Dyes/Pigments

Color-Tunable Solid-State Fluorescence Emission from Carbazole-Based BODIPYs**

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Abstract: Several carbazole-based boron dipyrromethene (BODIPY) dyes were synthesized by organometallic approaches. Thiazole, benzothiazole, imidazole, benzimidazole, triazole, and indolone substituents were introduced at the 1-position of the carbazole moiety, and boron complexation of each dipyrrin generated the corresponding compounds 1, 2 a, and 3–6. The properties of these products were investigated by UV/Vis and fluorescence spectroscopy, cyclic voltammetry, X-ray crystallography, and DFT calculations. These compounds exhibited large Stokes shifts, and compounds 1,

Introduction

Boron dipyrromethene (BODIPY) and its related BF₂ complexes have received considerable attention because of their high molecular coefficients and $\Phi_{\rm F}$ values, good thermal- and photo-stability, and versatile functionality.^[1] Such properties allow these dyes to be applied as fluorescent probes and sensors, as well as in biolabeling. To date, various BODIPY derivatives and congeners have been synthesized, including peripherally functionalized and core-modified compounds. For example, the fusion of a benzene, furan, or thiophene unit with the BODIPY skeleton results in expanded π conjugation.^[2] Aza-BODIPYs, in which the *meso*-bridged atom is replaced with a nitrogen atom, exhibit redshifted absorption and emission spectra relative to the spectra of regular BODIPYs.^[3] Despite their intense fluorescence in solution, most BODIPYs exhibit fluorescence quenching in the solid state.^[4]

Carbazole derivatives have also been extensively studied as potential electron conductors, catalysts, sensors, and biologically active alkaloids.^[5] A carbazole is simply a benzene-fused pyrrole, therefore incorporation of a carbazole unit into fused porphyrinoids presents interesting possibilities.^[6–9] We have previously investigated the synthesis and photophysical prop-

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| [**] | BODIPY = boron dipyrromethene. |
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2a, and **3–5** fluoresced both in solution and in the solid state. Complex **2a** showed the highest fluorescence quantum yield ($\Phi_{\rm f}$) in the solid state, therefore boron complexes of the carbazole–benzothiazole hybrids **2b–f**, which had several different substituents, were prepared and the effects of the substituents on the photophysical properties of the compounds were examined. The fluorescence properties showed good correlation with the results of crystal-packing analyses, and the dyes exhibited color-tunable solid-state fluorescence.



Scheme 1. Synthesis of carbazole-based BODIPYs. (Bpin)₂ = bis(pinacolato)diboron, cod = 1,5-cyclooctadiene, dtbpy = 4,4'-di-*tert*-butyl-2,2'-dipyridyl, XPhos = 2-dicyclohexylphosphino-2',4',6'-triisopropyl-biphenyl.

erties of carbazole-based porphyrinoids and recently reported the facile synthesis of carbazole-based BODIPYs (Scheme 1).^[8] Various substituents could be introduced onto the carbazole moiety and efficient substituent effects were confirmed. However, these carbazole-based BODIPY dyes showed extensive fluorescence quenching due to intramolecular charge transfer (ICT). To develop fluorescent dyes, new carbazole-based BODI-PYs were designed in the present work (Figure 1). Here, a thiazole, benzothiazole, imidazole, benzimidazole, 1,2,3-triazole, or indolone moiety was attached at the 1-position of the carbazole and the BF₂ complexes **1**, **2a**, and **3–6** were subsequently synthesized. These unsymmetrical BODIPYs exhibited large Stokes shifts and several were fluorescent even in the solid state. Herein, we report the synthesis and photophysical properties of these carbazole-based BODIPYs.

Results and Discussion

Scheme 2 outlines the synthesis of the new BODIPY derivatives 1–6. Thiazole substituents were introduced into the carbazole

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Figure 1. Structures of carbazole-based BODIPYs 1, 2a, and 3-6. Bn = benzyl.

skeleton by Ir-catalyzed borylation of 3,6-di-*tert*-butylcarbazole (**7 a**) then subsequent Suzuki–Miyaura coupling of the product



Scheme 2. Synthesis of **1**, **2a**, and **3–6**. NBS = *N*-bromosuccinimide, TBAF = - tetrabutylammonium fluoride.

with 2-bromothiazole or 2-bromobenzothiazole. Boron complexation of the resulting dipyrrins 8 and 9a with BF₃·OEt₂ provided the corresponding BODIPYs 1 and 2a, respectively. In contrast, imidazole substituents were attached by Pd-catalyzed direct arylation of 1-bromo-3,6-di-tert-butylcarbazole (10), which was prepared by bromination of 7 a with N-bromosuccinimide (NBS). The reaction of 10 with 1-methylimidazole or 1methylbenzimidazole gave 11 and 12, which were subsequently converted into complexes 3 and 4, respectively. We introduced 1,2,3-triazole and indolone substituents by a cyclization strategy. 3,6-Di-tert-butyl-1-ethynylcarbazole (13) was prepared by Stille coupling of 10 and subsequent TMS deprotection. The click reaction of 13 with benzylazide and subsequent boron complexation of triazolylcarbazole 14 provided 5. An indolone moiety was introduced by Sonogashira coupling of 13 with 2-iodoaniline to generate 15, followed by Znl₂-catalyzed cyclization of 15 to provide indolylcarbazole 16. Oxidation of 16 afforded 17,^[10] and finally boron complexation of 17 gave 6. In this manner, BODIPYs 1, 2a, and 3-6 were prepared and then fully characterized by both NMR and mass spectroscopy. Single crystals of 2a, 3, and 4 suitable for X-ray diffraction analysis were also prepared: the X-ray crystal structures of these products unambiguously confirmed the BODIPY skeletons (Figure 2).^[11]

The UV/Vis absorption and fluorescence spectra of the target compounds are shown in Figure 3 and the associated data are summarized in Table 1. The absorption maxima were redshifted in the following order: 5 < 3 < 4 < 1 < 2a < 6. Thus, the absorption of thiazole-appended compound 1 was redshifted relative to the absorptions of 3-5, whereas benzothiazole-appended complex 2a was even further redshifted and was also intensified absorption. Time-dependent DFT calculations suggested that the main absorption bands at $\lambda \approx 400$ and 300 nm may be assigned to the HOMO-LUMO and respectively, HOMO-2-LUMO transitions, whereas the HOMO-1-LUMO transition generates a somewhat weaker band (Figure S26 in the Supporting Information). Unlike 1, 2a, and 3-5, 6 generated a broad absorption spectrum that stretched to the NIR region, which suggests the presence of ICT. Complexes 1, 2a, 3, and 4 exhibited fluorescence with moderate-to-high $\Phi_{\rm F}$ values, whereas the fluorescence of 5 was weak and that of 6 was significantly quenched (Fig-

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Figure 2. X-ray crystal structures and crystal packing of a) **2 a**, b) **3**, and c) **4**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 50% probability level. Interplanar distances are shown between the mean planes of the molecules, excluding the peripheral substituents and the two fluorine atoms.



Figure 3. a) UV/Vis absorption spectra of **1–6** in CH₂Cl₂ and b) fluorescence spectra in CH₂Cl₂ (dotted line) or in the solid state (solid line). c) Photographic images of the powdered compounds under black light ($\lambda = 365$ nm).

ure 3 b).^[12] These dyes were also observed to fluoresce in the solid state, and the $\Phi_{\rm F}$ of **1**, **2a**, and **3–5** for solid-state fluorescence were all greater than 0.13. Among these compounds, **2a**

| Table 1. Selected photophysical properties of the carbazole-based BODIPYs in solution in CH_2Cl_2 or in the solid state. | | | | | | |
|---|--|--|--|---|--|---|
| Compound | $\lambda_{abs}^{[a]}$ | $\lambda_{ m em}^{(b)}$ | $\Delta { u_{ m St}}^{[c]}$ [cm ⁻¹] | $\Phi_{ m F}$ (CH ₂ Cl ₂) | λ_{powder} [nm] | $arPsi_{	extsf{F}}$ (powder) |
| 1 2a 3 4 5 | 436 458 394 419 382 663 | 513 ^[d] 534 ^[e] 427 ^[f] 477 ^[g] 477 ^[g] 793 ^[h] | 3440 3110 1960 2900 5210 2470 | 0.334 0.320 0.424 0.547 0.074 | 530 ^[d] 542 ^[e] 428 ^[f] 478 ^[g] 431 ^[g] _ ^[i] | 0.165 0.214 0.130 0.141 0.150 _ ^[i] |
| [a] Absorption wavelength. [b] Emission wavelength. [c] Stokes shift. [d] Excited at λ =420 nm. [e] Excited at λ =450 nm. [f] Excited at λ =360 nm. | | | | | | |

[g] Excited at $\lambda =$ 380 nm. [h] Excited at $\lambda =$ 660 nm. [i] Not detected.

had the highest value in the solid state ($\Phi_{\rm F}$ (powder) = 0.214). The fluorescence maxima of 1 and 2a in the solid state were redshifted compared to those in solution, which suggested Jtype packing of these two products.[13] Indeed, the crystal packing of 2a was confirmed to have a J-type arrangement, with an interplanar distance of 3.67 Å and a zigzag pattern (Figure 2a). This type of packing in conjunction with a large Stokes shift tends to minimize self-absorption (self-quenching), $^{[3d-e,4a,\,14-15]}$ which leads to the relatively strong fluorescence of 2a in the solid state. In contrast, the fluorescence maxima of 3 and 4 were not shifted, which indicated that Jtype interactions were not dominant for these compounds. The $\Phi_{\rm F}$ values of **3** and **4** in the solid state were much lower than those in solution. Interestingly, the $\Phi_{\rm F}$ value of 5 in the solid state was 0.150, which is higher than the value measured in solution ($\Phi_{\rm F}(\rm CH_2\rm Cl_2) = 0.074$). This effect most likely results from the flexible benzyl moiety, which accelerates nonradiative deactivation in solution but not in the solid state. In addition, the large Stokes shift of 5 reduces self-absorption, and therefore aggregation-induced emission enhancement is observed.^[16]

The redox potentials ($E_{reduction}$ and $E_{oxidation}$), of **1**, **2a**, and **3–6** were determined by cyclic voltammetry (Table 2, and Figure S28 in the Supporting Information). The thiazole-appended compound **1** showed higher potentials than **3–5**, whereas **2a** and **6** generated even higher potentials than **1**. The associated electrochemical HOMO–LUMO gaps (ΔE_{CV}) are in good agree-

| Table 2. Electrochemical properties. ^[a] | | | | | | | |
|---|--|--|--|--|--|--|--|
| Compound | $E_{\rm red}$ [V] | $E_{\rm ox}$ [V] | $\Delta E_{\rm CV}$ [V] | $\Delta E_{\rm opt}$ [V] | $\Delta E_{\rm DFT} [V]^{\rm [b]}$ | | |
| 1 2a 3 4 5 6 | -2.087 -1.859 _ ^[c] -2.341 _ ^[c] -0.665 | 0.831 0.932 0.770 0.808 0.716 1.073 | 2.914 2.791 _ ^[d] 3.149 _ ^[d] 1.738 | 2.84 2.71 3.15 2.96 3.25 1.87 | 3.12 3.07 3.64 3.37 3.60 2.12 | | |

[a] Determined by cyclic voltammetry; solvent: $CH_2Cl_{2^{\prime}}$ supporting electrolyte: Bu_4NPF_6 (0.10 M), reference electrode: Ag/Ag^+ , scan rate: 0.1 V s⁻¹. [b] Calculated at the B3LYP/6-31G* level. [c] Not detected. [d] Not calculated.

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ment with the absorption spectroscopy results (ΔE_{opt}) and with the calculated values (ΔE_{DFT}). The HOMO–LUMO gap for **6** is notably narrow because **6** showed an exceptionally redshifted absorption.

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DFT calculations were performed to examine the electronic states of the HOMOs and LUMOs of **1**, **2a**, and **3–6** (Figure 4).^[17] The HOMOs exhibit large electronic coefficients



Figure 4. HOMO (bottom) and LUMO (top) of a) 1, b) 2a, c) 3, d) 4, e) 5, and f) 6, calculated at the B3LYP/6-31G* level.

on the carbazole moieties, whereas the LUMOs show large electronic coefficients on each heterocycle. In fact, these latter coefficients are remarkably high in the case of **5** and **6** (Figure 4e and f). This result, as well as the broad absorption spectrum of **6**, suggests that the fluorescence quenching observed for **6** is due to ICT from the carbazole moiety to the indolone moiety.^[7b, 18]

Because **2a** showed both a redshifted absorption and relatively high Φ_F values both in solution and in the solid state, we decided to synthesize the BF₂ complexes of carbazole–benzothiazole hybrids to generate **2b–f** and examine the substituent effects (Scheme 3). Compounds **2b–f** were synthesized from **7b–f**, respectively, by sequential Ir-catalyzed borylation, Suzuki–Miyaura coupling, and boron complexation.

The photophysical properties of 2a-f are presented in Figure 5 and summarized in Table 3. Compound 2d, which



Scheme 3. Synthesis of 2 a-f. Mes = mesityl.

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Figure 5. a) UV/Vis absorption spectra of 2a-f in CH₂Cl₂ and b) fluorescence spectra in CH₂Cl₂ (dotted line) or in the solid state (solid line). c) Photographic images of the various powdered samples under irradiation by a $\lambda = 365$ nm lamp.

| Table 3. Selected photophysical properties of the carbazole-based BODI- PYs $2a-f$ in solution in CH_2CI_2 or in the solid state. | | | | | | |
|---|-------------------------|-------------------------|--|--|-------------------------------|------------------------------|
| Compound | λ_{abs} [nm] | λ _{em} [nm] | $\Delta u_{ m St}$ [cm ⁻¹] | $\Phi_{\rm F}$ (CH ₂ Cl ₂) | $\lambda_{ m powder}$ [nm] | $arPsi_{	extsf{F}}$ (powder) |
| 2a | 458 | 534 ^[a] | 3110 | 0.320 | 542 ^[a] | 0.214 |
| 2b | 495 | 579 ^[b] | 3010 | 0.008 | 651 ^[b] | 0.027 |
| 2c | 440 | 510 ^[c] | 3120 | 0.380 | 575 ^[c] | 0.158 |
| 2d | 420 | 483 ^[d] | 3110 | 0.296 | 485 ^[d] | 0.119 |
| 2e | 469 | 540 ^[a] | 2800 | 0.205 | 573 ^[a] | 0.106 |
| 2 f | 457 | 529 ^[a] | 2980 | 0.358 | 560 ^[a] | 0.248 |
| [a] Excited at λ =450 nm. [b] Excited at λ =490 nm. [c] Excited at λ = 430 nm. [d] Excited at λ =380 nm. | | | | | | |

contains an electron-withdrawing group, had a blueshifted absorption band, whereas the compounds with electron-donating or aryl groups exhibited redshifted absorption and fluorescence bands in solution. The methoxy-substituted product **2b** was redshifted the furthest, although its fluorescence intensity was very weak, most likely due to ICT. For the other complexes Φ_F (CH₂Cl₂)=0.2-0.4 Φ_F (powder)=0.1-0.25. Both **2a** and **2f** showed stronger fluorescence in the solid state than the other complexes studied, presumably because they contain larger substituents that reduce intermolecular interactions.^[19] The solid-state fluorescence bands of **2f** and **2a** were redshifted relative to the bands observed in solution, which suggests J-



type packing. The fluorescence maximum of 2d was not shifted and its solid-state Φ_F was low, similar to the results obtained for 3 and 4. It is noteworthy that 2c generated the most highly redshifted fluorescence band in the solid state, which suggests the formation of an excimer.

Single crystals of **2c** and **2e** were obtained and their structures were elucidated by X-ray diffraction (Figure 6).^[11] In their



Figure 6. Crystal packing of a) **2c** and b) **2e**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are at the 50% probability level. Interplanar distances are shown between the mean planes of the molecules, excluding the peripheral substituents and the two fluorine atoms.

crystal packings, both molecules self-stack, at interplanar intervals of 3.38 and 3.67 Å in the case of 2c and 3.41 and 3.43 Å in the case of 2e. It is noteworthy that 2c forms a H-type cofacial dimeric structure with a distance of 3.34 Å (not shown) between the nearest carbon atoms. This packing motif, in conjunction with the fluorescence spectroscopy results, strongly supports the formation of an excimer of 2c in the solid state.

Conclusion

We successfully synthesized a series of carbazole-based BODI-PYs by using organometallic reactions. Thiazole substituents were introduced at the 1-position of the carbazole by Suzuki-Miyaura coupling; imidazole substituents were introduced by Pd-catalyzed direct arylation. In addition, 1,2,3-triazole and indolone moieties were attached by cyclization reactions. These dipyrrins smoothly formed the boron complexes 1, 2a, and 3-6. The structures of these compounds were characterized by NMR and mass spectroscopy and by X-ray diffraction. Each compound showed characteristic properties; 6 exhibited a redshifted absorption in the NIR region, whereas 1, 2a, 3, and 4 fluoresced with relatively high $\Phi_{\rm F}$ values both in solution and in the solid state. Product 2a had the highest $\Phi_{\rm F}$ value in the solid state ($\Phi_{\rm F}$ (powder)=0.214). The carbazole-benzothiazole hybrids 2b-f were synthesized and the substituent effects on the photophysical properties were examined. With the exception of 2b, these compounds showed large Stokes shifts and exhibited solid-state fluorescence with $\Phi_{\rm F}$ (powder)=0.11-0.25. Complex 2c formed an excimer and showed the greatest extent of redshifted emission in the solid state. These fluorescence properties were consistent with the results of crystalpacking analyses, and these compounds exhibited color-tunable solid-state fluorescence. The further development of carbazole-based fluorescent dyes is currently underway in our laboratory.

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Keywords: boron dipyrromethene (BODIPY) · carbazoles · dyes/pigments · fluorescence · solid-state emission

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- [10] During preparation of this manuscript, Shinokubo reported a facile synthesis of 17 from carbazole 7 a and isatin.^[18b]
- [11] Crystallographic data for **2a**: $C_{54}H_{54}N_4S_2B_3F_4$; $M_r = 920.75$; monoclinic; space group P2₁/n; a = 15.413(2), b = 13.1802(14), c = 23.360(3) Å; $\beta =$ 100.591(4)°; $V = 4664.7(10) \text{ Å}^3$; Z = 4, $\rho_{calcd} = 1.311 \text{ g cm}^{-3}$; T = -180 °C; 30555 measured reflections; 8239 unique reflections ($R_{int} = 0.0205$); $R_1 =$ 0.0300 ($l > 2\sigma(l)$); $wR_2 = 0.0818$ (all data); GOF = 1.056. Crystallographic data for **2c**: $C_{19}H_{11}N_2SBF_2$; $M_r = 348.17$; monoclinic; space group $P2_1/c$; a = 8.2201(19), b = 12.158(3), c = 14.854(4) Å; $\beta = 93.027(9)^{\circ}$; V = 14.854(4)1482.4(6) Å³; Z=4; ρ_{calcd} =1.560 g cm⁻³; T=-180 °C; 9911 measured reflections; 2678 unique reflections ($R_{int} = 0.0204$); $R_1 = 0.0293$ ($l > 2\sigma(l)$); $wR_2 = 0.0832$ (all data); GOF = 1.011. Crystallographic data for **2e**: 4(C₃₁H₁₉N₂SBF₂)•5(CH₂Cl₂); *M*_r=2426.03; monoclinic; space group *P*2₁/*c*; 11065(3) Å³; Z=4; $\rho_{\rm calcd}$ =1.456 g cm⁻³; T=-180 °C; 65315 measured $2\sigma(I)$; $wR_2 = 0.2789$ (all data); GOF = 1.068. Crystallographic data for 3: 4($C_{24}H_{28}N_3BF_2$)·CH₃OH; M_r =1661.26; triclinic; space group $P\overline{1}$; a =14.279(6), b = 15.589(5), c = 21.281(7) Å; $\alpha = 101.867(3)$, $\beta = 98.133(15)$, $\gamma = 100.4090(10)^{\circ}; V = 4480(3) Å^3; Z = 2; \rho_{calcd} = 1.231 \text{ g cm}^{-3}; T =$ -180 °C; 54094 measured reflections; 14196 unique reflections ($R_{int} =$ 0.1083); $R_1 = 0.0675$ ($l > 2\sigma(l)$); $wR_2 = 0.1884$ (all data); GOF = 1.003. Crystallographic data for 4: C₂₈H₃₀N₃BF₂·CH₂Cl₂; M_r=542.29; triclinic; space group $P\bar{1}$; a = 8.849(2), b = 12.152(3), c = 12.830(4) Å; a = 92.7805(10), $\beta =$ 101.133(10), $\gamma =$ 98.924(5)°; V = 1332.9(6) Å³; Z = 2; $\rho_{calcd} =$ 1.351 g cm⁻³, T = -180 °C; 17039 measured reflections; 4535 unique reflections ($R_{int} = 0.0575$); $R_1 = 0.0441$ ($l > 2\sigma(l)$); $wR_2 = 0.1207$ (all data); GOF = 1.013. CCDC 1437585 (2 a), 1437586 (2 c), 1437587 (2 e), 1437588 (3), and 1437589 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystal Data Centre via www.ccdc.cam.ac.uk/data_request/ cif.
- [12] These dyes showed shorter absorption lengths and lower $\Phi_{\rm F}$ values than regular BODIPYs. The former is due to weak conjugation between the carbazole and heterocycle moieties, which is supported by the alternating bond lengths (Figure S31 in the Supporting Information). The $\Phi_{\rm F}$ value is probably low because the fluorescence is quenched to some degree by the heavy-atom effect of the sulfur atom and/or ICT.
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