

# Novel Fluorescent Dyes with Fused Perylene Tetracarboxylic Diimide and BODIPY Analogue Structures

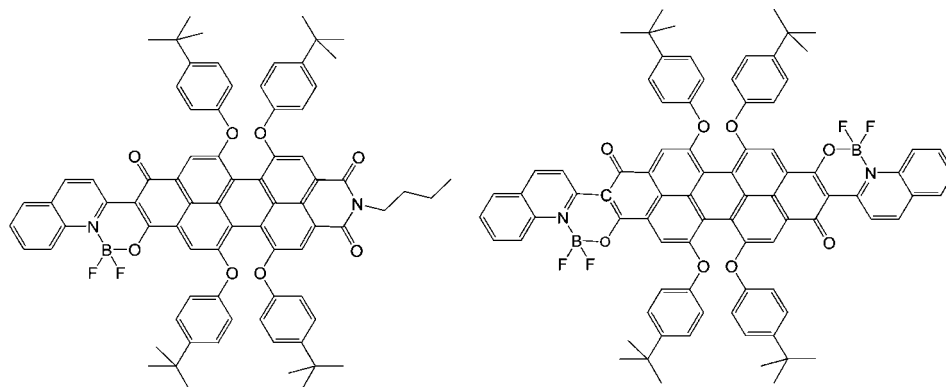
Junqian Feng,<sup>†,‡</sup> Baolong Liang,<sup>†</sup> Delou Wang,<sup>†</sup> Lin Xue,<sup>†</sup> and Xiyou Li<sup>\*,†</sup>

Department of Chemistry, Shandong University, 250100, China, and College of Shandong Policeman, Shandong, 250014, China

xiyouli@sdu.edu.cn

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## ABSTRACT



Two novel fluorescent dyes based on perylene tetracarboxylic diimides and BODIPY were designed and synthesized. Significant features, such as longer wavelength absorption and emission, high fluorescence quantum yields, and strong electron accepting abilities, are observed for these compounds.

Perylene tetracarboxylic diimides (PDIs) are currently being investigated as photoactive materials for use in a variety of fields because of their excellent thermal and photochemical stability, high luminescence efficiency, and novel optoelectronic properties.<sup>1,2</sup> Driven by the demands of various applications, the molecular modification aimed at changing the photophysical properties of PDIs has stimulated a lot of

interest in the past decade.<sup>3</sup> The modification of the molecular structure of PDIs can be achieved by introducing side groups either to the imide nitrogen atoms or at the bay positions.<sup>4</sup> Incorporation of substituents onto the imide nitrogen atoms could improve the solubility of PDIs in organic solvents and

<sup>†</sup> Shandong University.

<sup>‡</sup> College of Shandong Policeman.

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affect the packing mode of PDI molecules in the solid state, but did not change the photophysical properties significantly. However, the substituents at the bay positions could change the photophysical properties of PDIs efficiently, depending on their electron withdrawing or donating abilities and steric hindrance. PDIs with longer wavelength absorption and emission are required for a laser dye as well as the photodynamic therapy applications. Electron donating groups at the bay positions can shift the absorption and emission of PDIs to the longer wavelength, but induce a significant drop on fluorescence quantum yield and electron affinity at the same time.<sup>5</sup> To change the absorption of PDI to a longer wavelength without significant effect on their other physical properties is always a challenge.

The difluoroboradiazaindacene compounds (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene, abbreviated as BODIPY), which were known as “porphyrin’s little sister”, have similar fascinating features with PDIs.<sup>6</sup> The excellent thermal and photochemical stability, high fluorescence quantum yield, together with intense absorption profile have made them a kind of important biological probe.<sup>7</sup> To improve the properties of BODIPY as a biological probe, great efforts aimed at expanding the absorption and emission windows have been made. Fusion of aromatic rings to the pyrrole units in BODIPY was proved to be an efficient way to achieve this purpose.<sup>8</sup>

To create a new PDI dye with strong long-wavelength absorption and emission while keeping the excellent heat and photochemical stabilities unchanged, the combination of PDI and BODIPY in one molecule is a rational design. The one and only example that combined both PDI and BODIPY in one molecule to date has been reported by Akkaya and co-workers.<sup>9</sup> The BODIPYs were connected at the bay positions of PDI by a long and flexible linkage. Because of the large distance between BODIPY and PDI, there is no interaction between them at ground states and therefore there is no change on the absorption spectra relative to their precursors. We present here another example that combined both BODIPY and PDI unites in one molecule. In contrast to that reported by Akkaya, the BODIPY and PDI units in **1** and **2** are closer together and so are in conjugation with one another (Scheme 1). These new compounds are expected to show different absorption and emission spectra from their precursors while keeping the

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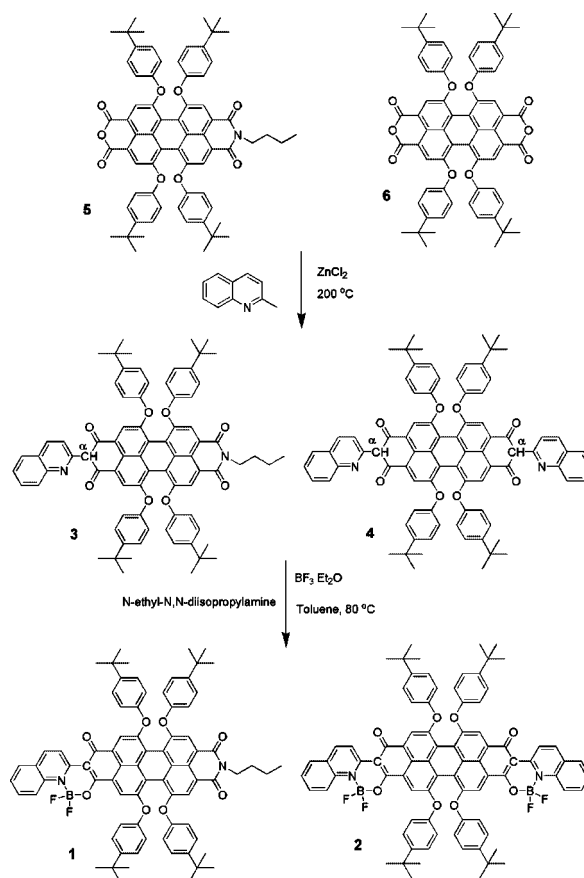
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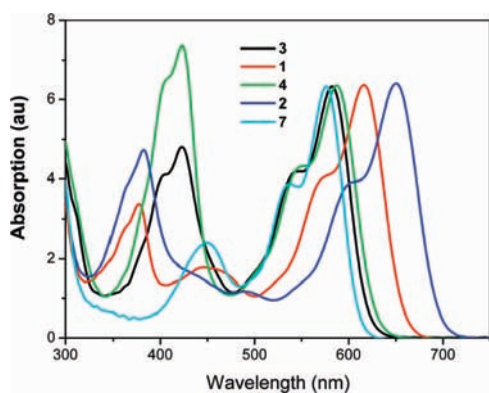
Scheme 1. Synthesis of **1–4**



good photochemical stabilities and high fluorescence quantum yields unchanged.

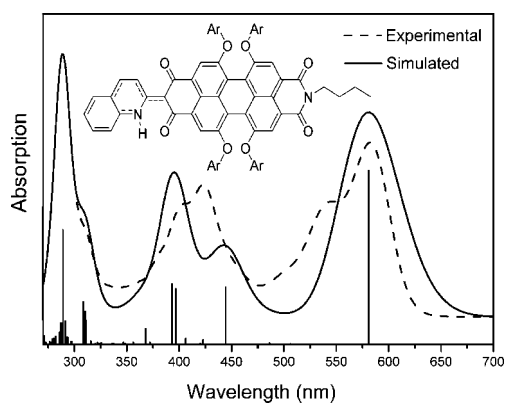
The synthetic procedures for **1** and **2** are described in Scheme 1. Condensation of **5** or **6** with 2-methylquinoline was carried out without solvent by using zinc chloride as a catalyst following a modified literature method.<sup>10</sup> Products **3** and **4** were obtained with yields of 63% and 58%, respectively, and were reacted further with  $\text{BF}_3\cdot\text{OEt}_2$  in toluene at 60 °C in the presence of *N*-ethyl-*N,N*-diisopropylamine for 2.5 h to give **1** or **2** in yields of 72% or 68%, respectively. Other methods, such as coordination in dichloromethane, can also afford the products, but with lower yields. All these compounds show good solubility in conventional halogenated organic solvents with good stability. However, slow decomposition in alcoholic solvents was observed. The structures of these compounds were fully characterized by different spectroscopic methods, including  $^1\text{H}$  and  $^{13}\text{C}$  NMR, MALDI-TOF mass spectrometry, as well as elemental analysis. It is worth noting that the signals corresponding to the proton  $\alpha$  to the quinoline (Scheme 1) in compounds **3** and **4** were not observed, probably because of the strong acidity of these protons which induce a quick exchange with the protons of solvents. Compound **2** should

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**Figure 1.** Normalized absorption spectra of compounds **1–4** compared with that of **7** in dichloromethane.

be theoretically collected as a mixture of *cis*- and *trans*-isomers. The  $^1\text{H}$  NMR spectrum recorded on a 300 MHz instrument did not show any clue of the existence of isomers; however, the spectrum recorded on a 600 MHz instrument indeed showed the presence of *cis*- and *trans*-isomers (Supporting Information). Attempts to separate the isomers by different chromatography methods failed.



**Figure 2.** Comparison of the simulated absorption spectrum with the experimental recorded spectrum of **3**.

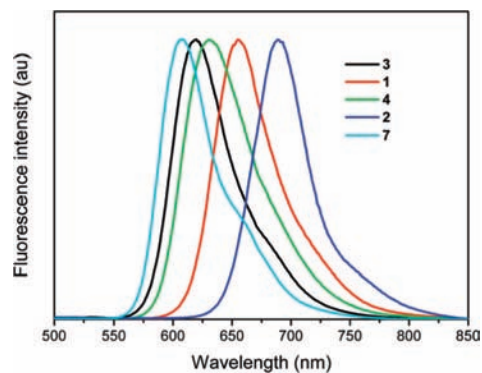
Figure 1 compares the electronic absorption spectra of compounds **1–4** with that of model compound *N,N'*-dibutyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)perylene-3,4:9,10-tetracarboxylic diimide (**7**)<sup>11</sup> in dichloromethane. All of these compounds show intense absorption in the UV–vis region. The maximal absorption peaks of compounds **3** and **4** red-shifted for about 6 and 11 nm, respectively, compared with that of **7** because of the introduction of quinoline. To reveal the origin of this red-shift, the absorption spectra of **3** were simulated with the TD-DFT method<sup>12</sup> based on three

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minimized structures with DFT calculation (Figure 2 and Figure S8 in the Supporting Information). It was found that the simulated absorption spectrum of the tautomeric structure in which the nitrogen is protonated was the most similar to that observed experimentally. In this structure the conjugated system of PDI is expanded and the absorption was shifted to red. This structure also explains the missing signals of the protons at the  $\alpha$  position in the  $^1\text{H}$  NMR spectra. These calculations have also been carried out for compound **4** (Figure S9 in the Supporting Information) and similar results were obtained.

The maximal absorption peaks of **1** and **2** were further red-shifted to 616 and 650 nm, respectively. This significant red-shift can be ascribed to the expanded aromatic system in the structures of **1** and **2** because the coordination of boron has driven the quinoline to take a precisely coplanar conformation with PDI. The minimized structure with DFT calculation of **1** and **2** confirmed this speculation and the simulated absorption spectra agree well with the experimental results (Figures S10 and S11 in the Supporting Information).



**Figure 3.** Normalized fluorescence spectra of **1**, **2**, **3**, and **4** compared with that of **7** in dichloromethane (excited at 450 nm).

The fluorescence spectra of compounds **1–4** in different organic solvents were recorded and the fluorescence quantum yields ( $\Phi_f$ ) are calculated with **7** as the standard. In addition, the fluorescence lifetimes ( $\tau$ ) are measured by the phase

**Table 1.** Photophysical Properties of Molecules **1–4** and **7**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>7</b>
$\lambda_{\text{abs}}$ (nm)	616	650	582	588	576
$\lambda_{\text{em}}$ (nm)	655	689	620	632	607
$\Phi_f$ (%)					
toluene	53.6	35.0	56.8	55.1	100
THF	47.1	34.2	46.4	44.6	100
$\text{CH}_2\text{Cl}_2$	50.0	34.7	66.2	58.8	100
$\tau$ (ns)					
toluene	5.01	4.42	3.52	3.37	6.40
THF	4.97	4.41	3.46	3.33	6.97
$\text{CH}_2\text{Cl}_2$	5.45	4.77	4.29	3.89	6.85

modulation method with a scattering solution as reference. The fluorescence spectra of **1–4** and **7** are shown in Figure 3 and the fluorescence quantum yields and lifetimes are summarized in Table 1.

Similarly, the maximal emission peaks for compounds **1–4** red-shifted significantly relative to that of **7**. This can be ascribed to the extension of the conjugation system because of the connection of quinoline. The fluorescence quantum yields of compounds **1–4** are almost half of that of **7**. This might be attributed to the increased flexibility of the molecules because of the incorporation of the quinoline unit, which induces mass nonradioactive decay. The fluorescence lifetimes of these compounds are in the range of 3.3 to 5.5 ns, which are smaller than that of **7**. Similarly the shorter lifetimes might also be caused by the enhanced nonradioactive decay. Amidines prepared by condensation of perylene-tetracarboxylic dianhydride with arylamine show similar red-shifted absorption and emission. But the fluorescence quantum yields and lifetimes of these compounds have not been reported so far, probably because of their low emission efficiency.<sup>13</sup>

**Table 2.** Half-Wave Redox Potentials<sup>a</sup> (vs SCE) of Compounds **1–4** and **7** in CH<sub>2</sub>Cl<sub>2</sub>

compd	oxd <sub>2</sub>	oxd <sub>1</sub>	red <sub>1</sub>	red <sub>2</sub>	red <sub>3</sub>	$E_{1/2}^{0,b}$
<b>1</b>	1.60	1.27	−0.57	−0.70	−1.65	1.79
<b>3</b>	1.52	1.21	−0.82	−1.19		2.03
<b>2</b>	1.54	1.25	−0.50	−1.57	−1.65	1.75
<b>4</b>	1.42	1.15	−0.80	−1.26	−1.73	1.95
<b>7</b>	1.78	1.28	−0.72	−0.95		2.00

<sup>a</sup> Values obtained by DPV in dry CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M TBAP as the supporting electrolyte and Fc/Fc<sup>+</sup> as internal standard. <sup>b</sup>  $E_{1/2}^{0} = \text{oxd}_1 - \text{red}_1$ .

Both BODIPY and PDIs are good electron acceptors as revealed by the previous report.<sup>6,14</sup> Therefore the newly synthesized compounds in this work are expected to show good electron accepting abilities. The electrochemical behaviors of these compounds are investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The half-wave redox potential values vs SCE of **1–4** together with that of model **7** are summarized in Table 2. Within the electrochemical window of CH<sub>2</sub>Cl<sub>2</sub>, compounds **1–4** undergo at least one reversible one-electron oxidation and two quasi-reversible one-electron reductions.

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The introduction of quinoline groups onto the PDI ring induces a negative shift for both first oxidation and reduction potentials of **3** and **4**. The first oxidation potential decrease from 1.28 V for **7** to 1.21 V for **3** and 1.15 V for **4** while the first reduction potential decreased significantly from −0.72 V for **7** to −0.82 and −0.80 V for **3** and **4**, respectively. This result suggests that quinoline is an electron donating group and it makes compound **3** and **4** more stable toward reduction.

The comparison of the first oxidation and reduction potentials of compounds **1** and **2** with that of **7** reveals that the coordination of boron fluoride shifts the first reduction potential to the positive direction while the first oxidation potentials remain unchanged. This allows compounds **1** and **2** to be better electron acceptors than **7**. The experimentally recorded redox potentials correspond well with the calculated energy levels of HOMO and LUMO (Figure S12 and S13 in the Supporting Information). Higher HOMO and LUMO energy levels relate with small oxidation and reduction potentials while the lower HOMO and LUMO energy levels always go with larger oxidation and reduction potentials. The PDIs with strong electron withdrawing abilities were reported to be good *n*-type organic semiconductors by several groups.<sup>3c,15</sup> Seeking new PDIs with larger electron withdrawing ability is now a fascinating direction for organic semiconductor research.<sup>16</sup> The condensation of BODIPY with PDI seems a promising way to achieve this purpose.

In summary, we have synthesized two novel fluorescent dyes with longer wavelength absorption and emission by closely combining BODIPY and PDI in one molecule. These compounds show good solubility in conventional organic solvents and reasonable fluorescence quantum yields. The most significant is these new compounds are better electron acceptors than their parent analogues and therefore they are promising candidates for *n*-type organic semiconductors.

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**Supporting Information Available:** Experimental methods, detailed synthetic procedures and structure characterizations, <sup>1</sup>H and <sup>13</sup>C NMR spectra and simulated absorption spectra of **1–4**, and HOMO and LUMO orbital maps and energy levels of **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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