# Synthesis and Photophysical Properties of Glass-Forming Bay-Substituted Perylenediimide Derivatives

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A series of perylenediimide-based small molecules (PDI1-PDI5) containing electron-deficient groups in the bay region were synthesized and characterized. The PDI derivatives were found to be capable of forming molecular glasses with glass transition temperatures ranging from 50 to 102 °C. Detailed investigations of the optical properties of the synthesized derivatives were performed and compared with those obtained from quantum chemical calculations. Optimized molecular structures of the PDI derivatives exhibited core-twisting by 16° and torsional angle between the bay substituent and the perylene core in the range of  $60-72^{\circ}$ . The PDI derivatives exhibited absorption maxima in the range of 2.27-2.36 eV and emission maxima in the range of 2.10-2.28 eV. The impact of the bay substituents on the emission, fluorescence quantum yield, and lifetimes in solutions and thin films was established. The red shift of emission maxima (from 2.282 to 2.095 eV) observed for various PDIs in solutions was accompanied by significant reduction in the emission quantum yield (from 0.73 to 0.44) and corresponding increase of the fluorescence lifetime (from 4.5 to 6.8 ns). This was in agreement with quantum chemical calculations indicating decrease of the radiative relaxation rate due to reduction of the oscillator strength and remarkable decrease of the torsional activation barrier. The spectral properties of the wet-casted perylenediimide films featuring different bay substituents were also studied. The variation in the emission peak (of 0.25 eV) and the considerable increase of the Stokes shift (of 0.4 eV) are explained in terms of the formation of the amorphous state. The influence of the bay substituents on the thermal and spectral properties of the films are discussed.

## Introduction

Perylenediimides (PDIs) are widely investigated organic materials with important applications in optoelectronics. Although the key application of PDIs so far is in laser dyes,<sup>1</sup> such as the famous perylene orange and red dyes, other potential applications of PDIs in organic field-effect transistors,<sup>2</sup> photovoltaic cells,<sup>3</sup> and light-emitting diodes<sup>4</sup> are being explored. Chemical, thermal stability, and photostability accompanied by high luminescence efficiency and good solution processability<sup>5,6</sup> make optoelectronic applications of PDIs viable. It is interesting to note that the high photostability of PDIs as compared to other organic compounds is advantageous for optoelectronic applications.

For PDI-based light-emitting devices, it is essential to provide tunability of the emission wavelength. Although the imide nitrogen substituted PDI derivatives demonstrate excellent thermal and photostability, and show superior luminescence quantum yield (QY) (up to 100%), these molecules have negligible spectral tunability.<sup>6</sup> Additionally, the planar structure of perylenediimide core facilitates the formation of H aggregates (face to face) in the concentrated solutions and solid state, which

generally result in significant luminescence quenching. An alternative way for tuning the absorption/emission wavelength either by modification of the diimide groups or by substitution at perylene core has been proposed.<sup>6</sup> The modifications of the diimide group via the ring opening of the imide moiety, replacement of the carbonyl groups by imino groups and their incorporation into a six-membered rings,<sup>6</sup> alteration of the ring sizes, etc. enabled reasonable spectral tuning through extended conjugation and in some cases yielded luminescence efficiency close to 100%. However, efforts in achieving amplified emission from the derivatives with modified diimide group were unsuccessful.<sup>7</sup> PDI derivatives substituted at the bay positions of the perylene core (Figure 1) using C-O, C-C, and C-N coupling are considered to be promising,<sup>8</sup> owing to the fact that the steric hindrance and perylene core twisting induced by the bay substituents could prevent  $\pi - \pi$  stacking,<sup>9</sup> and thus reduce luminescence quenching. Also the majority of perylene dyes favor H-type aggregation with weak fluorescence,<sup>10</sup> owing to the steric inhibition of substituents. However, a few reports on the perylene core substituted PDI derivatives, like tetrachloro-,<sup>11</sup> cholesterol-,<sup>12</sup> and various aryl-substituted<sup>7,13</sup> perylenes, showed reduced luminescence quantum yield (<85%) as compared to those substituted at the imide nitrogen. Recently, we have reported optical and charge transport properties of core substituted perylenediimide derivatives.14

Here we report the luminescence properties of a series of perylenediimide derivatives with electron accepting substituents

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Figure 1. Chemical structure of PDI derivatives.



**Figure 2.** Molecular structure of the bay-substituted PDI derivative, PDI5.  $\alpha$ , dihedral angle between the two subplanes (half-units) of the PDI core;  $\beta$ , dihedral angle between the planes of the bay substituent and half-unit of the core.

at the bay positions of the perylene core (Figure 1). By estimating quantum yield (QY) and luminescence decay time, the connection between the (non) radiative relaxation rates and the QY of the PDI derivative with respect to the bay substituent was established. This allows better understanding of the substituent-induced luminescence properties and assists in selecting the PDI derivatives for further applications.

**DFT Calculations.** Quantum chemical calculations of the PDI derivatives were carried out using density functional theory (DFT) as implemented in the Gaussian 03<sup>15</sup> software package. Molecular structure of the ground electronic state was optimized using B3LYP functional theory with the 6-311G basis set. Excited-state energies and oscillator strengths for singlet transitions were obtained by means of the ZINDO procedure. The optimized molecular structure of the bay-substituted PDI derivatives achieved via total energy minimization revealed two important structure distortions which could be attributed to all PDI molecules studied, in particular, twisted perylene core as well as the twisted bay substituent around the methyl bridge connecting it to the core, in accordance with previous reports.<sup>16,17</sup> The twist planes and angles for one of the PDI derivatives, PDI5, are illustrated in Figure 2.

It is known that PDIs with twisted core have important implications for their arrangement in well-organized supramolecular structures with controlled optical and electronic properties, and thus, are considered to be promising for organic electronics.<sup>16,17</sup>

Our calculations imply that the dihedral angle  $\alpha$  between the two subplanes of the core is similar ( $\alpha = 16^{\circ}$ ) for PDI2-PDI5 derivatives, i.e., independent of the substituents at the bay region. The determined dihedral angle is in good agreement with the angle  $15-18^{\circ}$  reported in the literature for diphenoxy and



**Figure 3.** Calculated total energy of the ground state  $S_0$  and the first excited state  $S_1$  (a) and oscillator strength for the transition  $S_0 \rightarrow S_1$  (b) as a function of dihedral angle  $\beta$  (at fixed angle  $\alpha$ ,  $\alpha = 16^{\circ}$ ) for PDI2 derivative. Dashed line designates energy minimum of  $S_1$  state. Solid lines are the guides for the eye.

dipentafluorophenoxy substituents attached to the bay positions of PDIs.<sup>16</sup> Literature reported core-twist angle for the bromosubstituted PDI (the case of PDI1) and calculated by semiempirical AM1 method is somewhat larger (21°).<sup>17</sup> The dihedral angle  $\beta$  formed by the planes of the bay substituent and halfunit of the core is determined to be substituent dependent. Quantum chemical calculations also revealed an insignificant 8° inclination of the long axis of the bay substituents with respect to the half-units of the core.

The differences in the state energies and oscillator strengths of the two selected PDI derivatives, PDI2 and PDI5, imposed by the torsional motions of their bay substituents are revealed. The selection of the representative derivative PDI2 from the group of PDI1–PDI2 and the derivative PDI5 from the group of PDI3–PDI5 having nitrogen in the bay substituents was based on the pronounced difference in the optical properties (spectral positions of the fluorescence and absorption bands, fluorescence quantum yields) of these groups, which are discussed below.

Figure 3 demonstrates total energies of the ground state  $S_0$ and the first excited state  $S_1$  as well as the oscillator strength for the transition  $S_0 \rightarrow S_1$  as a function of dihedral angle  $\beta$ calculated for the PDI2 molecule. Since the attachment of different bay substituents resulted in the similarly twisted perylene core for PDI2–PDI5, calculations are presented for the fixed dihedral angle  $\alpha$ . For comparison, an analogous figure showing  $\beta$  angle dependences of the state energies and oscillator strength for PDI5 molecule is displayed in Figure 4.

Energies of the S<sub>0</sub> and S<sub>1</sub> states in PDI2 molecule exhibit minima at the same dihedral angle  $\beta$  ( $\beta = 72^{\circ}$ ), indicating unchanged orientation of 2,4-di(trifluoromethyl)phenyl substituent upon transition from the ground to the first excited state. The energy minima of S<sub>0</sub> and S<sub>1</sub> states in PDI5 correspond to different  $\beta$  angles, 70° and 60°, respectively, implying torsion of 4-pyridyl substituent plane toward the core plane upon excitation. Very similar torsions (by ~10°) of the bay substituents were also revealed for PDI3 and PDI4 molecules upon their excitation. Deeper energy minima obtained for PDI2 as compared to that for PDI5 (see Figures 3a and 4a) indicate higher torsional activation barrier needed for the bay substituent to accomplish this motion. High torsional activation barrier can significantly affect optical properties of the molecules and obstruct close packing of the molecules in the films.



**Figure 4.** Calculated total energy of the ground state  $S_0$  and the first excited state  $S_1$  (a) and oscillator strength for the transition  $S_0 \rightarrow S_1$  (b) as a function of dihedral angle  $\beta$  (at fixed angle  $\alpha$ ,  $\alpha = 16^{\circ}$ ) for PDI5 derivative. Dashed line designates energy minimum of  $S_1$  state. Solid lines are the guides for the eye.

Calculated  $S_0 \rightarrow S_1$  transition energies for PDI2 and PDI5 derivatives are 2.27 and 2.2 eV, respectively. Estimate of the oscillator strength for the transition  $S_0 \rightarrow S_1$  in PDI2 as predicted by quantum chemical calculations is 0.92, whereas, his estimate for PDI5 molecule is 0.73 (dashed lines in Figures 3b and 4b). Similar oscillator strengths of the order of 0.7 were also obtained for PDI3 and PDI4 molecules with nitrogen atoms in the bay substituents. Theory predicted 1.3 times lower oscillator strengths for the PDI3–PDI5 derivatives as compared to that for PDI2 and indicated diminished absorbance and fluorescence quantum yield.

Figure 5 illustrates a change of the molecular charge density and the main directions of this change corresponding to the  $S_0 \rightarrow S_1$  transition in representative PDI2 and PDI5 molecules. Obviously, upon excitation the charge redistribution in both molecules occurs only within the half units of the perylene core due to its twisted conformation. In PDI2 molecule 2,4di(trifluoromethyl)phenyl substituents attached to the bay position of the core act as strong electron acceptors, and thus, the electron cloud is attracted toward the substituents (see Figure 5a). Meanwhile, in PDI5 molecule (Figure 5b) as well as in other PDI3 and PDI4 molecules, the charge redistribution is more limited to the half units of the core without marked influence of the bay substituents.

### **Experimental Section**

**Materials and Methods.** All chemicals and reagents were purchased from Aldrich and used as received. All reactions were done in distilled anhydrous solvents under inert atmosphere. The NMR spectral data of all synthesized samples were recorded on a Bruker ACF 300 spectrometer operating at 300 and 75.5 MHz for <sup>1</sup>H and <sup>13</sup>C nuclei, respectively, using CDCl<sub>3</sub> solvent and TMS as internal standard. The absorbance and fluorescence spectra were recorded on a Shimadzu 3101 PC spectrophotometer and RF-5301PC Shimadzu spectrofluorometer, respectively. Tetrahydrofuran solutions of the PDI derivatives (concentration  $1 \times 10^{-5}$  M) in  $10 \times 10$  mm<sup>3</sup> quartz cells were used for luminescence measurements. Neat films of the PDI derivatives used in the investigations were prepared from  $1 \times 10^{-3}$  M THF solutions on the glass substrates by drop-casting in an ambient



**Figure 5.** Redistribution of molecular charge density corresponding to the  $S_0 \rightarrow S_1$  transition calculated for PDI2 (a) and PDI5 (b). Open circles indicate a decrease, filled circles an increase of the molecular charge. The big circles correspond to the amount of the charge density changed. Arrows show main directions of molecular charge redistribution.

air. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA Instruments Q100 (heating rate 20 °C. min<sup>-1</sup> for TGA and heating/cooling rate of 10 °C. min<sup>-1</sup> for DSC measurements) using nitrogen as carrier gas.

Fluorescence Kinetics and Quantum Yield Studies. PDI derivatives were excited using light-emitting diode (Nichia NSPB500AS) coupled to monochromator to produce emission at 490 nm with a full width at half-maximum of 13 nm. Photoluminescence (PL) spectra were measured using backthinned CCD spectrophotometer PMA-11 (Hamamatsu) and corrected for the wavelength-dependent sensitivity of the CCD. Fluorescein in 0.1 M NaOH aqueous solution with QY of 0.92 has been used as a reference.<sup>18</sup> The QY of the PDI solutions was estimated by comparing wavelength-integrated PL intensity of the solution with that of the reference. Optical densities of the reference and solutions of the PDI derivatives were kept below 0.05 to avoid reabsorption effects. Estimated QY was verified by using an alternative method of an integrating sphere (Sphere Optics) coupled to the CCD spectrometer.<sup>19,20</sup> The integrated sphere method was also employed in the QY estimations of the PDI films.

PL decay curves of the PDI derivatives were measured using time-correlated single-photon-counting system PicoHarp 300 (PicoQuant GmbH). Pulsed excitation at 1 MHz repetition rate was provided by picosecond diode laser with the pulse duration of 70 ps and the emission wavelength of 375 nm.

**Synthesis of 1,7-Dibromo-***N***,***N***'-didodecylperylenediim-ide (PDI1).** Synthesis and characterization of 1,7-dibromo-perylenedianhydride and 1,7-dibromoperylenediimide were reported earlier.<sup>14</sup>

Synthesis of Perylenediimide Derivatives (PDI2-5). PDI1 (1.12 mmol) and aryl monoboronic acid (2.8 mmol) were dissolved in 50 mL of THF (AR grade) and heated to 70 °C for 15 min under nitrogen atmosphere. About 20 mL of 1 M K<sub>2</sub>CO<sub>3</sub> aqueous solution and 10 mol % Pd(PPh<sub>3</sub>)<sub>4</sub> was added to the mixture. The contents were heated at 75 °C under nitrogen atmosphere for 20–24 h. After completion, the reaction mixture was diluted with ethyl acetate (300 mL) and extracted with water (3 × 300 mL). The crude product was purified by column chromatography using a mixture of 20% ethyl acetate and 80% hexane as eluent and silicagel (200–400 mesh) as stationary phase.

*N*,*N*'-Bis(dodecyl)-1,7-bis(2,4-di(trifluoromethyl)phenyl)perylene-3,4,9,10-diimide (PDI2). Yield: 75% (0.75 g); Red orange solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 8.52 (s, 2H, Per-H), 8.21–8.27 (m, 4H, Per-H and Ar–H), 7.97–8.00 (m, 2H, Per-H), 7.54–7.57 (d, 4H, Ar–H), 4.18–4.13 (t, 4H, N–CH<sub>2</sub>), 1.82–1.77 (m, 6H, alkyl-CH<sub>2</sub>), 1.39–1.25 (m, 24H, alkyl-CH<sub>2</sub>), 0.88 – 0.64 (m, 12H, alkyl-CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 163.2, 163.0, 154.9, 140.8 138.9, 137.2, 134.7, 134.1, 129.9, 128.9, 128.7, 127.1, 122.0, 121.7, 105.9, 77.4, 77.0, 76.5, 61.2, 56.6, 40.8, 31.9, 29.6, 29.5, 29.4, 29.3, 28.1, 27.2, 22.6, 14.0. EI-MS *m*/*z*: 1150.72 (Exact Mass: 1150.45). Anal. Calcd for C<sub>64</sub>H<sub>62</sub>F<sub>12</sub>N<sub>2</sub>O<sub>4</sub>: C, 66.77; H, 5.43; F, 19.80; N, 2.64; O, 15.10. Found. C, 66.73; H, 5.37; F, 19.86; N, 2.38.

*N*,*N*'-**Bis(dodecyl)-1,7-bis(4-cyanophenyl)perylene-3,4,9,10diimide (PDI3).** Yield: 75% (0.7 g); Red color solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ ppm) 8.64 (s, 2H, Per-H), 8.20–8.18 (d, 2H, Per-H), 7.83–7.79 (m, 4H, Ar–H), 7.71–7.67 (m, 6H, Per-H and Ar–H), 7.31–7.30 (d, 2H, Ar–H), 7.20–7.17 (t, 2H, Tp-H), 4.20–4.15 (t, 4H, N–CH<sub>2</sub>), 1.80–1.65 (m, 4H, alkyl-CH<sub>2</sub>–), 1.45–1.30 (m, 26H, alkyl-CH<sub>2</sub>), 0.88–0.65 (m, 8H, alkyl-CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, δ ppm) 163.0, 162.9, 146.5, 138.9, 134.6, 133.9, 132.4, 130.7, 130.0, 129.8, 129.0, 127.9, 122.9, 122.6, 118.0, 112.8, 77.4, 77.0, 76.5, 40.7, 31.9, 29.6, 29.5, 29.34, 29.3, 28.1, 27.0, 22.6, 14.0. EI-MS: *m/z* 928.02 (Exact Mass: 928.49). Anal. Calcd for C<sub>62</sub>H<sub>64</sub>N<sub>2</sub>O<sub>4</sub>: C, 80.14; H, 6.94; N, 6.03; O, 6.89. Found: C, 80.32; H, 6.97; N, 5.78.

*N*,*N*'-Bis(dodecyl)-1,7-bis(3-nitrophenyl)perylene-3,4,9,10diimide (PDI4). Yield: 80% (0.77 g); Red solid. <sup>1</sup>H MNR (300 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 8.61 (s, 2H, *Per-H*), 8.59–8.35 (m, 4H, *Per-H and Ar–H*), 8.20–8.15 (d, 2H, *Per-H*), 7.94–7.92 (d, 2H, *Per-H*), 7.77–7.67 (m, 4H, *Ar–H*), 4.19–4.14 (t, 4H, N-*CH*<sub>2</sub>), 1.74–1.65 (m, 6H, alkyl-*CH*<sub>2</sub>-), 1.52–1.24 (m, 30H, alkyl-*CH*<sub>2</sub>), 0.88–0.80 (m, 8H, alkyl-*CH*<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 163.5, 163.4, 158.7, 141.0, 137.2, 135.6, 134.4, 130.1, 129.9, 129.3, 128.0, 127.3, 122.3, 121.8, 119.7, 106.0, 55.4, 40.6, 31.9, 29.6, 29.5, 29.4, 29.3, 28.1, 27.1, 22.6, 14.0, –0.0. EI-MS *m/z*: 968.17 (Exact Mass: 968.47). Anal. Calcd for C<sub>60</sub>H<sub>64</sub>N<sub>4</sub>O<sub>8</sub>: C, 74.36; H, 6.66; N, 5.78; O, 13.21. Found: C, 74.22; H, 6.76; N, 5.38.

*N*,*N*'-Bis(dodecyl)-1,7-bis(4-pyridyl)perylene-3,4,9,10-diimide (PDI5). Yield: 85% (0.7 g); Black color solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ ppm) 8.85–8.70 (m, 4H, *Pyr-H*), 8.55 (s, 2H, *Per-H*), 8.20–8.30 (m, 2H, *Per-H*), 7.78–7.75 (d, 2H, *Per-H*), 7.65–7.60 (d, 4H, *Pyr-H*), 4.22–4.15 (t, 4H, N-*CH*<sub>2</sub>), SCHEME 1: Synthesis of Perylenediimide Derivatives: (i) R-B(OH)<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, 1M K<sub>2</sub>CO<sub>3</sub>, THF, N<sub>2</sub>, 75°C



 TABLE 1: Thermal Characteristics of Perylenediimide

 Derivatives

PDI derivatives	$T_{\rm m}$ (°C)	$T_{\rm g}$ (°C)	$T_{\rm cr}$ (°C)	<i>T</i> <sub>ID-5%</sub> (°C)
PDI1	155	50	_	436
PDI2	_	57	_	443
PDI3	245	99	155	460
PDI4	_	102	_	443
PDI5	_	81	_	450

1.72–1.63 (m, 8H, alkyl-*CH*<sub>2</sub>-), 1.44–1.29 (m, 30H, alkyl-*CH*<sub>2</sub>), 0.92–0.84 (m, 12H, alkyl-*CH*<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 162.8, 134.3, 132.4, 130.1, 128.8, 128.0, 124.2, 123.05, 122.7, 77.4, 77.0, 76.5, 40.6, 31.9, 29.6, 29.6, 29.5, 29.3, 28.1, 27.1, 22.6, 22.5, 14.1. EI-MS *m*/*z*: 880.67 (Exact Mass: 880.49). Anal. Calcd for C<sub>58</sub>H<sub>64</sub>N<sub>4</sub>O<sub>4</sub>: C, 79.06; H, 7.32; N, 6.36; O, 7.26. Found: C, 78.85; H, 7.26; N, 6.05.

### **Results and Discussion**

**Synthesis of Perylenediimide Derivatives.** The chemical structures of perylenediimide derivatives (PDI1-PDI5) are shown in Figure 1. The electron-deficient substituents such as bromo (PDI1), 2,4-di(trifluoromethyl)phenyl (PDI2), 4-cyanophenyl (PDI3), 3-nitrophenyl (PDI4), and 4-pyridyl (PDI5) were incorporated in the bay region of perylenediimide core.

The optical behavior of PDI2-PDI5 were compared with 1,7dibromoperylenediimide (PDI1) and the effect of substituents were studied. The PDI derivatives were synthesized using Suzuki coupling in 70–80% yield and illustrated in Scheme 1.<sup>13,14</sup> PDI1 was synthesized using bromination of perylene dianhydride followed by condensation with *n*-dodecylamine.<sup>14a</sup> PDI1 was purified by column chromatography (20% ethyl acetate:hexane) followed by repeated washing with dichloromethane:methanol (1:1) mixture and the pure 1,7-dibromoPDI was obtained in 65% yield. The PDI derivatives were characterized using <sup>1</sup>H and <sup>13</sup>CNMR (see Supporting Information), EI-MS, and elemental analysis.

**Thermal Properties.** Thermal stability, glass transition, and crystallization behavior of PDI derivatives were studied using TGA and DSC techniques, and the results are summarized in Table 1. TGA traces were recorded at a heating rate of 20 °C/ min under nitrogen atmosphere and are presented in Figure 6. The substituted PDI2-PDI5 derivatives showed higher thermal stability than PDI1, which might be due to increase in rigidity after incorporation of bay substituents. The perylene derivatives were found to be thermally stable up to ca. 440 °C with 5% weight loss temperature (*T*<sub>ID</sub>) ranging from 436 to 460 °C. The first major weight loss observed from 450 to 500 °C might be due to loss of two *n*-dodecyl chains (2 × C<sub>12</sub>H<sub>25</sub>). Irrespective



**Figure 6.** TGA traces of PDI derivatives recorded at a heating rate of  $20 \text{ }^{\circ}\text{C} \text{ min}^{-1}$  under nitrogen atmosphere.



**Figure 7.** DSC curves of (A) PDI1, PDI4, and PDI5, (B) PDI2 (dotted line) and PDI3 (solid line). Heating rate: 10 °C min<sup>-1</sup> under nitrogen atmosphere.

of the substitutents in the bay region, all the PDI derivatives showed similar thermal decomposition curves.<sup>14a</sup> Values of  $T_{\rm g}$ ,  $T_{\rm cr}$ , and  $T_{\rm m}$  of PDI derivatives were obtained from DSC thermogram and are recorded at a heating rate of 10 °C/min and summarized in Table 1. All DSC curves are presented in Figure 7, A and B. Glass transition, melting, and crystallization temperature were recorded during second heating and cooling cycle, respectively. The DSC curves showed that all perylenediimide derivatives were amorphous materials, except PDI3. The typical DSC curves for PDI2 and PDI3 are shown in Figure 7B. PDI2 which was obtained as an amorphous compound showed only glass transition at 57 °C in the DSC scans. PDI3 showed endothermic melting signal at 245 °C in the first DSC heating scan. During the slow cooling scan PDI3 did not show recrystallization. It was transformed into amorphous (glassy) state and in the second heating scan a glass transition at 99 °C was observed. However, further heating revealed an exothermic recrystallization peak with a maximum at 155 °C and an endothermic melting peak with a maximum at 245 °C.

**Spectral Properties.** The spectral properties of the PDI derivatives were investigated using UV–vis and PL spectroscopy. The absorption and emission spectra of the PDI solutions shown in Figure 8 were recorded in chloroform at a concentration of  $10^{-5}$  M. The absorption and emission spectra of the PDI films are displayed in Figure 9. The peak energies of the absorption ( $E_{abs}$ ) and emission ( $E_{em}$ ) spectra, PL quantum yields



**Figure 8.** Absorption (dashed line) and PL (solid line) spectra of the PDI derivatives in chloroform.



Figure 9. Absorption (dashed line) and PL (solid line) spectra of the films of PDI derivatives.

(QY), PL decay time constants ( $\tau$ ), and CIE 1931 color coordinates of the PDI1–PDI5 derivatives are summarized in Table 2.

The introduction of electron-withdrawing groups induces rather small changes to the shape and maxima of the absorption spectra of the PDI derivative solutions as compared to the changes imposed by the electron-donating groups.14 This observation can be explained by the lack of charge transfer from electron-withdrawing substituents to the perylene core.<sup>8,9,14</sup> The main absorption peak energies of the PDI1 (2.36 eV) and PDI2 (2.37 eV) derivatives are similar to those of PDIs with symmetrical substitution at the imide nitrogen positions and can be attributed to the  $\pi - \pi^*$  transition in the perylene core.<sup>13</sup> In accordance with our theoretical calculations, the absorption band of PDI3-PDI5 derivatives is red-shifted by ca. 0.07 eV as compared to that of PDI1-PDI2. The main absorption peaks of the PDI2 (2.37 eV) and PDI5 (2.3 eV) derivatives were found to be 0.1 eV larger as compared to the calculated  $S_0 \rightarrow S_1$ transition energies for PDI2 (2.27 eV) and PDI5 (2.2 eV) derivatives. This discrepancy between the experiment and theoretical calculations is apparently caused by the solvation, which was not taken into account in the calculations. The absorption and PL spectra of the PDI derivatives are found to be nearly mirror images of each other with clearly resolved

TABLE 2: Optical Properties of PDIs in Solution and Solid State

PDI derivatives	solution state				solid state					
	$E_{\rm abs}~({\rm eV})$	$E_{\rm em}~({\rm eV})$	QY	$\tau$ (ns)	CIE $(x,y)$	$E_{\rm abs}~({\rm eV})$	$E_{\rm em}~({\rm eV})$	QY	$\tau_{\text{initial}}$ (ns)	CIE $(x,y)$
PDI1	2.361, 2.530, 2.705	2.282	0.73	4.45	0.496, 0.481	2.126, 2.460	1.994	< 0.005	< 0.07	0.664, 0.336
PDI2	2.368, 2.537, 2.71	2.268	0.61	4.66	0.521, 0.465	2.342, 2.510	1.994	< 0.005	< 0.07	0.606, 0.394
PDI3	2.272, 2.422, 2.633	2.095	0.44	6.80	0.641, 0.647	2.153, 2.333	1.748	< 0.005	< 0.07	0.651, 0.349
PDI4	2.282, 2.439, 2.645	2.121	0.45	6.31	0.622, 0.366	2.205, 2.372	1.748	< 0.005	< 0.07	0.673, 0.327
PDI5	2.301, 2.452, 2.66	2.149	0.47	6.00	0.661, 0.324	2.225, 2.402	1.748	< 0.005	< 0.07	0.637, 0.363

vibronic structures, in particular, for the PDI1 and PDI2 derivatives. A pronounced progression of the vibronic peaks with the strongest  $\pi - \pi^*$  transitions is commonly observed in perylenediimides due to their rigid core structure.<sup>11</sup>

Absorption and PL band broadening results in an obscured vibronic structure for PDI3–PDI5 solutions and can be caused either by increased conjugation between the substituents and the PDI core<sup>12</sup> or by the substituent-induced twisting of the core.<sup>14,21</sup> Our quantum chemical calculations indicate the possible increase of conjugation between the substituents and the core for PDI3–PDI5 due to the reduction of torsional angle between the planes of the core and substituents. However, the calculations also indicate that the substituent-induced twisting of the core remains almost unchanged for all the PDIs studied.

Introduction of different substituents at the bay position of the PDI core results in the red shift of the absorption maximum from 2.36 to 2.27 eV and twice as large red shift of the PL maximum from 2.28 to 2.10 eV. The pronounced bathochromic shift of the emission maxima of the PDI3-PDI5 as compared to the PDI1 and PDI2 by 0.17 eV is also in agreement with our theoretical predictions that indicate lower  $S_0 \rightarrow S_1$  transition energies as well as lower torsional activation barrier for PDI3-PDI5. Continuous decrease of the PL quantum yield following the red shift of the PL peak is observed in the PDI derivatives. The origin of such behavior is caused by the interplay between radiative and nonradiative relaxation processes, which are discussed below.

Absorption and PL spectra of the PDI1-PDI5 films are shown in Figure 9. The spectra of the films are broadened and red-shifted as compared to that of the solutions. Despite the spectral broadening, the persistent vibronic modes in the absorption spectra of the films closely resemble those in the absorption spectra of dilute PDI solutions, where molecules are considered as noninteracting. This suggests amorphous state of the films of PDI2-PDI5 composed of the randomly oriented molecules. Large torsion angles ( $\sim 70^{\circ}$ ) between the planes of the perylene core and aromatic bay substituents revealed by the calculations inhibit close packing of the PDI2-PDI5 molecules, thus preventing their aggregation. An exception is the PDI1 film composed of the molecules with the comparatively small 1,7dibromo substituents, which allow much closer packing of the molecules. This is evidenced by the appearance of a new redshifted absorption band at 2.126 eV associated with aggregates. Another distinctive feature is the 2-4 times larger Stokes shift observed in the PDI films as compared to that in the solutions. This is typical for amorphous systems, where owing to exciton migration, lowest energy states have larger impact on the emission properties. Drastically reduced emission efficiency of the PDI films (QY < 0.005) as compared to the solutions is attributed to enhanced exciton migration to quenching sites associated with molecular oxygen unintentionally introduced in the PDI films during their preparation in ambient conditions.

CIE 1931 chromaticity coordinates (x,y) of the PDI solutions and thin films measured using KonicaMinolta CS-100A chromameter are shown in Figure 10. The color coordinates of PDI1–PDI2 solutions correspond to the yellow region, whereas coordinates of PDI3–PDI5 solutions to the reddish-orange region. The color coordinates of all the PDI films studied correspond to the reddish-orange region, except the PDI2 film with coordinates matching the orange region. Fluorescence image of the thin films of PDI2, PDI3, and PDI4 is given in the Supporting Information (Figure S1).

Photoluminescence Decay Study. PL transients provide information on the dominating excited-state relaxation processes. Figure 11 depicts PL transients measured at the PL band maxima of the dilute chloroform solutions of the substituted PDI derivatives. As revealed by fitting of the experimental data, the curves display mainly single-exponential decays with time constants ( $\tau$ ) in the range of 4.5–6.8 ns with respect to the substituents. PDI5 containing pyridyl substituents exhibits double-exponential decay with the dominant relaxation time  $(\tau_2)$ of 6.0 ns contributing up to 92% of overall PL intensity decay. The origin of the minor decay component  $(\tau_1)$  with the fractional intensity of only 8% is unclear; however, it might result from insignificantly small traces of PDI1 used in the synthesis of PDI5, and due to the spectral overlap of the PL bands of PDI1 and PDI5. The PDI derivative containing bromine (PDI1) showed the fastest PL decay ( $\tau = 4.5$  ns), whereas the derivative with benzonitrile (PDI3) showed the slowest decay ( $\tau = 6.8$ ns). PL decay time is found to be longer for the PDI derivative solutions exhibiting larger Stokes shift.

PL decay curves measured in the neat PDI films bear multiexponential character with the initial dominant decay times of at least  $\sim 10^2$  shorter as compared to those in the solutions. Since the shortest  $\tau$  that can be reliably determined using our photon-counting setup is limited roughly by the pulse width of



**Figure 10.** CIE 1931 *xy* chromaticity diagram of the PDIs in solution (circles) and in the solid state (squares).



**Figure 11.** PL transients (points) of the PDI derivatives in chloroform. Lines represent exponential fits of the measured curves with decay time constants  $\tau$ .



**Figure 12.** PL quantum yield (squares) and decay time (circles) of  $10^{-5}$  M chloroform solutions of the PDI derivatives containing different substituents as a function of Stokes shift. Lines are guides for the eye.

the excitation source, the initial  $\tau$  in the films were shorter than 0.07 ns, and thus the decay closely followed the excitation pulse. The multiexponential (or nonexponential) PL decay in the films is usually explained by excitation delocalization over the neighboring interacting chromophores followed by excitation migration toward lower energy sites and subsequent emission of photons. Exciton migration increased the probability of collisional quenching with molecular oxygen thus causing the dramatic reduction in fluorescence efficiency of the films.

In Figure 12, PL QY and decay time as functions of Stokes shift are shown for the PDI derivatives. Decreased fluorescence quantum yield from 0.61 in PDI2 to 0.47 in PDI5 agrees well with the 1.3 times lower oscillator strength obtained from the calculations for the transition  $S_0 \rightarrow S_1$  in PDI5 as compared to that in PDI2. A clear tendency of decreasing QY and simultaneous increasing of the decay time followed by the increasing Stokes shift for the PDI derivatives can be observed. Usually increased energy (Stokes) losses indicate enhanced probability for the excitation to relax via nonradiative pathways. Thus, about twice as large Stokes shifts observed for pyridine-, nitrobenzene-, and benzonitrile-substituted PDI derivative solutions result in significantly lower QYs (~0.45) as compared to that of



Figure 13. Radiative (squares), nonradiative (triangles), and measured (circles) PL decay time as a function of PL quantum yield for a series of PDI derivatives containing different substituents in chloroform solution  $(10^{-5} \text{ M})$ . Lines are guides for the eye.

bromine-substituted derivative (QY = 0.73) and can be accounted for by enhanced nonradiative relaxation. Increased Stokes losses can be attributed to the lower torsional activation barrier for the aromatic bay substituents in PDI3–PDI5 derivatives as confirmed by quantum chemical calculations. A complete domination of nonradiative decay processes for this series of PDI derivatives decreases the decay time with increase of the Stokes shift, and thus behavior similar to that of QY should be observed. However, the opposite behaviors of the PL decay time together with high PL QYs point out importance of the radiative decay processes.

In order to unveil the competition of radiative and nonradiative decay processes and explain an increase of the measured  $\tau$ with the Stokes shift, radiative ( $\tau_R$ ) and nonradiative ( $\tau_N$ ) decay time constants for each of the PDI derivative was estimated by using the following relations

$$QY = \tau/\tau_R$$
$$\tau^{-1} = \tau_R^{-1} + \tau_N^{-1}$$

Here the term  $\tau_N^{-1}$  takes into account of all possible nonradiative decay pathways including intersystem crossing to triplet states. The deduced  $\tau_{\rm R}$  and  $\tau_{\rm N}$  are plotted in Figure 13 as a function of the PL QY, which represent a particular PDI derivative with different bay substituents. Obviously, attachments of various substituents at the bay positions of the perylene core induce more rapid changes in radiative decay rate as compared to that of nonradiative one. In particular, 10-fold decrease in radiative decay ( $\tau_{\rm R}$ ) and only 3-fold increase in nonradiative decay ( $\tau_N$ ) followed by an increase of PL QY from 0.44 to 0.73, was deduced for this series of PDI derivatives (see Figure 13). This plot unambiguously demonstrates the governing role of radiative decay in the bromine (PDI1), 2,4bis(trifluoromethyl)benzene (PDI2), pyridine (PDI5), nitrobenzene (PDI4), and benzonitrile (PDI3) substituted PDI derivative solutions, which is responsible for increase of the measured  $\tau$ with the Stokes shift and behaves oppositely to the PL QY (see Figure 13).

The larger variation of  $\tau_R$  as compared to that of  $\tau_N$  induced by the attachment of different substituents at the perylene core is most likely determined by the interaction between the  $\pi$ -systems of the core and the substituents. Experimentally estimated reduction of the radiative decay rate in PDI5 as compared to that in PDI2 is in good agreement with the weakening of the oscillator strength as predicted by our calculations. Meanwhile, the tendency of an increase of nonradiative decay rate in PDI1–PDI5 can be attributed to an increase of torsional motion of the bay substituents. This tendency is inline with the increase of glass forming temperature from 57 to 102  $^{\circ}$ C for the PDI derivatives evaluated from DSC measurements.

The small perturbation of the core by 2,4-bis(trifluoromethyl)phenyl substituents results from nearly orthogonal orientation (torsion angle 72°) of the substituents with respect to the core accompanied by high torsional activation barrier of the substituents. This may be due to the steric repulsion of the orthosubstituted trifluoromethyl moiety from the perylene core. The similar steric effects resulting in orthogonally oriented perylene and aromatic substituents have been observed for other 1,7diaryl-substituted PDIs.<sup>13</sup> The significant red shift in absorption and PL spectra, and low PL QYs of pyridyl-, nitrophenyl-, and cyanophenyl-substituted PDI derivatives imply the increased  $\pi$ -interaction between the perylene core and the substituents due to the presence of nonbonded electron in the bay region and lower torsional activation barrier of the bay substituents.

#### Conclusion

A series of perylenediimide derivatives substituted at the bay positions of the pervlene core have been synthesized in good yields. The new derivatives demonstrated glass-forming properties with the glass transition temperatures ranging from 57 to 102 °C. Photophysical studies indicated high luminescence quantum yield in the solution (0.44-0.73). The bay substitution induced red shift of the emission wavelength (of 0.18 eV) in solution, which was followed by the increase of the Stokes shift (0.1 eV) and 1.5-fold increase in the fluorescence lifetime. Analysis of the luminescence lifetime and quantum yield indicated that the substitution at the bay positions of the perylene core invoked drastic changes in radiative decay rate and relatively small ones in nonradiative decay rate. The large variation of radiative relaxation rate was attributed to the orientation-dependent interaction of the  $\pi$ -systems of the core and the substituents due to potential steric effects at the bay position, as was confirmed by quantum chemical calculations.

The spectral properties of the wet-casted perylenediimide films resembled those of the molecules. Additionally, the larger variation in the emission peak (of 0.25 eV) and considerable increase of the Stokes shift (of 0.4 eV) implied formation of the amorphous (glassy) state, which was also confirmed by differential scanning calorimetry measurements.

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**Supporting Information Available:** <sup>1</sup>H and <sup>13</sup>C NMR, and MS spectra of all synthesized PDI derivatives are given. This material is available free of charge via the Internet at http:// pubs.acs.org.

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