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Perylene-Fused BODIPY Dye with Near-IR Absorption/Emission and High Photostability

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ABSTRACT

A N-annulated perylene unit was successfully fused to the meso- and β-positions of a boron dipyrromethene (BODIPY) core. The newly synthesized BODIPY dye 1b exhibits intensified near-infrared (NIR) absorption and the longest emission maximum ever observed for all BODIPY derivatives. In addition, this dye possesses excellent solubility and photostability, beneficial to practical applications.

4,4-Difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene, also known as boron dipyrromethene (BODIPY, Figure 1), represents an extraordinary class of fluorophore.[1] Its unusual and remarkable properties, such as high fluorescence high quantum yield, large molar extinction coefficients, and outstanding chemical, thermal, and photochemical inertness, make it attractive for a variety of applications

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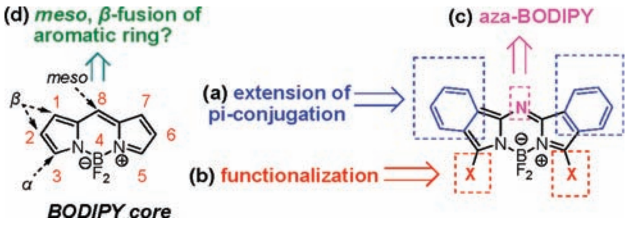
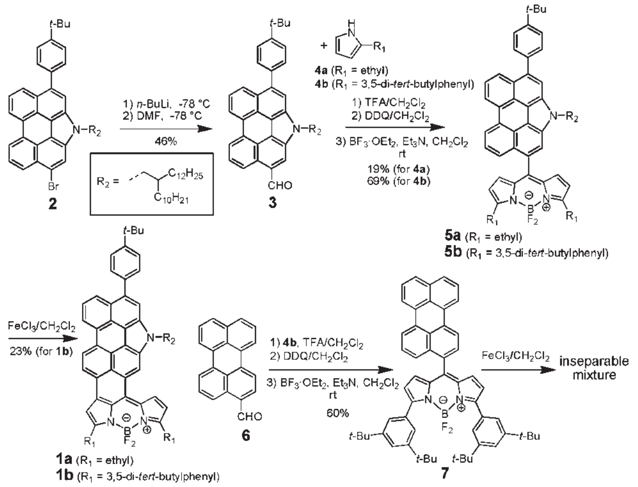


Figure 1. Molecular appoaches toward BODIPY dyes with longer absorption and emission.

including luminescent devices,[2] chemical sensors,[3] biological labeling,[4] and photovoltaic devices.[5] BODIPY chromophores generally possess visible absorption and fluorescent emission located between 470 and 550 nm. Considering the increasing interest in the preparation of near-infrared (NIR) absorption as well as NIR emission dyes,[6] promotion of the absorption and emission of a BODIPY dye to the far-red and even to the NIR spectral region by structural modifications is crucial and necessary. As shown in Figure 1, such modifications currently include (a) extension of π-conjugation by fusing a rigid ring to the pyrrole unit,[7] (b) functionalization at the α- and/or *meso*-position to generate a "push—pull" motif,[8] and (c) replacement of the 8-carbon atom with a nitrogen atom to form aza-BODIPY dyes.[9]

The fusion of polycyclic aromatic compounds to porphyrin cores has recently attracted considerable interest,[10] and these fused hybrid molecules usually show intensified NIR absorption and in some cases also exhibit moderate NIR emission.[10h] BODIPY dye, porphyrin's little sister, provides a nice "zig-zag" geometry for fusion of an aromatic unit to the *meso*- and β-positions (method (d), Figure 1). Such a fusion is beneficial to the bathochromic shift of the absorption and emission to a far-red and NIR spectral region. Despite the structural similarities between BODIPY and porphyrin, fusion of a polycyclic aromatic compound onto the zig-zag edge (i.e., *meso*- and β-positions) of a BODIPY core, to the best of our knowledge, has never been reported. Herein, we report the first example of polycyclic aromatic unit fused BODIPY **1b** (Scheme 1) which exhibits an intensified NIR absorption and acceptable NIR emission.

Scheme 1



The *N*-annulated perylene-fused BODIPY **1b** was synthesized as shown in Scheme 1. Initially, we attempted to prepare its analog **1a** in which two ethyl groups are attached to the α-positions of the BODIPY core. The perylene aldehyde **3** was first prepared in 46% yield by lithiation of monobrominated *N*-annulated perylene **2**[11] followed by reaction with anhydrous DMF. Acid-catalyzed condensation of the obtained aldehyde **3** with 2 equiv of 2-ethyl pyrrole **4a** led to the corresponding dipyrromethane derivative in good yield. Due to high reactivity, this dipyrromethane was used for the next step without further purification. Subsequent oxidation by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and complexation with $BF_3 \cdot OEt_2$ afforded the *N*-annulated perylene-BODIPY dyad **5a** with an overall yield of 19% in three steps. Iron(III) chloride, a well-known mild oxidant, has proven to be effective to promote cyclodehydrogenation of many branched oligophenylenes into polycyclic aromatic hydrocarbons.[12] Herein, intramolecular ring fusion of **5a** by using 2 equiv of $FeCl_3$ as an oxidant yielded a mixture with a longer absorption between 600 and 800 nm, indicating formation of the desired ring-fused product **1a**. However, separation of this mixture turned out to be extremely difficult due to strong aggregation of the products in both the solid state and solution, despite the presence of bulky 4-*tert*-butylphenyl and branched aliphatic chains attached to the *N*-annulated perylene unit. Such a troublesome problem was also observed for aromatic ring-fused porphyrin systems, which can be somewhat alleviated by the

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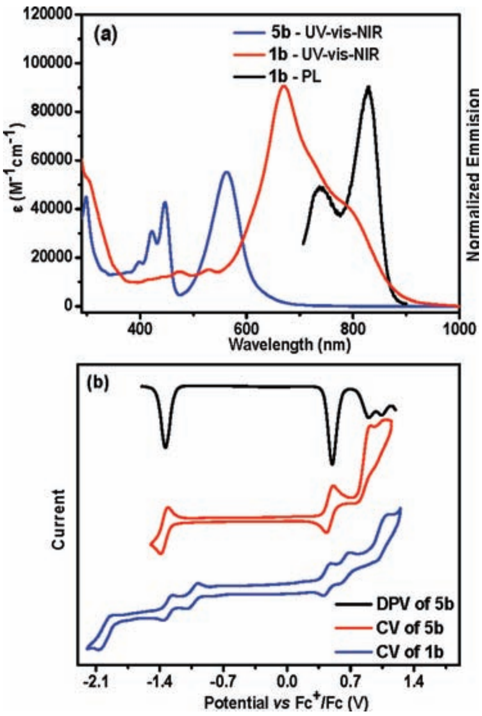

Figure 2. (a) UV−vis−NIR absorption spectra of **1b** and **5b** in toluene (1.0×10^{-5} M) and photoluminescence (PL) spectrum (1×10^{-6} M) of compounds **1b** in toluene (excitation wavelength is 670 nm). (b) Cyclic voltammograms (CV) of **1b** and **5b** in DCM with 0.1 M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mV/s. The differential pulse voltammogram (DPV) of **5b** was shown to distinguish the oxidation waves. Fc/Fc$^+$ was used as external reference.

introduction of a bulky 3,5-di-*tert*-butylphenyl group to the *meso*-positions of porphyrin.[10f,g] Inspired by this strategy, we thus modified the structure of the target compound by attaching two bulky 3,5-di-*tert*-butylphenyl groups directly onto the α-positions of the BODIPY core (**1b**). Accordingly, the 3,5-di-*tert*-butylphenyl-substituted pyrrole **4b** was prepared (see Supporting Information (SI) for synthetic details) and used for the acid-catalyzed condensation reaction with **3**. Compound **5b** was then obtained in an overall yield of 69% in three steps, through the same synthetic route used for **5a**. Oxidative cyclization of precursor **5b** was carried out with $FeCl_3$ in dichloromethane (DCM) to give the desired product **1b** in 23% yield. The final compound **1b** has very good solubility, and it did not show strong aggregation in solution and allowed us to separate and characterize it more conveniently (see SI). In addition, fusion of unmodified perylene to the BODIPY core was also attempted by using the same strategy starting from the reaction between the perylene aldehyde **6**[13] and **4b**. The obtained perylene-BODIPY dyad **7** was submitted to a similar cyclization with $FeCl_3$. However, a strongly aggregated mixture with a deep green color was obtained, which cannot be further purified.

The absorption spectrum of precursor **5b** in toluene displays the characteristic bands of respective BODIPY and *N*-annulated perylene while the fused compound **1b** demonstrates a significant bathochromic shift of the absorption maximum with respect to **5b** (Figure 2a). Compound **1b** shows intensified absorption bands with the absorption maximum at 670 nm (ε = 91 000 M^{-1} cm^{-1}) together with a shoulder around 780 nm. The absorption behavior of **1b** is nearly independent of solvent polarity. However, the photoluminescence (PL) spectrum of this molecule exhibits solvent dependence (Figure S1 in the SI). Dye **1b** in different solvents displays two distinct emission bands (band I located between 700 and 758 nm and band II located between 790 and 860 nm). Upon increasing the polarity of the solvent from hexane to toluene and to chloroform, the ratio of band I intensity to band II intensity successively increases (Figure S1 and Table S1 in the SI). Band I could be assigned to the original PL band whereas band II at a longer wavelength is attributed to the formation of aggregates of the dye molecules in solution, which is reflected by the fact that the ratios of the intensity of band II to band I in emission spectra successively increase upon increasing the concentration of dye **1b** in toluene (Figure S2 in the SI). Since many highly conjugated π-systems prefer to form aggregates in a nonpolar solvent *via* $\pi-\pi$ interactions,[14] such a solvent dependence of PL spectra can be explained by the different degrees of aggregation in different solvents. The excitation spectra of **1b** at the two main fluorescence peaks disclosed that even the absorption spectrum of **1b** is the superposition of the monomer and aggregates (Figure S3 in the SI). Also noteworthy is that dye **1b** in toluene exhibits emission with the maximum at 830 nm (Figure 2a), which is the longest NIR emission maximum ever observed for all BODIPY derivatives. Relatively low photoluminescence quantum yields up to 0.8% were observed for **1b** in toluene mainly due to the dye aggregation in solution. Of course, other factors such as conformation change of the excited molecules and weak photoinduced intramolecular charge transfer from *N*-annulated perylene to the BODIPY core can also decrease the fluorescence quantum yield.

The electrochemical properties of **1b** and **5b** were investigated by voltammetry in deoxygenated DCM solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. As shown in Figure 2b, three reversible reduction waves with half-wave potentials at −1.04, −1.31, −2.00 V (vs Fc$^+$/Fc) and three reversible oxidation waves with half-wave potentials at 0.50, 0.64, 1.16 V were observed for **1b**. A HOMO energy level of −5.16 eV and a LUMO energy level of −3.83 eV were estimated based on the onset potential of the first oxidation and the first reduction wave, respectively.[15] An energy gap

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(15) The HOMO and LUMO energy levels were calculated from the onset of the first oxidation and reduction waves according to equations HOMO = $-(4.8 + E_{ox}^{onset})$ and LUMO = $-(4.8 + E_{red}^{onset})$.

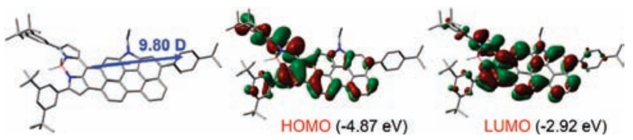

Figure 3. Optimized molecular structure, dipole moment (indicated by arrow), and the frontier molecular orbital profiles of molecule **1b** (the branched aliphatic chain is replaced by an ethyl group during the calculations).

of 1.33 eV was then obtained which is in agreement with the optical band gap (1.38 eV). In contrast, the precursor **5b** exhibits one reversible oxidation wave corresponding to a perylene subunit with a half-wave potential at 0.47 V and two oxidation waves corresponding to the BODIPY core with half-wave potentials at 0.84 and 1.02 V and one reversible reduction wave with a half-wave potential at −1.35 V (Table S2 in the SI). Compared with **1b**, a larger energy gap (2.06 eV) was observed for **5b**, and this is also consistent with the optical band gap (2.02 eV).

To gain better insight into the geometric and electronic structure, time-dependent density function theory (TDDFT at B3LYP/6-31G**) calculations were performed and the optimized molecular structure, dipole moment, and frontier molecular orbital profile are shown in Figure 3. The perylene moiety in **1b** somewhat deviates from the BODOPY plane due to the steric congestion between the protons in the 7-position of BODIPY and the *meta*-proton of the *N*-annulated perylene core. The asymmetry in **1b** also generates a large dipole moment, which is calculated as 9.80 D. The calculations also predict that compound **1b** will show major absorption bands at 705 and 594 nm (Figure S5 and Table S4 in the SI), which are in good agreement with the experimental data.

A solution of **1b** in air-saturated toluene remains unchanged over months at ambient conditions, indicating the excellent photostability of **1b**. To reveal the effect of BODIPY moieties on the photostability, compound **1b** was compared with the *N*-annulated perylene-fused porphyrin dye **8**[10h] as well as the electron-rich bis-*N*-annulated quarterrylene dye **9**.[11] Upon irradiation with UV light (4 W) for 4000 min, the absorbance of dye **1b** in air-saturated toluene remained almost constant and only lost 5% of the initial intensity. In contrast, a half-life time ($t_{1/2}$) of around 244 min was measured in the case of compound **8** while dye **9** cannot even survive for longer than 10 min under the same condition (Figure 4). This observation clearly demonstrates that the fused BODIPY unit is the most effective building block to stabilize the highly electron-rich *N*-annulated perylene. Moreover, the excellent photostability of **1b** is of great importance for practical applications.

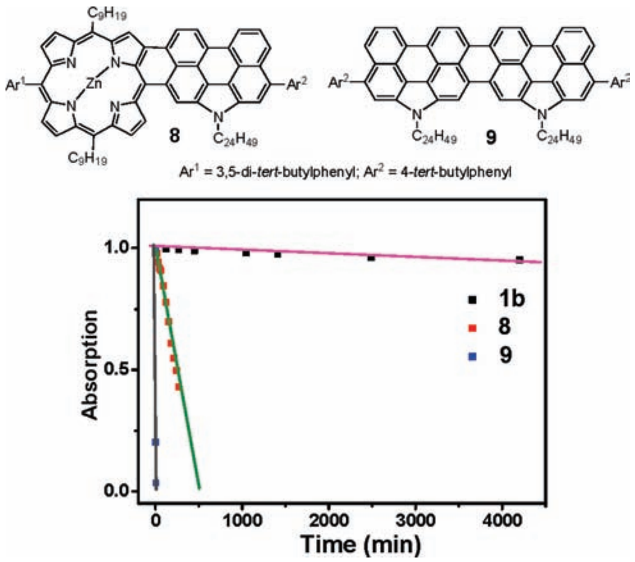

Figure 4. Change of optical density of **1b**, **10**, and **11** at the absorption maximum wavelength with the irradiation time. The original optical density before irradiation was normalized at the absorption maximum. Solutions of compounds **1b**, **10**, and **11** in toluene were irradiated under 4 W UV light (emitting at 254 nm).

In summary, a successful fusion of a *N*-annulated perylene to the *meso*- and β-positions of a BODIPY core was achieved for the first time. Use of the bulky groups on both *N*-annulated perylene and the BODIPY moiety is crucial for the purpose of suppressing aggregation. The obtained dye has a largely delocalized π-system and therefore shows NIR absorption and emission. Noteworthy is that the perylene-fused BODIPY dye exhibits excellent photostability which is important for practical applications. Although the photoluminescence quantum yield is relatively low in the case of **1b**, our approach opens opportunities to prepare a series of new active aromatic unit-fused BODIPY dyes with tunable NIR absorption and emission, and this work is currently underway in our laboratories.

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Supporting Information Available. Experimental details and characterization data of all new compounds, and theoretical calculation data. This material is available free of charge via the Internet at http://pubs.acs.org.