-carboxy diimide **3** (78 mg, 0.10 mmol) was added. The reaction mixture was stirred for 4 h at 90 °C under argon atmosphere. After being cooled to room temperature, the solvent was removed by rotary evaporation. The solid residue was thoroughly washed with several portions of water and dried. The crude product was dissolved in chloroform and purified twice by column chromatography on

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silica 60 using chloroform as eluent to afford the regioisomeric mixture of product (72 mg, 72.4%).

The regioisomers were isolated on the basis of their different solubility in toluene. In a typical procedure, 400 mg of 70:30 mixture of N,N'-dioctyl-1,7- and 1,6-di(2,4-di-*tert*-butylphenoxy)-perylene diimide was taken in 40 mL of toluene and sonicated for 10 min. The 1,6-isomer completely dissolved in toluene, whereas, the 1,7-isomer remained as suspension. Within few hours, the suspension of 1,7-isomer settled at the bottom of the vial. The precipitate was filtered off and dried. <sup>1</sup>H NMR spectrum of precipitate showed the presence of only 13% of 1,6-isomer. The procedure was repeated twice with 15 and 10 mL of toluene to afford pure 1,7-isomer (160 mg, 40%). The mother liquor, which contained 140 mg of 89:11mixture of 1,6- and 1,7-isomer (85 mg, 21%) was obtained by repetition of above-mentioned separation process two times with 10 mL of toluene.

*N*,*N*<sup>'</sup>-Dioctyl-1,7-di(2,4-di-*tert*-butylphenoxy)perylene-3,4,9,10tetracarboxy Diimide (1,7-5). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 9.65$  (br d, J = 28.4 Hz, 2H), 8.56 (d, J = 8.3 Hz, 2H), 8.30 (s, 2H), 7.58 (d, J = 2.4 Hz, 2H), 7.24 (br, 2H), 6.86 (br d, J =50.1 Hz, 2H), 4.13 (t, J = 7.6 Hz, 4H), 1.71 (m, 4H), 1.50 (d, J =23.5 Hz, 18H), 1.39 (s, 18H), 1.37–1.18 (m, 20H), 0.86 (t, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 163.7$ , 163.4, 156.1, 151.7, 148.1, 140.8, 133.9, 130.3, 129.8, 128.3, 125.4, 125.2, 125.1, 124.4, 124.1, 122.2, 120.3, 40.9, 35.3, 35.0, 32.0, 31.9, 30.8, 29.9, 29.5, 29.4, 28.3, 27.4, 22.8, 14.4. MS (ESI-TOF): [M + Na]<sup>+</sup> calcd for C<sub>68H<sub>82</sub>N<sub>2</sub>O<sub>6</sub>Na, 1045.6071; found, 1045.6035.</sub>

*N*,*N***-Dioctyl-1,6-di**(2,4-di-*tert*-butylphenoxy)perylene-3,4,9,10tetracarboxy diimide (1,6-5). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 9.60$  (br d, J = 27.5 Hz, 2H), 8.63 (d, J = 8.6 Hz, 2H), 8.20 (s, 2H), 7.58 (d, J = 2.4 Hz, 2H), 7.25 (br, 2H), 6.85 (br d, J = 35.2Hz, 2H), 4.19 (t, J = 7.6 Hz, 2H), 4.07 (t, J = 7.5 Hz, 2H), 1.70 (m, 4H), 1.49 (d, J = 14.7 Hz, 18H), 1.39 (s, 18H), 1.37–1.18 (m, 20H), 0.86 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta =$ 163.9, 163.1, 157.2, 151.8, 148.2, 140.9, 134.1, 131.4, 128.9, 127.3, 127.1, 125.4, 125.2, 124.1, 123.2, 122.7, 122.4, 121.3, 120.3, 41.1, 40.8, 35.3, 35.0, 32.1, 32.0, 31.8, 30.9, 29.6, 29.5, 29.4, 28.4, 28.2, 27.4, 27.3, 22.9, 22.8, 14.4, 14.2. MS (ESI-TOF): [M + Na]<sup>+</sup> calcd for C<sub>68</sub>H<sub>82</sub>N<sub>2</sub>O<sub>6</sub>Na, 1045.6071; found, 1045.6075.

Synthesis of N,N-Dioctyl-1,7- and 1,6-Di(4-tert-butylphenoxy)perylene-3,4,9,10-tetracarboxy Diimide (6). Prepared from 4-tertbutylphenol (62.4 mg, 0.42 mmol), K<sub>2</sub>CO<sub>3</sub> (111 mg, 0.83 mmol) and 18-Crown-6 (422 mg, 1.66 mmol) and N,N'-dioctyl-dibromoperylene-3,4,9,10-tetracarboxy diimide 3 (80 mg, 0.104 mmol) according to the procedure described above for compound 5. The crude product was chromatographed on silica 60 using chloroform as eluent to afford the regioisomeric mixture of product 6 (78.4 mg, 83%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 9.40$  (d, J =8.5 Hz, 1.4H), 9.33 (d, J = 8.5 Hz, 0.6H), 8.43 (d, J = 8.5 Hz, 0.7H), 8.40 (d, J = 8.5 Hz, 1.3H), 8.19 (s, 1.3H), 8.12 (s, 0.6H), 7.46 (d, J = 8.7 Hz, 4H), 7.08 (d, J = 8.7 Hz, 4H), 4.08 (t, J = 7.6 Hz, 400 Hz)4H), 1.69 (m, 4H), 1.38 (s, 18H), 1.32-1.21 (m, 20H), 0.86 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 163.4, 163.3, 162.9, 162.8,$ 156.6, 155.5, 152.7, 152.5, 148.6, 148.4, 133.4, 133.3, 131.1, 130.9, 130.1, 129.1, 128.8, 128.6, 127.6, 127.7, 127.4, 124.9, 123.8, 123.6, 123.5, 123.3, 122.4, 122.2, 122.1, 121.2, 119.6, 119.4, 40.9, 34.8, 32.1, 31.7, 29.6, 29.4, 28.3, 27.4, 22.9, 14.3. MS (ESI-TOF): [M + Na]<sup>+</sup> calcd for C<sub>60</sub>H<sub>66</sub>N<sub>2</sub>O<sub>6</sub>Na, 933.4819; found, 933.4824.

Synthesis of *N*,*N*-Dioctyl-1,7 and 1,6-Dipyrrolidinylperylene-3,4,9,10-tetracarboxy Diimide (1,7-8 and 1,6-8). *N*,*N*'-Dioctyldibromoperylene-3,4,9,10-tetracarboxy diimide 3 (2 g, 2.59 mmol) was dissolved in 150 mL of pyrrolidine. The reaction mixture was stirred at 55 °C under an argon atmosphere for 18 h. After being cooled to room temperature, solvent was evaporated under reduced pressure and solid residue was dissolved in chloroform. The crude product was purified on silica 60 using chloroform as eluent. First, the green band was collected and concentrated by rotary evaporation to afford the product (1.56 g, 80%), which was found to be regioisomeric mixture of 1,7- and 1,6-dipyrrolidinylperylene diimide in a 74:26 ratio (according to <sup>1</sup>H NMR analysis). The isomers were separated by column chromatography on silica 100 using DCM as eluent. First, a blue fraction was collected, and after that, green. From the <sup>1</sup>H NMR analysis, the blue fraction was identified as 1,6-dipyrrolidinylperylene diimide 1,6**-8**, whereas the green fraction was identified as 1,7-dipyrrolidinylperylene diimide 1,7**-8**.

*N*,*N*<sup>'</sup>-Dioctyl-1,7-dipyrrolidinylperylene-3,4,9,10-tetracarboxy Diimide (1,7-8). Yield = 1.15 g. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 8.36 (s, 2H), 8.31 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 4.21 (t, *J* = 7.5 Hz, 4H), 3.67 (br s, 4H), 2.74 (br s, 4H), 1.98 (br, 8H), 1.75 (m, 4H), 1.50–1.17 (m, 20H), 0.87 (t, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  = 164.3, 146.6, 134.3, 130.0, 126.8, 123.9, 122.2, 121.9, 120.9, 119.2, 118.2, 52.4, 40.8, 32.1, 29.7, 29.5, 28.5, 27.5, 26.1, 22.9, 14.4. MS (ESI-TOF): [M]<sup>+</sup> calcd for C<sub>48</sub>H<sub>56</sub>N<sub>4</sub>O<sub>4</sub>, 752.4302; found, 752.4284.

*N*,*N*<sup>\*</sup>-Dioctyl-1,6-dipyrrolidinylperylene-3,4,9,10-tetracarboxy diimide (1,6-8). Yield = 0.41 g. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): δ = 8.68 (d, *J* = 8.1 Hz, 2H), 8.34 (s, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 4.24 (t, *J* = 7.5 Hz, 2H), 4.20 (t, *J* = 7.6 Hz, 2H), 3.71 (br s, 4H), 2.76 (br s, 4H), 2.00 (br, 8H), 1.84–1.67 (m, 4H), 1.53–1.16 (m, 20H), 0.87 (distorted triplet, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, TMS): δ = 164.6, 164.3, 150.2, 135.9, 131.3, 130.4, 128.7, 128.5, 123.5, 123.1, 117.9, 117.8, 117.2, 117.1, 52.4, 40.9, 40.7, 32.0, 32.1, 29.8, 29.6, 29.4, 29.5, 28.5, 28.4, 27.5, 27.4, 25.9, 22.9, 22.89, 14.4. MS (ESI-TOF): [M]<sup>+</sup> calcd for C<sub>48</sub>H<sub>56</sub>N<sub>4</sub>O<sub>4</sub>, 752.4302; found, 752.4303.

Synthesis of 1,7-Dipyrrolidinylperylene-3,4,9,10-tetracarboxy Dianhydride (1,7-9). *N,N'*-Dioctyl-1,7-dipyrrolidinylperylene-3,4,9,10-tetracarboxy diimide *1,7-8* (200 mg, 0.27 mmol) was taken in 2-propanol (20 mL) and subsequently KOH (1.9 g, 33.8 mmol) was added. The reaction mixture was stirred under an argon atmosphere at reflux for 4 h. After being cooled to room temperature, the reaction mixture was poured into acetic acid (50 mL) and stirred overnight. The resulting green precipitate was collected by filtration, washed with water and methanol, and dried. The green solid was purified by column chromatography (silica 100, CHCl<sub>3</sub>) to yield the product (61 mg, 43%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 8.50$  (s, 2H), 8.44 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 3.75 (br s, 4H), 2.85 (br s, 4H), 2.08 (br, 8H). MS (ESI-TOF): [M]<sup>+</sup> calcd for C<sub>32</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>, 530.1479; found, 530.1457.

# **Results and Discussion**

Synthesis and Characterization. The 1,7- and 1,6-regioisomers of diphenoxy and dipyrrolidinyl substituted PDIs (1,7-5, 1,6-5, 1,7-8, and 1,6-8) were synthesized from perylene-3,4,9,10-tetracarboxylic dianhydride 1 in three steps according to the route depicted in schemes 1, 2, and 4. First, dibromoperylene-3,4,9,10-tetracarboxylic dianhydride was prepared by the I<sub>2</sub>-catalyzed bromination of perylene-3,4,9,10-tetracarboxylic dianhydride 1 in 96% sulfuric acid. As mentioned in the literature, this reaction led to the crude product 2, which was a mixture of 1,7- and 1,6-dibromoperylene dianhydride along with a very small amount of 1,6,7-tribromoperylene dianhydride.<sup>12</sup> The presence of 1,7and 1,6-regioisomers can only be detected by high-field (600 MHz) <sup>1</sup>H NMR in concentrated D<sub>2</sub>SO<sub>4</sub>. Moreover, the





Scheme 2. Synthetic Route to Compound 1,7-5 and 1,6-5



crude product 2 is insoluble in all organic solvents. Therefore, we subjected the crude product to imidization without characterization and further purification (Scheme 1).

Imidization of crude product **2** with *n*-octylamine in refluxing propionic acid yielded perylene diimides **3** and **4**. The product mixture was subjected to silica gel column chromatography with CH<sub>2</sub>Cl<sub>2</sub> as eluent. *N*,*N'*-dioctyl-1,6,7-tribromoperylene diimide **4** was successfully separated from the product mixture in ca. 1% yield and characterized by <sup>1</sup>H and <sup>13</sup>C NMR and MS. However, 1,7- and 1,6-dibromoperylene diimides could not be separated by column chromatography. Additionally, 300 MHz <sup>1</sup>H NMR spectrum of mixture **3** could not differentiate the two isomers. Subsequently, mixture **3** was reacted with 2,4-di-*tert*-butylphenol to afford regioisomeric mixture of *N*,*N'*-dioctyl-1,7- and 1,6-di(2,4-di-*tert*-butylphenoxy)perylene diimide by the nucleophilic substitution of both bromine atoms (Scheme 2).

The product, after silica gel column chromatography with CHCl<sub>3</sub>, was characterized by <sup>1</sup>H NMR spectroscopy (300 MHz, CDCl<sub>3</sub>) and mass spectrometry. The <sup>1</sup>H NMR spectrum exhibited two sets of signals with different intensities

Scheme 3. Structure of *N*,*N*-Dioctyl-1,7- and 1,6-Di(4-*tert*-butylphenoxy)perylene Diimide 6



in the aromatic region indicating the presence of 1,7- and 1,6-regioisomers in the product. Two well-resolved doublets and singlets were observed in the region between 8.1 and 8.7 ppm (Figure 2a). In addition, two broad doublets are overlapped at around 9.6 ppm. The integration areas of the doublets at 8.56 and 8.63 ppm revealed that 1,7-5 and 1,6-5 are present in the product in a ratio 70:30. These

Scheme 4. Synthetic Route to Compound 1,7-8 and 1,6-8



two regioisomers, 1,7-5 and 1,6-5, could not be separated by conventional column chromatography. Fortunately, these two regioisomers have shown very different solubility in toluene. The minor isomer 1,6-5 is well-soluble in toluene and exhibit solubility as high as 15 mg/mL, whereas the major isomer 1,7-5 has very poor solubility in toluene (ca. 0.2 mg/mL). We successfully separated them from each other on the basis of this pronounced solubility difference. The process must be repeated at least three times in order to achieve complete separation of both regioisomers. The separation process was monitored thoroughly by 300 MHz <sup>1</sup>H NMR (see Figures S9 and S10 in the Supporting Information). An even more pronounced solubility difference for the two isomers was observed in benzonitrile, but we preferred toluene for the separation process over benzonitrile because of its simplicity of use. Such a large difference in the solubility of these regioisomers may be attributed to the presence of bulky 2,4-di-tert-butylphenoxy groups at bay region. Because of the steric hindrance caused by bulky tert-butyl groups located at ortho position, the orientation of phenoxy groups is restricted relative to the perylene core. This hypothesis of restricted orientation of phenoxy groups is beefed up by two peculiar features observed in <sup>1</sup>H NMR spectrum of both 1,7-5 and 1,6-5. First, the signal of 6-H, 12-H protons (bay protons of the perylene core) at 9.65 ppm is significantly broadened (Figure 2b,c). Second, at the same time, a clear broadening is observed for the protons of *o-tert*-butyl groups in comparison to that of *p-tert*-butyl groups (see Figures S7 and S8 in the Supporting Information). This broadening of the signals was presumably due to the spatial closeness of o-tertbutyl group protons with 6-H and 12-H protons of the pervlene core, caused by rigidified conformation. In addition, slowdown of the interconversion of two atropisomers caused by bulky 2,4-di-tert-butylphenoxy substituent may also be an additional contributing factor in the above-mentioned broadening of NMR signals.<sup>21</sup> To further strengthen our hypothesis of restricted rotation of the phenoxy group around the perylene core and to correlate it with the solubility difference of two regioisomers, we synthesized a model compound 6 with 4-tertbutylphenoxy groups at the bay region in place of



**Figure 2.** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectra: (a) regioisomeric mixture of 1,7-5 and 1,6-5, (b) pure 1,7-5 regioisomer, (c) pure 1,6-5 regioisomer, (d) product 6 (1,7- and 1,6-regioisomers in a ratio 72:28).

2,4-di-*tert*-butylphenoxy groups (Scheme 3). In the case of **6**, the signal corresponds to the 6-H and 12-H protons at 9.40 ppm that is observed to be sharp just like usual disubstituted PDIs (Figure 2d). Moreover, the <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>) of **6** clearly revealed the presence of 1,7- and 1,6-regioisomers in a 72:28 ratio (Calculated from the integration areas of the doublets at 9.40 and 9.33 ppm). But, quite expectedly, these two regioisomers exhibited the same solubility in toluene or benzonitrile.

To the best of our knowledge, this is the first time the 2,4-di-*tert*-butylphenoxy group has been linked to the perylene core. Earlier, 4-*tert*-butylphenoxy, 3,5-di-*tert*-butylphenoxy, and 4-1,1,3,3-tetramethylbutylphenoxy groups were attached in which *tert*-butyl groups are located away from the PDI core and consequently do not cause restricted orientation of the phenoxy groups around perylene core. <sup>13a,14c,16,19b</sup>

In view of the fact that PDI dyes readily form  $\pi - \pi$  aggregates, which also causes broadening and shifting in the NMR spectrum,<sup>16a</sup> variable-concentration <sup>1</sup>H NMR measurements of 1,7-5 were carried out in CDCl<sub>3</sub> (20 mg/mL to 1 mg/mL), but no noticeable difference in the spectra was observed. Additionally, no aggregation was observed for both 1,7-5 and 1,6-5 in concentration-dependent steady-state absorption and emission measurements in that concentration domain.

It is to be noted that the characteristic signals of the regioisomers 1,7-5 and 1,6-5 in the <sup>1</sup>H NMR spectra (Figure 2), one singlet and two doublets of perylene core protons, exhibit significant differences in the chemical shift values (0.1 ppm for the singlets and 0.08 ppm for the doublets at 8.53-8.66). Because of this difference, the two regioisomers can be distinguished by 300 MHz<sup>1</sup>H NMR. However, a convenient unequivocal assignment of the NMR spectrum to the individual regioisomers 1,7-5 and 1,6-5 was performed on the basis of the signal of methylene protons next to the imide nitrogen at 4.13 ppm. Because of the same chemical environment, all four methylene protons of major regioisomer 1,7-5 appear as one triplet at 4.13 ppm (Figure 2b). On the other hand, for minor regioisomer 1,6-5 two separate triplets (at 4.19 and 4.07 ppm) were observed for the same four methylene protons (Figure 2c). In this way, an unambiguous characterization has been made successfully on the basis of 300 MHz <sup>1</sup>H MNR.

Dipyrrolidinyl-substituted PDIs 1,7-8 and 1,6-8 were synthesized from the regioisomeric mixture of N,N'-dioctyl-1,7- and 1,6-dibromoperylene diimide 3 by substitution of bromine atoms with pyrrolidine groups according to the procedure described earlier in literature.<sup>12</sup> As expected, the substitution reaction yielded a mixture of 1,7- and 1,6-dipyrrolidinyl perylene diimide derivatives. Separation of 1,7-8 and 1,6-8 regioisomers was performed by conventional column chrmatogrphy on Silica 100 using DCM as mobile phase. The minor regioisomer 1,6-8 came first and subsequently the major regioisomer 1,7-8 was collected.

Both regioisomers were characterized on the basis of 300 MHz <sup>1</sup>H NMR. Similar to previously mentioned regioisomers 1,7-5 and 1,6-5, an unequivocal assignment of the <sup>1</sup>H NMR spectrum to the individual regioisomers 1,7-8 and 1,6-8 was based on the signal of methylene protons next to the imide nitrogen at 4.21 ppm (Figure 3). Additionally, in the aromatic region two doublets and one singlet of the regioisomers 1,7-8 and 1,6-8 exhibit large differences in chemical shift values (ca. 0.35 ppm). Surprisingly, these aromatic signals for 1,6-8 appear in different order (doublet, singlet, doublet) compared to that of 1,7-8 (singlet, doublet, doublet). This different pattern of appearance of singlet and doublets makes them even more easily recognizable by 300 MHz <sup>1</sup>H NMR.

The two regioisomers are very different in color too; 1,7-8 is deep green in color, whereas 1,6-8 is deep blue. Both regioisomers are soluble in wide range of solvents including hexane, toluene, chloroform, dichloromethane, benzonitrile and ethanol. Keeping in mind that 1,7-dipyrrolidinylperylene dianhyride has been used as an important building block for the synthesis of many useful complex systems, we have also optimized the reaction conditions to convert 1,7-8 to corresponding dianhyride 1,7-9 through saponification. We observed that complete removal of *n*-octylamino groups of 1,7-8, in 2-propanol with 100-fold excess of KOH, takes longer time compare to cyclohexylamino groups of N,N'-dicyclohexyl-1,



**Figure 3.** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectra of regioisomers 1,7-8, and 1,6-8.

#### Scheme 5. Conversion of 1,7-8 to Corresponding Dianhydride



Table 1. Redox Potentials (*V* vs Ag/AgCl) of 1,7-5, 1,6-5, 1,7-8, and 1,6-8 Obtained by DPV<sup>a</sup>

compd	$E_{1 \text{ox}}$	$E_{2 \text{ox}}$	$E_{1red}$	$E_{2red}$
1,7-5	$+1.47^{b}$		-0.61	-0.85
1,6-5	+1.46		-0.64	-0.89
1,7-8	+0.63	+0.77	-0.83	-0.99
1,6-8	+0.77	$+1.28^{b}$	-0.83	-0.99

<sup>a</sup> Scan rate: 0.05 V/s. <sup>b</sup> Irreversible processes.

7-dipyrrolinylperylene diimide reported earlier.<sup>12</sup> Therefore, a 125-fold excess of KOH was used for the saponification reaction to afford 1,7-9 (Scheme 5).

**Electrochemical Properties.** To compare the relative electron donor and acceptor capabilities of 1,6- and 1,7- regioisomers, redox properties of both sets of isomers (1,7-5 and 1,6-5; 1,7-8 and 1,6-8) were investigated by differential pulse voltammetry in benzonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte. Obtained redox potentials (*V* vs Ag/AgCl) are summarized in Table 1 and differential pulse voltammograms of 1,7-8 and 1,6-8 are shown in Figure 4.

The two regioisomers of diphenoxy substituted PDIs (1,7-5 and 1,6-5), which are mainly known for their electron acceptor capabilities, displayed very similar redox characteristics. Both the isomers undergo two reversible reductions, which reflect the first and the second one-electron reductive process. The two reversible one-electron reductions of 1,7-5 occur at -0.61 V and -0.85 V, whereas for 1,6-5, both first and second reductions are



Figure 4. Differential pulse voltammograms of 1,7-8 (green) and 1,6-8 (blue) in PhCN vs Ag/AgCl reference electrode.

slightly shifted to more negative values by 30 and 40 mV, respectively. As far as oxidation potential is concerned, only one irreversible oxidation peak was observed at around +1.47 V for both compounds. Thus, two regioisomers 1,7-5 and 1,6-5 have virtually the same oxidation and reduction capabilities.

On the other hand, the two regioisomers of dipyrrolidinyl substituted PDIs (1,7-8 and 1,6-8), which are mainly known for their electron donating capabilities, display some interesting features and notable differences in their oxidation characteristics (Figure 4). The regioisomer 1,7-8 exhibits two one-electron oxidation peaks at moderate potentials ( $E_{1 \text{ox}} = +0.63 \text{ V}, E_{2 \text{ox}} = +0.77 \text{ V}$ ). Both the first and the second oxidations are reversible. In the case of second regioisomer 1,6-8, the oxidation of both pyrrolidinyl units takes place at the same potential, i.e., +0.77 V. This two-electron oxidation is reversible. In addition, this blue isomer also exhibits an irreversible one-electron oxidation peak at very high potential, i.e., +1.28 V. Surprisingly, the first oxidation of 1,6-8 occurs at exactly same potential at which second oxidation of 1,7-8 takes place, i.e., +0.77 V. Significantly higher values of oxidation potentials for 1,6-8 clearly indicating that the removal of electrons from 1,6-8 is more difficult in comparison to 1,7-8.

Both 1,7-8 and 1,6-8 exhibit two reversible one-electron reduction peaks at exactly same potentials ( $E_{1red} = -0.83$  V,  $E_{2red} = -0.99$  V) indicating that both regioisomers have same electron acceptor abilities. The improved value for first oxidation potential of 1,7-8 (+0.63 V) obtained by us in comparison to the literature value (+0.72 V) clearly suggests that the previously reported 1,7-dipyrrolidinyl substituted PDI was contaminated with 1,6-regioisomer.<sup>11a</sup>

Steady-State Absorption Studies. The ground-state absorption spectra of 1,7- and 1,6-diphenoxy substituted PDIs (1,7-5 and 1,6-5) in chloroform are depicted in Figure 5. The absorption spectra of both regioisomers are dominated by characteristic  $\pi - \pi^*$  transitions and resemble with each other.

For both regioisomers, the absorption bands attributed to  $S_0-S_1$  electronic transition are at around 555 nm in CHCl<sub>3</sub>. However, the molar extinction coefficient is significantly lower for 1,6-5 in comparison to 1,7-5. The main difference in the absorption characteristic of two



Figure 5. Steady-state absorption spectra of 1,6-5 (black) and 1,7-5 (red) in chloroform.



Figure 6. Steady-state absorption spectra of 1,7-8 (green) and 1,6-8 (blue) in chloroform.

isomers is in the wavelength range 375-475 nm. For 1,7-5 the absorption band belongs to  $S_0-S_2$  electronic transition is located at 408 nm, whereas in the case of 1,6-5, the same band is centered at ca. 468 nm. The absorption properties of these two regioisomers were also investigated in nonpolar toluene and polar benzonitrile, but no other noticeable differences were observed between the two.

In contrast to 1,7-5 and 1,6-5, the dipyrrolidinyl-substituted regioisomers 1,7-8 and 1,6-8 display large differences in their absorptive features. The absorption spectra in chloroform are shown in Figure 6.

For these two regioisomers the lowest energy bands, which correspond to  $S_0-S_1$  electronic transitions, are highly red-shifted with respect to that of unsubstituted PDIs ( $\lambda_{max} = 527 \text{ nm}$ ),<sup>13c</sup> reflecting pronounced electronic interaction between PDI core and pyrrolidinyl groups. In the case of 1.7-8, the lowest energy band is centered at 702 nm and has a small shoulder at ca. 650 nm. Whereas for regioisomer 1,6-8, this lowest energy band and the shoulder have approximately same molar extinction coefficients. In addition, this band is significantly weaker and blue-shifted by ca. 15 nm with respect to that of 1,7-8. These lowest energy bands of both the regioisomers are dependent on polarity of the solvent and exhibit significant red shift upon increase in the polarity of the surrounding medium (see Figures S1 and S2 in the Supporting Information). In addition to the lower energy absorption at ca. 700 nm, isomer 1,7-8 exhibits a higher energy  $S_0-S_2$  electronic



**Figure 7.** Normalized steady-state emission spectra of 1,7-5 (red) and 1,6-5 (black) in CHCl<sub>3</sub> ( $\lambda_{ex} = 474$  nm).

transition at 428 nm, but, corresponding band is almost absent in the case of 1,6-8. We presume that the absence of higher energy band is responsible for the deep blue color of regioisomer 1,6-8. Quite surprisingly, 1,6-8 has one additional strong band centered at 550 nm, which looks very similar to the lowest energy band of the diphenoxy substituted PDIs (1,7-5 and 1,6-5). Because of these peculiar absorption characteristics, isomer 1,6-8 covers a larger part of the visible region (450–750 nm) compared to that of 1,7-8. Therefore, 1,6-8 may be of particular interest for some specific applications where larger absorption crosssection in the visible region is required (e.g., photovoltaic devices).

Steady-State and Time-Resolved Emission Studies. Further insight into the optical properties of both set of regioisomers (1,7-5 and 1,6-5; 1,7-8 and 1,6-8) was gained by steady-state emission and time-correlated single photon counting (TCSPC) methods. 1,7- and 1,6-diphenoxy substituted PDIs (1,7-5 and 1,6-5) were examined in three different solvents, i.e., toluene, chloroform, and benzonitrile. The emission spectra of these compounds in chloroform are depicted in Figure 7 and fluorescence decays are shown in Figure 8. The emission data are summarized in Table 2.

As expected, on the basis of absorption studies, both 1,7-5 and 1,6-5 exhibit approximately similar emission characteristics too. The emission bands of both regioisomers are approximately the mirror image of their  $S_0 - S_1$ absorption bands with Stokes shift of around 35 nm. However, the emission band of 1,6-5 ( $\lambda_{max} = 593$  nm) is slightly broader and red-shifted in comparison to that of 1,7-5 ( $\lambda_{\text{max}} = 587 \text{ nm}$ ) in chloroform as shown in Figure 7. The emission maxima of both isomers show small bathochrmic shift (ca. 14-16 nm) upon moving from nonpolar toluene to moderately polar chloroform (Table 2). Both regioisomers are highly emissive, in all the investigated solvents, with fluorescence quantum yields greater than 0.92. For fluorescence lifetime measurements, the solutions of both regioisomers were excited at 483 nm and emission time profiles were collected at corresponding emission maximum. Similar to emission maxima and quantum yields, both 1,7-5 and 1,6-5 also displayed approximately same singlet-state lifetimes. However, 1,6-5 exhibited slightly higher fluorescence lifetimes in



**Figure 8.** Fluorescence decay time profiles of 1,7-5 (red,  $\lambda_{mon} = 587$  nm) and 1,6-5 (black,  $\lambda_{mon} = 593$  nm) in CHCl<sub>3</sub> ( $\lambda_{ex} = 483$  nm).

 Table 2. Optical Properties of 1,7-5, 1,6-5, 1,7-8, and 1,6-8 in

 Different Solvents

compd	solvent	$\lambda_{\mathrm{abs}}$	$\lambda_{ m em}$	$\Phi_{ m f}$	$ au_{\rm f}({\rm ns})$
1,7-5	toluene	548	573	0.97	4.91
	chloroform	556	587	0.97	5.39
	benzonitrile	553	583	0.98	4.79
1,6-5	toluene	545	577	0.96	5.52
	chloroform	554	593	0.94	5.81
	benzonitrile	550	590	0.92	5.35
1,7 <b>-8</b>	hexane	661	703	0.54	6.08
	toluene	687	724	0.40	4.48
	chloroform	702	743	0.32	3.47
	ethanol	699	770	0.07	1.03
1,6 <b>-8</b>	hexane	647	728	0.09	1.27
	toluene	671	735	0.07	1.26
	chloroform	688	752	0.06	1.01
	ethanol	688	778	0.02	0.51

all the three solvents with respect to that of 1,7-5 (1,6-5,  $\tau_{\rm f}$  [ns] = 5.52 in toluene, 5.81 in CHCl<sub>3</sub>, 5.35 in benzonitrile; 1,7-5,  $\tau_{\rm f}$  [ns] = 4.91 in toluene, 5.39 in CHCl<sub>3</sub>, 4.79 in benzonitrile). It is noteworthy that for both of these isomers fluorescence life times were found to be maximum in moderately polar chloroform in comparison to nonpolar toluene and polar benzonitrile.

The emission properties of 1,7- and 1,6-dipyrrolidinylsubstituted PDIs (1,7-8 and 1,6-8) were investigated in four different solvents, i.e., hexane, toluene, chloroform, and ethanol. The emission spectra of these compounds in chloroform are depicted in Figure 9 and fluorescence decays are shown in Figure 10. The emission data are summarized in Table 2.

In contrast to 1,7-5 and 1,6-5, the 1,7- and 1,6-regioisomers of dipyrrolidinyl PDIs (1,7-8 and 1,6-8) display large differences in emission properties. Additionally, for these compounds, emission properties namely emission maximum, fluorescence quantum yield and fluorescence lifetime were found to be dependent on polarity of surrounding medium due to the presence of electron donating pyrrolidine groups at the perylene core (Figure S3, S4, S5 and S6, Supporting Information). Emission maxima of both isomers exhibit significant bathochromic shift upon increasing the solvent polarity: 1,7-8,  $\lambda_{max} = 703$  nm in hexane and 770 in ethanol; 1,6-8,  $\lambda_{max} = 728$  nm in hexane and 778 in ethanol (Table 2). In both polar and nonpolar solvents, the emission band of



Figure 9. Normalized steady-state emission spectra of 1,7-8 (green) and 1,6-8 (blue) in CHCl<sub>3</sub>.



**Figure 10.** Fluorescence decays of 1,7-8 (green,  $\lambda_{mon} = 724 \text{ nm}$ ) and 1,6-8 (blue,  $\lambda_{mon} = 735 \text{ nm}$ ) in tolune ( $\lambda_{ex} = 483 \text{ nm}$ ).

1,6-8 is found to be broader compare to that of 1,7-8. In addition, the emission maxima of regioisomer 1,6-8 is bathochromically shifted by ca. 10 nm relative to that of 1,7-8 in polar and weakly polar solvents (i.e., ethanol, chloroform, and toluene). On the other hand, in nonpolar hexane, the emission maxima of 1,6-8 is bathochromically shifted by 25 nm compare to that of 1,7-8. The fluorescence quantum yields of both isomers were also determined in solvents ranging from nonpolar to polar. Quite unexpectedly, a large difference is observed in the quantum yields of these two isomers. In nonpolar and weakly polar solvents, 1,7-8 has high to moderate quantum yields ( $\Phi_f = 0.54$  in hexane, 0.40 in toluene, and 0.32 in chloroform), whereas emission quantum yields of the regioisomer 1,6-8 are found to be significantly lower than that of 1,7-8 ( $\Phi_f = 0.09$  in hexane, 0.07 in toluen, and 0.06 in chloroform). However, both regioisomers have weak emission in polar ethanol (1,6-8,  $\Phi_f = 0.02$ ; 1,7-8,  $\Phi_f =$ 0.07). For fluorescence lifetime measurements, solutions of both regioisomers were excited at 648 nm and emission time profiles were collected at corresponding emission maximum. Similar to fluorescence quantum yields, fluorescence life times of isomer 1,6-8 were also found significantly lower with respect to that of 1,7-8 in all the investigated solvents (1,6-8,  $\tau_f$  [ns] = 1.27 in hexane, 1.26 in toluene, 1.01 in CHCl<sub>3</sub>, and 0.51 in ethanol; 1,7-8,  $\tau_{\rm f}$  [ns] = 6.08 in hexane, 4.48 in toluene, 3.47 in CHCl<sub>3</sub>, and 1.03 in ethanol).

# Conclusions

To conclude, we have synthesized, separated, and characterized 1,6- and 1,7-regioisomers of diphenoxy and dipyrrolidinyl substituted PDI dyes. The regioisomers of diphenoxy substituted PDIs (1,7-5 and 1,6-5) were separated easily utilizing their very different solubility in toluene. On the other hand, regioisomers of dipyrrolidinyl substituted PDIs (1,7-8 and 1,6-8) were separated by conventional silica gel column chromatography. Our studies have also shown that these 1,7- and 1,6-isomers can readily be characterized even by 300 MHz <sup>1</sup>H NMR. Subsequently, a comparative study of their electrochemical and optical properties was also carried out. Eventually, 1,7-dipyrrolidinylperylene diimide 1,7-8 was successfully converted to corresponding dianhydride 1,7-9, which can be used as building block for the synthesis of complex systems.

One of the rationale of this work was to clear the chaos present in literature over the presence of 1,6-regioisomeric impurity in 1,7-difunctionalized perylene diimide dyes. Our results further confirm the observation of Würthner et al. that the bromination and subsequent imidization of perylene dianhydride **1** leads to a mixture of regioisomeric 1,7- and 1,6-dibromoperylene diimides rather than only 1,7-regioisomer. Additionally, comparison of redox potentials of regioisomerically pure 1,7-dipyrrolinylperylene diimide 1,7-**8** with published values confirm their prediction that the previously reported difunctionalized PDIs were contaminated with 1,6-regioisomers.

Our studies have also shown that introduction of phenoxy groups at the 1,7- and 1,6-positions of PDI core leads to the regioisomers that are very similar in redox and optical properties. Therefore, a mixture of regioisomeric 1,7- and 1,6-diphenoxy PDIs may be used for various applications, i.e., construction of light harvesting systems, photovoltaic devices, etc. On the contrary, in the case of dipyrrolidinyl-substituted PDIs, redox and optical properties depend significantly on the positions of two pyrrolidine groups relative to each other. Consequently, the two regioisomers obtained by the substitution of pyrrolidine groups at the 1,7- and 1,6-positions exhibit profound differences in their electrochemical and optical characteristics. We found that 1,6-dipyrrolidinylperylene diimide has significantly diminished electron donor ability and inherently low emission characteristics compared to respective 1,7-regioisomer. In view of our results, we therefore strongly emphasize that impurity of 1,6-regioisomer must be removed from 1,7-dipyrrolidinylperylene diimide prior to any use, otherwise it will significantly reduce the efficiency of the whole system. The final conclusion that can be drawn from this work is that 1,6difunctionalized PDIs, depending on the substituents, may or may not have characteristics similar to respective 1,7-derivative. We expect these results and findings will further motivate material chemists to take especially cautious approach to this regioisomeric impurity problem particularly when a strong electron-donating groups, e.g., pyrrolidine, are attached to the PDI core.

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**Supporting Information Available:** Steady-state absorption and emission spectra of 1,7-8 and 1,6-8 in different solvents (S2 & S3); fluorescence decay time profiles of 1,7-8 and 1,6-8 in different

solvents (S4); <sup>1</sup>H NMR spectra of aliphatic region of 1,7-5 and 1,6-5 in CDCl<sub>3</sub> (S5); <sup>1</sup>H NMR spectroscopic monitoring of separation of regioisomers *1*,7-5 and *1*,6-5 (S6); <sup>1</sup>H and <sup>13</sup>C NMR spectra of all synthesized compounds (S7–S13) (PDF). This material is available free of charge via the Internet at http:// pubs.acs.org.