BODIPY-Fused Porphyrins as Soluble and Stable Near-IR Dyes**

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Dye chemistry is believed to be one of the most explored areas in industrial organic chemistry. An area of recently increasing interest is the design and synthesis of so-called near-infrared (NIR) dyes,^[1,2] which function (absorb and/or emit light) in the NIR spectral region, ranging from 700 to 2000 nm, with diverse applications in solar cells,^[3] nonlinear optics,^[4] and bioimaging.^[5] For instance, in organic solar cells, the materials should have good light-harvesting capability, not only in the UV/Vis spectral range, but also at the NIR range, because 50% of the sunlight radiation energy is in the infrared region. In in vivo bioimaging, NIR fluorescent dyes have obvious advantages over traditional visible dyes, because biological samples have low background fluorescence and a concomitant high signal-to-noise ratio in the NIR region. Moreover, NIR light can penetrate sample matrices deeply due to low light scattering.

Porphyrin is one of the most widely investigated, nitrogen-containing, macrocyclic, aromatic compounds. Porphyrins and metalloporphyrins generally have an intense absorption in the 400-450 nm region, called the Soret band, and relative weak absorptions in comparison with the Soret band in the 500-700 nm region, named Q bands. Due to the insufficient absorption property of the porphyrin monomer in the visible and in particular in the NIR region, efforts have been made toward the design and synthesis of π -extended porphyrins, such as porphyrin tapes.^[6] To fuse polycyclic aromatic hydrocarbons (PAHs, e.g., pyrene, anthracene, azulene, and perylene)^[7] to the porphyrin core is another important option for such a purpose and this strategy has proven to fill the aforementioned research gap. A general method towards PAH-fused porphyrins is the intramolecular ring cyclization of singly linked porphyrin-PAH dyads; this usually requires activation of the PAH unit by appropri-

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[**] BODIPY=boron dipyrromethene

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ate substitution. As a result, the obtained, fused systems normally possess high electron density, which inevitably makes them unstable upon long-term exposure to air and light. In our previous work,^[8] the replacement of the relatively electron-rich, N-annulated perylene unit in a perylene-fused porphyrin compound with a perylene monoimide, which contains an electron-withdrawing dicarboxylic imide group, was found to stabilize the highly conjugated system. However, the introduction of electron-deficient units leads to decreased reactivity, which makes fusion reactions or fusion of more building blocks, to achieve longer NIR absorption, difficult. Consequently, how to balance reactivity with stability remains a long-standing challenge for aromatic, ring-fused, porphyrin systems.

Boron dipyrromethene (BODIPY) is a strongly UV/Visabsorbing, small dye with a relatively sharp fluorescenceemission peak with high quantum yield.^[9] Its unusual and remarkable optical and chemical properties enable BODIPY to play important roles in the fields of luminescent devices, chemical sensors, biological labeling, and photovoltaic devices. Similarly to porphyrin, BODIPY also has some undesirable characteristics, such as relatively shorter wavelength absorption and emission in the UV/Vis range. Although three strategies for achieving a bathochromic shift for the BODIPY core have been investigated: 1) replacement of pyrrole with an isoindole unit,^[10] 2) functionalization at the α and/or meso position to generate a "push-pull" motif,^[11] and 3) preparation of aza-BODIPY dyes.^[12] Fusing the BODIPY core to the other aromatic rings has rarely been reported.^[13] In the past year we have been working on the synthesis of BODIPY-fused porphyrins, such as compounds 1 and 2 (Scheme 1). The design is based on the following considerations: 1) The BODIPY core provides a nice "zigzag" edge geometry for fusion of an aromatic unit (e.g., porphyrin) to the *meso* and β positions. Because perylene-fused



Scheme 1. Structures of BODIPY-fused porphyrins 1 and 2.

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BODIPY dyes exhibit absorption between 600 and 800 nm, as we have reported previously,^[13] porphyrin-fused BODIPY dye is supposed to display enhanced NIR absorption, due to the larger conjugation in the latter. 2) The electron-withdrawing ability of the boron atom can lower the HOMO energy level of the fused dye. Our previous studies have pointed out that a fused BODIPY unit is the most effective building block, reported so far, for stabilization of the highly electron-rich, N-annulated perylene.^[13] As a result, the porphyrin-fused BODIPY compound is expected to be a stable NIR dye in spite of its narrow band gap. 3) Generally speaking, the BODIPY core has relatively high reactivity and can undergo electrophilic substitution.^[9a] This high reactivity is beneficial to ring-closure reactions, so that fusion of double or even multiple BODIPY units into the porphyrin backbone becomes possible. Herein, we report the successful synthesis of the two novel NIR dyes, 1 and 2, which show the desired photophysical properties and photostability.

In the design of the highly conjugated, hybrid-molecules **1** and **2**, bulky 3,5-di(*tert*-butyl)phenyl groups were chosen as substituents, because such bulky groups, not only surmounts the solubility problem, but also eliminate the aggregation of the chromophores in solution.^[2b,7g,f,8a] Scheme 2 outlines the synthetic route for compounds **1** and **2**. Singly linked, aromatic, dipyrromethane, dyad compounds (e.g., compound **5**) can be prepared in a good yield by a trifluoroacetic acid (TFA)-catalyzed condensation of the corresponding aromatic aldehyde with 2 equivalents of pyrrole derivative. However, only a small amount of the desired product **5** could be detected under general TFA-catalyzed conditions in our case, probably owning to the steric hindrance. Adding more



Scheme 2. Synthetic route for compounds 1 and 2: a) TsOH·H₂O, CHCl₃, reflux; b) DDQ, CH₂Cl₂, RT; c) BF₃·OEt₂, Et₃N, CH₂Cl₂, reflux; d) FeCl₃, CH₂Cl₂, CH₃NO₂, RT; e) Ni(acac)₂, toluene, reflux; f) FeCl₃, CH₂Cl₂, CH₃NO₂, reflux.

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TFA or increasing the reaction temperature led to the formation of an inseparable mixture, so efforts were directed toward promoting the condensation of 3,5-di(tert-butyl)phenyl-substituted pyrrole $4^{[13]}$ with porphyrin-aldehyde $3^{[14]}$ Fortunately, para-toluene sulfonic acid monohydrate (TsOH·H₂O) was found to accelerate the transformation and this strategy also reduced the degree of side reactions. The dipyrromethane-derivative 5 was quantitatively obtained under optimized conditions by using a catalytic amount of TsOH·H₂O. Considering the high reactivity of dipyrromethane derivatives, 5 directly underwent oxidation by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), without further purification, and subsequent complexation with BF₃·OEt₂ afforded the porphyrin-BODIPY-dyad 6 with an overall yield of 72% for the three steps. Iron(III) chloride, as a mild oxidant, has been successfully used to prepare aromatic, ring-fused porphyrins^[2b,7c,d,f,g,8b] and very recently this reagent has proven to be effective to promote ring closure of N-annulated perylene at the *meso* and β positions of a BODIPY core.^[13] Therefore, FeCl₃ was utilized to promote intramolecular ring fusion of 6 and the fully fused product 1 was achieved in 72% yield. Further extension of the π -conjugation length of 1 by fusing another BODIPY subunit to the highly conjugated skeleton is supposed to lead to a more redshifted and intense NIR absorption. Compound 8 was thus synthesized in an overall yield of 34% in three steps, through the same synthetic route used for 6. Metallation of 8 with Ni(acac)₂ yielded precursor 9 in 95% yield. However, when 9 was treated with 20 equivalents of $FeCl_3$ in CH_2Cl_2 , a complicated mixture of partially fused compounds, except the desired compound 2, was obtained. To increase the reaction temperature turned out to be effective to promote intramolecular ring fusion and the fully fused compound 2 was eventually purified in 15% yield. The relatively low yield is attributed to the significant decomposition of BODIPY derivatives under refluxing conditions in the presence of FeCl₃.

Aromatic-compound-fused porphyrins are considered to have a strong tendency to form highly packed aggregates, therefore, obtaining well-resolved ¹H NMR spectra without the presence of coordinating solvents^[15] or NaBH₄,^[2b] has proven to be challenging. Due to the attachment of sufficiently bulky groups around the aromatic core, compounds 1 and 2 are highly soluble in common organic solvents, thus facilitating purification and characterization. More importantly, sharp as well as well-split ¹H NMR signals are achievable even at RT without additives. The absorption spectra of the unfused precursors 6 and 9 display the superposition of the porphyrin monomer and BODIPY subunit (Figure 1). Extension of the π system by fusing one or two BODIPY units definitely narrows the HOMO-LUMO band gap. UV/ Vis-NIR spectroscopic measurement clearly demonstrates that both fused compounds, 1 and 2, show broad absorption spectra that cover the entire visible and a part of the NIR spectral regions (Figure 1). The strong absorption bands in the visible range, at 560 nm for 1 and 616 nm for 2, result in a violet and a blue color for 1 and 2 in solution, respectively.

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Figure 1. UV/Vis–NIR absorption spectra of 1, 2, 6, and 9 in toluene $(1.0 \times 10^{-5} \text{ m})$.

Owing to the higher conjugation in 1 than in 6, the absorption spectrum of the fused dye 1 in toluene displays a significant bathochromic shift with an absorption maximum at 890 nm ($\varepsilon = 49 \ 000 \,\mathrm{m}^{-1} \,\mathrm{cm}^{-1}$). Moreover, the further π -extended compound 2 shows absorption deep beyond 1000 nm absorption maximum at 1040 nm with an $(\varepsilon = 68)$ $000 \,\mathrm{m}^{-1} \mathrm{cm}^{-1}$). Despite the similar molecular size of BODIPY, anthracene, and azulene, comparison of the NIR absorbance of bisBODIPY-fused porphyrin 2 (λ_{max} = 1040 nm) with bisanthracene-fused porphyrin $(\lambda_{\rm max} =$ 973 nm)^[7f] and bisazulene-fused porphyrin $(\lambda_{\rm max} =$ $1014 \ nm)^{[7c]}$ reveals bathochromic shifts of 67 nm and 26 nm, respectively. Therefore, fusion of BODIPY to the porphyrin core appears to be an effective method for bathochromic shifts of the absorbance. On the other hand, BODIPY-fused porphyrins show longer NIR absorption than BODIPYfused perylene dye. Also noteworthy is that dye 2 possesses the longest NIR absorption maximum ever observed for a BODIPY derivative. Both dyes 1 and 2 exhibit very weak fluorescence, which is common for Ni-porphyrins.^[16]

The electrochemical properties of **1** and **2** were investigated by cyclic voltammetry (CV) in a deoxygenated CH_2Cl_2 solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte and the results are summarized in Table 1 (see the Supporting Information for details). As shown in Figure 2, compound **1** exhibits two reversible oxidation waves with half-wave potentials at 0.45

Table 1. Summary of electrochemical properties of compounds 1 and 2.

	$egin{array}{c} E_{ m ox}^1 \ [{ m V}]^{[a]} \end{array}$	$E^1_{ m red} \ [{ m V}]^{[a]}$	HOMO [eV] ^[b]	LUMO [eV] ^[b]	$E_{ m g}$ [eV] ^[c]	E_{g} [eV] ^[d]
1	0.45	-0.94	-5.15	-3.95	1.20	1.31
2	-0.34	-1.55	-4.39	-3.38	1.01	1.00

[a] E_{ox}^n and E_{red}^n are half-wave potentials for respective redox waves with Fc/Fc⁺ as reference. [b] 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 = $-(4.8+E_{red}^{onset})$.^[17] [c] Obtained from cyclic voltammograms. [d] Obtained from the low-energy absorption onset in the absorption spectra.



Figure 2. Cyclic voltammograms (CV) and differential-pulse voltammogram (DPV) of compounds **1** and **2** in CH_2Cl_2 with 0.1 \times Bu₄NPF₆ 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⁻¹. Fc/ Fc⁺ was used as external reference.

and 1.08 V (versus Fc⁺/Fc), whereas five reversible or quasireversible oxidative waves were observed with half-wave potentials at -0.34, -0.16, 0.34, 0.49, and 0.79 V for 2; these are distinguishable by differential-pulse voltammetry (DPV). It is obvious that bisBODIPY-fused porphyrin 2 has a larger extended π system, which is able to stabilize more charges. Furthermore, two reversible reduction waves were found for both 1 and 2 with half-wave potentials at -0.94and -1.50 V for **1** and at -1.55 and -2.10 V for **2**, indicating that they can be reduced into the corresponding radical anions and dianions, which also can be stabilized by the delocalized π system. HOMO energy levels of -5.15 and -4.39 eV, and LUMO energy levels of -3.95 and -3.38 eV were estimated for 1 and 2, respectively, based on the onset potential of the first oxidation and the first reduction wave, respectively.^[16] Energy gaps of 1.20 eV for 1 and 1.01 eV for 2 were then calculated; this is in agreement with their optical band gaps (1.31 eV for 1 and 1.00 eV for 2). In contrast, the precursors exhibit one reversible reduction wave corresponding to a BODIPY subunit with half-wave potentials at -1.26 V for 6 and -1.21 V for 9, and another reversible reduction wave corresponding to a porphyrin core with halfwave potentials at -1.68 V for 6 and -1.60 V for 9. In addition, four oxidation waves were observed for both 6 and 9 (Table S1 and Figure S1 in the Supporting Information). Compared with the fused dyes 1 and 2, larger energy gaps, 1.75 and 1.77 eV, were obtained for 6 and 9, respectively; this is also consistent with their optical band gaps.

Despite the small band gaps, dyes 1 and 2 can be stored as solids at ambient conditions for several months. Solution of both 1 and 2 in air-saturated toluene remains unchanged over weeks upon direct exposure to visible light and air, suggesting excellent photostability of 1 and 2. Even upon irradiation with UV light (4 W) for 1740 min, the absorbance of dye 1 in air-saturated toluene remained almost constant and only lost 10% of the initial intensity. The half-life time ($t_{1/2}$) of around 743 min was measured in the case of compound 2



Figure 3. Changes of optical density of 1 and 2 at the absorption maximum wavelength with the irradiation time. The original optical density before irradiation was normalized at the absorption maximum. Solutions of compounds 1 and 2 in toluene were irradiated under 4 W UV light (emitting at 254 nm).

under the same conditions (Figure 3). This can be explained by the smaller band gap as well as a higher-lying HOMO energy level in dye 2. Nevertheless, in view of the longwavelength absorption behaviors of NIR-dyes 1 and 2, such unusual photostability is fairly remarkable; this once again proves that the fused BODIPY unit is the ideal building block to stabilize a highly conjugated system.

In summary, we have described the facile and efficient synthesis of BODIPY-fused porphyrin 1 and bisBODIPYfused porphyrin 2 as two new soluble and stable NIR dyes. Sufficiently bulky groups are crucial for the purpose of suppressing aggregation. Compounds 1 and 2 show remarkable properties, such as intense NIR absorption and good photostability. In particular, bisBODIPY-fused porphyrin 2 has a longer NIR absorption with respect to bisanthracene- and bisazulene-fused porphyrins. Moreover, compound 2 also possesses the longest NIR absorption maximum ever observed for a BODIPY derivative. The excellent photostability of molecules 1 and 2, together with the spectral coverage, as well as the amphoteric redox behavior (reversible oxidation and reduction waves), suggest that these BODIPYfused porphyrin dyes can be used as building blocks to construct photovoltaic devices in the future. Of course, appropriate functionalizations are necessary for this purpose.

Experimental Section

Synthesis of 6: TsOH·H₂O (8 mg, 0.04 mmol) was added to a solution of 3 (192 mg, 0.2 mmol) and 4 (112 mg, 0.44 mmol) in degassed anhydrous CHCl₃ (20 mL). The reaction mixture was stirred and heated to reflux for 1.5 h under nitrogen atmosphere and quenched by addition of a saturated NaHCO₃ solution. The organic layer was washed with saturated brine and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum to afford the crude product 5 (300 mg) as a brown solid. The crude product 5 was then dissolved in degassed anhydrous CH₂Cl₂ (15 mL). After addition of DDQ (58 mg, 0.26 mmol) in dry CH₂Cl₂ (6 mL), the solution was stirred at RT for 1 h under nitrogen atmosphere.

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Et₃N (0.8 mL, excess) and BF₃·OEt₂ (0.9 mL, excess) were successively added. The mixture was then stirred and heated to reflux overnight. After cooling, the solvents were removed under reduced pressure, and the residue was purified by column chromatography (silica gel, CH2Cl2/ hexane 1:6) to give a purple solid product (6, 210 mg, 70% in three steps). ¹H NMR (CDCl₃ 500 MHz, 25 °C, TMS): $\delta = 9.16$ (d, J = 5 Hz, 2H), 8.86 (d, J=5.1 Hz, 2H), 8.85 (d, J=5.1 Hz, 2H), 8.83 (d, J=5 Hz, 2H), 7.91 (d, J=1.9 Hz, 6H), 7.85 (d, J=1.3 Hz, 4H), 7.75-7.76 (m, 3H), 7.51-7.52 (m, 2H), 6.46 (d, J=4.4 Hz, 2H), 7.23 (d, J=3.8 Hz, 2H), 1.50 (s, 54H), 1.40 ppm (s, 36H); ¹³C NMR (CDCl₃, 125 MHz, 25 °C, TMS): $\delta\!=\!160.1,\,157.1,\,150.6,\,150.4,\,149.2,\,143.4,\,142.7,\,141.7,\,139.4,\,133.6,\,132.3,$ 132.1, 128.8, 128.0, 123.9, 123.8, 123.6, 121.6, 121.5, 35.1, 35.0, 31.6, 31.5 ppm; MS (MALDI-TOF): *m*/*z* calcd for C₉₉H₁₁₃BF₂N₆Ni: 1496.875; found: 1496.776 $[M]^+$ and 1477.605 $[M-F]^+$; elemental analysis calcd (%) for C₉₉H₁₁₇BF₂N₆Ni: C 79.35, H 7.87, N 5.61; found: C 79.38, H 7.65, N 5.40

Synthesis of 1: A solution of FeCl₃ (162 mg, 1 mmol) in nitromethane (2 mL) was added to a solution of 6 (150 mg, 0.1 mmol) in degassed anhydrous CH₂Cl₂ (30 mL). The reaction mixture was stirred at RT for 30 min and quenched by addition of a saturated NaHCO3 solution. The organic layer was washed with saturated brine and dried over anhydrous Na2SO4. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, CH2Cl2/hexane 1:4) to give a purple solid product (1, 108 mg, 72 %). ¹H NMR (CDCl₃, 500 MHz, 25°C, TMS): $\delta = 7.49$ (s, 4H), 7.46 (m, 3H), 7.32 (s, 2H), 7.24 (d, J =1.9 Hz, 2 H), 7.18 (d, J = 1.9 Hz, 4 H), 6.86 (d, J = 5.1 Hz, 2 H), 6.73 (d, J = 5.1 Hz, 2 H), 7.5 5.1 Hz, 2H), 6.03 (s, 2H), 5.50 (s, 2H), 1.35 (s, 36H), 1.33 (s, 18H), 1.27 ppm (s, 36 H); 13 C NMR (CDCl₃, 125 MHz, 25 °C, TMS): $\delta = 159.0$, 153.7, 151.3, 150.0, 149.9, 149.5, 148.7, 146.8, 137.3, 136.6, 136.5, 132.2, 131.8, 131.6, 130.8, 129.6, 129.4, 126.2, 125.4, 123.4, 121.9, 121.8, 121.7, 113.5, 106.1, 34.9, 31.5, 31.4 ppm; MS (MALDI-TOF): m/z calcd for C₉₉H₁₁₃BF₂N₆Ni: 1493.847; found: 1493.960 [M]⁺ and 1474.887 [M-F]⁺; elemental analysis calcd (%) for C₉₉H₁₁₃BF₂N₆Ni: C 79.56, H 7.62, N 5.62; found: C 79.80, H 7.73, N 5.70.

The synthesis and characterizations of all new compounds are described in the Supporting Information.

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Keywords: aromaticity • BODIPY • dyes/pigments • near-IR spectroscopy • porphyrins • ring closure

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- [16] The presence of Ni in the porphyrin is necessary based on the following considerations: 1) matching the energy level of porphyrin core to that of BODIPY so that fusion of these two subunits becomes possible; 2) preventing demetalation during the FeCl₃-promoted oxidative cyclodehydrogenation reaction. We also attempted to replace the Ni metal with Zn. However, treatment of dyes 1 and 2 with strong acid, such as CF₃COOH or H₂SO₄, led to significant decomposition perhaps due to the instability of BODIPY in the presence of the strong acid.
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