Red-emissive Polyphenylated BODIPY Derivatives: Effect of Peripheral Phenyl Groups on the Photophysical and Electrochemical Properties

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A series of red-emissive BODIPY derivatives **2**–**4** having five to seven phenyl groups on their periphery were synthesized, and their photophysical and electrochemical properties were investigated. While the 8-phenyl-substituted derivatives only have moderate fluorescence quantum yields in solution, they can show intense red fluorescence in the PMMA films. The peripheral phenyl groups also affect the redox reversibility in cyclic voltammetry.

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) derivatives have attracted much attention as fluorescence materials because of their excellent stability, intense absorption profiles, and high fluorescence quantum yields.[1] Significant efforts have been devoted to their structural modification in order to tune their fluorescence properties, so that some derivatives indeed show great potential not only as biological probes[1a] but also for various applications, such as organic light emitting diodes,[2] laser dyes,[3] and sensitizers for solar cells.[4] As a new family of BODIPY derivatives, we have now focused our attention on an all-phenyl-substituted BODIPY. The incorporation of phenyl groups on the periphery of the fluorophore can lead to some characteristic properties, such as increased morphological stability[5a] as well as aggregation-induced emission as seen in the tetraphenylsiloles.[5b] As for the phenyl-substituted BODIPY, the 1,3,5,7-tetraphenyl derivative **1** was reported in the literature.[6] In this study, we synthesized a series of BODIPY derivatives having five to seven phenyl groups on the periphery, i.e., the 1,3,5,7,8-pentaphenyl **2**, 1,2,3,5,6,7-hexaphenyl **3**, and 1,2,3,5,6,7,8-heptaphenyl derivatives **4** (Figure 1) and investigated the effects of the peripheral phenyl groups on their properties.

As shown in Scheme 1, the hexa- and heptaphenyl BODIPY derivatives **3** and **4** were synthesized using 2,3,4-triphenylpyrrole (**5**) as a key precursor, which was prepared by the threefold Suzuki–Miyaura coupling of 2,3,4-tribromopyrrole[7] with $PhB(OH)_2$. The reaction of **5** with formylpyrrole **6** or benzaldehyde followed by treatment with $BF_3 \cdot Et_2O$ and Et_3N afforded **3** and **4** as deep red solids in 17 and 53% yields, respectively.

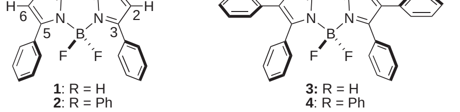
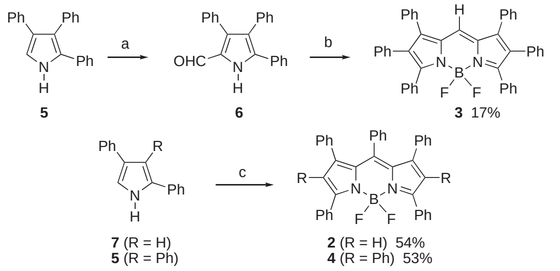


Figure 1. Phenyl-substituted BODIPY derivatives **1**–**4**.



Scheme 1. Reagents and conditions: a, $POCl_3$, DMF; b, i) **5**, $POCl_3$, CH_2Cl_2, 0 °C, ii) Et_3N, $BF_3 \cdot OEt_2$, toluene, 100 °C; c, i) benzaldehyde, TFA, CH_2Cl_2, then DDQ, ii) Et_3N, $BF_3 \cdot OEt_2$, toluene, 100 °C or CH_2Cl_2.

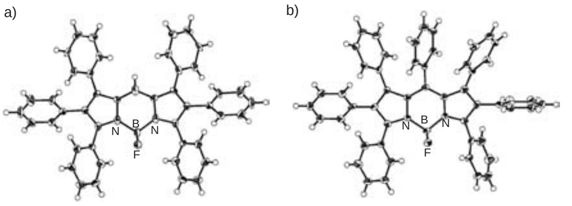


Figure 2. ORTEP drawings of a) **3** and b) **4**. Thermal ellipsoids are drawn at the 50% probability.

In a similar manner, the pentaphenyl derivative **2** was synthesized from 2,4-diphenylpyrrole (**7**)[8] as a deep red solid in 54% yield.[9]

The X-ray crystallographic analysis of **3** and **4** revealed that the peripheral phenyl groups are arranged in a propeller-like fashion having dihedral angles with the central BODIPY plane of 34.4–76.5° (Figure 2).[10] In **4**, the distance between the centers of the 8-phenyl ring and the 1- or 7-phenyl ring are 3.71 and 3.78 Å, respectively, which are shorter than those for the phenyl groups at the 1, 2, and 3 positions (4.59–4.85 Å in **3** and **4**). This suggests a substantial steric congestion in the consecutive three phenyl-substituted moieties at the 1, 7, and 8 positions. A similar steric congestion was also observed for the pentaphenyl derivative **2** with the distances of 3.75 and 3.78 Å between the 8-phenyl group and the 1- or 7-phenyl group, respectively.[10]

Table 1 summarizes the photophysical properties of the BODIPY derivatives. In the absorption spectra in THF, all the derivatives **1**–**4** showed strong absorption bands with maximum wavelengths (λ_{max}) around 561–578 nm ($\log \varepsilon = 4.7$–4.9), which are red-shifted by about 60–70 nm compared to the 1,3,5,7-tetramethyl BODIPY derivative (**8**: 509 nm)[11a] and 1,3,5,7-tetramethyl-8-phenyl BODIPY derivative (**9**: 500 nm).[11b] According to the DFT and TDDFT calculations (see

Table 1. Photophysical properties of the BODIPY derivatives

Compd	$\lambda_{\max}$/nm	λ_{em}/nm	Lifetime	Decay rate constants	
	(log ε)	(Φ_{F})[a]	τ_{s}/ns	$k_{\text{r}}/10^8\,\text{s}^{-1}$	$k_{\text{nr}}/10^8\,\text{s}^{-1}$
1 (THF)	571 (4.87)	601 (0.92)	5.2	1.8	0.15
(film)[b]	570	607 (0.83)	5.6	1.5	0.30
2 (THF)	561 (4.78)	597 (0.31)	2.1	1.4	3.2
(film)[b]	560	601 (0.87)	5.8	1.5	0.22
3 (THF)	576 (4.79)	608 (0.96)	5.3	1.8	0.075
(film)[b]	572	608 (0.75)	5.4	1.4	0.46
4 (THF)	573 (4.87)	613 (0.20)	1.4	1.4	5.7
(film)[b]	570	609 (0.73)	6.7	1.1	0.40
8 (toluene)[11a]	509	516 (0.92)	6.1	1.5	0.13
9 (THF)[11b]	500	510 (0.56)	3.1	1.8	1.4

[a] Absolute quantum yield determined by a calibrated integrating sphere system. [b] Spin-coated film prepared from a CH_2Cl_2 solution of PMMA (50 mg/mL) containing 1 wt % of the sample.

Supporting Information),[9] these substantial red shifts are mainly due to the π conjugation expanded with the 3,5-phenyl groups as well as the electron-withdrawing effect of the peripheral phenyl groups. The former effect is responsible for the elevation of the HOMO levels, while the latter contributes to the decrease in the LUMO levels.

In the fluorescence spectra in THF, compounds **1**–**4** showed red emissions with the maxima (λ_{em}) at 597–613 nm, which are also red-shifted by about 100 nm compared to **8**[11a] and **9**.[11b] Although the λ_{em} of **1**–**4** are comparable to each other, significant difference was observed in their quantum yields (Φ_{F}). While the tetraphenyl and hexaphenyl BODIPYs **1** and **3** have extremely high Φ_{F} values of 0.92 and 0.96, respectively, those of the pentaphenyl and heptaphenyl BODIPYs **2** (0.31) and **4** (0.20) are only moderate. This difference should be ascribable to the effect of the phenyl group at the 8 position.

To gain an insight into the origin of the difference in Φ_{F} values, the excited state dynamics was investigated. On the basis of the Φ_{F} and fluorescence lifetime (τ_{s}), the radiative (k_{r}) and nonradiative (k_{nr}) decay rate constants from the singlet excited state were determined. While the k_{r} values of **1**–**4** are almost constant in the range of $1.4\text{–}1.8 \times 10^8\,\text{s}^{-1}$, the k_{nr} values of **2** ($3.2 \times 10^8\,\text{s}^{-1}$) and **4** ($5.7 \times 10^8\,\text{s}^{-1}$) are much greater than those of **1** ($1.5 \times 10^7\,\text{s}^{-1}$) and **3** ($7.5 \times 10^6\,\text{s}^{-1}$). As observed in the X-ray structures of **2** and **4**, the steric congestion around the 8-phenyl group may accelerate internal conversion.

To confirm this consideration, we also measured the fluorescence spectra in a rigid medium with a low-concentration condition. The PMMA films containing 1 wt % of the BODIPY derivatives were prepared by spin coating, and their fluorescence properties were measured. In contrast to the case in solution, the 8-phenyl-substituted derivatives **2** and **4** showed very intense emissions under this condition, with Φ_{F} values of 0.87 and 0.73, respectively, which are comparable to those of **1** (0.83) and **3** (0.75). This may be due to the restricted rotation of the phenyl rings in the solid state. In fact, in the doped PMMA films, the k_{nr} values of **2** ($2.2 \times 10^7\,\text{s}^{-1}$) and **4** ($4.0 \times 10^7\,\text{s}^{-1}$) are dramatically decreased and are comparable to those of **1** ($3.0 \times 10^7\,\text{s}^{-1}$) and **3** ($4.6 \times 10^7\,\text{s}^{-1}$).

The electrochemical properties of **1**–**4** were also investigated by cyclic voltammetry in CH_2Cl_2. All the compounds **2**–**4** showed not only reversible oxidation waves at $E_{1/2} = +0.84\,\text{V}$ for **2**, $+0.85\,\text{V}$ for **3**, and $+0.84\,\text{V}$ for **4** (vs. Fc/Fc^+) but also reversible reduction waves at $E_{1/2} = -1.34\,\text{V}$ for **2**, $-1.34\,\text{V}$ for **3**, and $-1.38\,\text{V}$ for **4**, respectively. These results indicate that both the generated radical cation and radical anion have sufficient stabilities under these conditions. This is in contrast to the fact that the 1,3,5,7-tetramethyl derivative **8** shows irreversible oxidation and reduction waves.[12a] In the case of the tetraphenyl BODIPY **1**, while a reversible oxidation wave was observed at $E_{1/2} = +0.83\,\text{V}$, the reversibility of the reduction wave ($E_{\text{pc}} = -1.34\,\text{V}$) is substantially decreased. For stabilization of their radical anion, the protection of the reactive 8-position may be important.[12b]

In summary, we synthesized a series of phenyl-substituted BODIPY derivatives. The study of their structure–property relationships revealed several findings, such as the effect of the 8-phenyl group on the fluorescence, their high fluorescence quantum yields in the polymer films, and the high reversibility in the redox process. These findings would be important for further structural modification of the BODIPY skeleton. These results also suggest the potential use of these compounds as red-emitting dopant materials.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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