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PAPER

Synthesis of pyrrolyldipyrrinato BF_2 complexes by oxidative nucleophilic substitution of boron dipyrromethene with pyrrole†

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Direct oxidative nucleophilic substitution of the 3-hydrogen of BODIPY dyes by pyrrole has been developed under reflux condition under oxygen, from which a series of pyrrolyldipyrrinato BF_2 complexes **1a–h**, as extended BODIPYs, have been synthesized. Most of these BODIPYs show strong fluorescence emissions at wavelengths over 600 nm in six solvents of different polarity. Removal of the BF_2 group from BODIPY **1e** gave the corresponding free base pyrrolyldipyrrin **7** as an analog of the natural product prodigiosin, in high yield.

Introduction

In recent years, boron dipyrromethene (BODIPY) dyes have received much attention due to their outstanding properties, such as large molar absorption coefficient, sharp fluorescence emissions, high fluorescence quantum yields and high photophysical stability.[1–3] Moreover, the rich chemistry of BODIPYs and their key synthetic precursors, such as pyrrole and dipyrromethane, allows the continuous generation of novel BODIPY dyes for various applications.[3–9]

The absorption and emission for the classical BODIPY chromophore center at wavelengths between 470 and 530 nm.[1,10] To extend their applications, it is very necessary to develop extended BODIPYs that absorb and emit at longer wavelengths.[11–13] To achieve this goal, several groups[14–26] recently have performed chemical modifications on some ready-made BODIPYs to fuse a ring at the pyrrolic-position(s) of the BODIPY core or to install aryl, vinyl, styryl and arylethynyl substituents at the 3,5-positions of the chromophore.

The direct connection of pyrrole at the 3-position of the chromophore to form pyrrolyldipyrrinato BF_2 complexes has been proven to be able to red shift the spectra,[27–29] for example BODIPY **A** marketed by Invitrogen as BODIPY 576/589 which has been used as a long wavelength labeling reagent for biological applications. However, few efforts have been devoted to their synthesis. Currently, pyrrolyldipyrrinato BF_2 complexes are generally achieved from the BF_3 complexation of 9-pyrrole substituted dipyrrins[30] known as pyrrolyldipyrrins, the skeleton of a natural red pigment prodigiosin **B** (Fig. 1).[31] Due to the complicated synthesis of pyrrolyldipyrrins as described in a patent,[28] BODIPY **A** is only available in small quantities. In a recent report for the preparation of highly fluorescent pyrrolyldipyrrinato Sn(IV) complexes[27] by Thompson and coworkers, the synthesis of pyrrolyldipyrrin is still tedious and requires the usage of an expensive Pd-catalyst for the coupling reactions. In this work, we report an alternative route for the efficient synthesis of pyrrolyldipyrrinato BF_2 complexes by oxidative nucleophilic substitution of the 3-hydrogen on BODIPY **2** with pyrrole (Scheme 1).

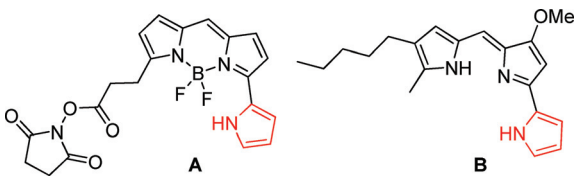
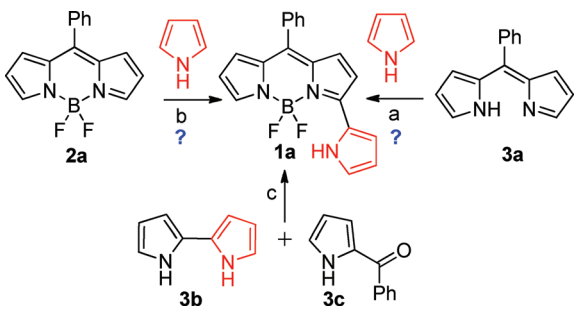


Fig. 1 Chemical structures of BODIPY 576/589 (**A**) and prodigiosin (**B**).



Scheme 1 Possible routes for the formation of BODIPY **1a**.

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†Electronic supplementary information (ESI) available: Copies of NMR, HRMS, UV-vis and fluorescence data for all new compounds, crystallographic information files (CIFs) for compounds **1b**, **1e** and **7**. CCDC reference numbers 863478–863481. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob06689k

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Results and discussion

Recently, we have been focused on the direct post-modification of some ready-made BODIPYs, like BODIPY **2a** for the facile introduction of various functionalities to the chromophore.[32–33] In our synthesis, BODIPY **2a** was obtained through a one-pot synthesis (Scheme S1, Supporting information†). Interestingly, during the column purification of the reaction mixture, we always isolated a small amount of a red fluorescent dye right before BODIPY **2a**. Later on, this less polar red dye was identified to be an extended BODIPY **1a**, a pyrrolyldipyrrinato BF_2 complex. This interesting result promoted us to study the possible routes for the formation of BODIPY **1a** and to improve the yield of this interesting molecule.

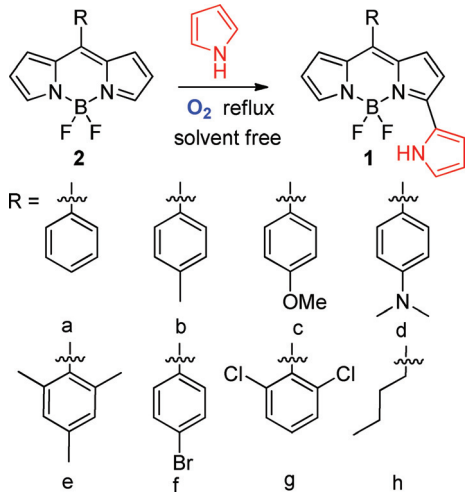
Since both the 1,9-positions of dipyrrin **3a** and the 3,5-positions of BODIPY **2a** are susceptible to the nucleophilic substitution/addition, both routes *a* and *b* could be responsible for formation of BODIPY **1a** (Scheme 1). In contrast, route *c* which has been proposed for the formation of a similar BODIPY in a patent[28] could be ruled out since it is not possible to form the key intermediate **3c** under our reaction conditions.

We then set up experiments to test the remaining two routes. To test route *a*, pyrrole was added into dipyrrin **3a** in dichloromethane in the presence of various acid catalysts ($POCl_3$, CF_3COOH, CF_3SO_3H, CH_3SO_3H or $BF_3{\cdot}Et_2O$) under air or molecular oxygen. After the subsequent additions of triethylamine and $BF_3{\cdot}Et_2O$, no BODIPY **1a** was obtained according to TLC. While we were preparing this manuscript, Ravikanth and coworkers reported the formation of BODIPY **1a** through the BF_3 complexation of an *in situ* generated 9-pyrrole substituted dipyrrin, which was obtained from the nucleophilic substitution of the corresponding dipyrromethane with pyrrole in the presence of an excess amount of DDQ.[29]

By adapting the reaction conditions used for the oxidative nucleophilic substitution of BODIPY recently disclosed by Dehaen,[34–35] pyrrole was added to BODIPY **2a** in dichloromethane in the presence or absence of acid catalyst (CF_3COOH, CF_3SO_3H, or $BF_3{\cdot}Et_2O$) under oxygen (route *b* in Scheme 1). No BODIPY **1a** was generated. Changing the solvent to 1,2-dichloroethane or dimethylformamide and varying the reaction temperature still failed to generate BODIPY **1a**.

Recently, Bergman and coworkers[36] have reported the solvent-free autoxidative coupling of quinolines with indoles and pyrroles. We thus performed the above reaction using an excess amount of pyrrole without further addition of any other solvents. In this condition, BODIPY **1a** was smoothly generated under reflux under air, and was easily isolated in a pure form by simply passing through a short silica gel pad. However, the isolated yield was only 10%, which may be attributed to the poor stability of the reactive intermediates **4** or **5** (Scheme S2, Supporting information†). To accelerate the conversion of these intermediates to BODIPY **1a**, we repeated this reaction under oxygen, and the yield was improved to 31% (Scheme 2). The usage of some common oxidant reagents, such as 2,3-dichloro-5,6-dicyanobenzoquinone or tetrachloroquinone for the reaction gave a dark reaction mixture and no BODIPY **1a** was obtained.

We further applied this optimized reaction condition to BODIPYs **2b–2h**, from which the desired BODIPYs **1b–1h** were isolated in 22–37% yields (Scheme 2). Among these,



Scheme 2 Syntheses of BODIPYs **1** *via* solvent free oxidative nucleophilic substitution.

meso-alkyl substituted BODIPY **2h** is more reactive than *meso*-aryl substituted BODIPYs **2a–2g**. Only 10 h was required for the completion of reaction. Furthermore, a larger amount (2.0 mmol) of BODIPY **2e** (620 mg) worked fine under our reaction condition, giving BODIPY **1e** in a similar yield (35%).

BODIPYs **1a–1h** were characterized by high resolution mass spectroscopy and NMR spectroscopy. Attempts to synthesize the double substituted product **C** (Scheme S2, Supporting information†) failed. This may be attributed to the electron-donating effect of the newly installed pyrrole substituent on the 3-position of the BODIPY core, which would increase the electron density of the chromophore and reduces the electrophilic ability of the 5-positional carbon.

Crystals of BODIPYs **1b** and **1e** suitable for X-ray analysis were obtained from the slow evaporation of their dichloromethane solutions. These two BODIPYs showed an almost planar structure for the BODIPY core (the central six-membered ring with two adjacent five-membered rings). The plane defined by F–B–F atoms for these BODIPY molecules is perpendicular to that of the BODIPY core as shown in Fig. 2. The B–N distance for these BODIPYs is within 1.55–1.56 Å, which indicates the usual delocalization of the positive charge. The dihedral-angles between the *meso*-aryl substituents and the BODIPY core are 52° and 83° for BODIPYs **1b** and **1e**, respectively. The larger dihedral-angle observed for BODIPY **1e** may be attributed to the steric hindrance effect from 1,6-dimethyl substituents on the *meso*-aryl group, which prohibited the free rotation of the *meso*-aryl substituent.

The uncoordinated pyrrole in BODIPY **1e** is out of the plane of the BODIPY core with a 16° dihedral angle similar to that described in the literature.[27,29] On the other hand, the uncoordinated pyrrole in BODIPY **1b** is almost coplanar with the BODIPY core with an unusually small dihedral angle at 2.8°. The observed NH–F distances were 2.09 and 2.45 Å for BODIPY **1b** and 2.01 and 2.66 Å for BODIPY **1e** as shown in Fig. 2.

BODIPYs **1a–1h** showed strong absorption bands at around 575 ± 15 nm and shoulder peaks at around 540 ± 15 nm in various solvents investigated despite their different polarities

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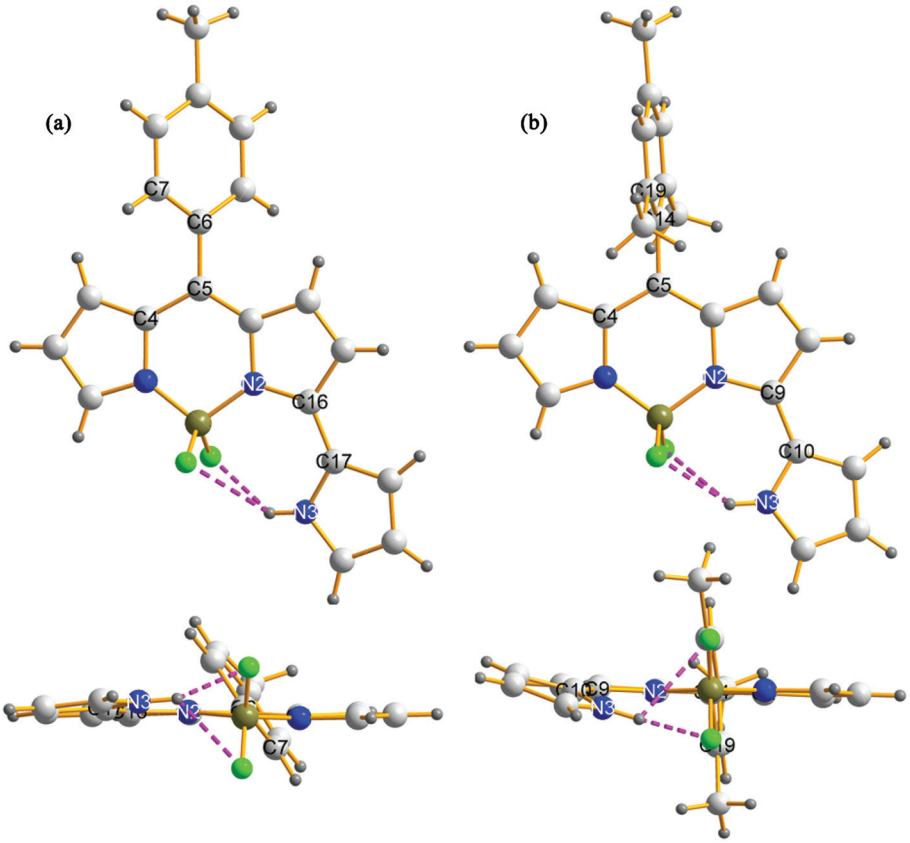

Fig. 2 X-Ray structures of BODIPYs **1b** (a) and **1e** (b). BODIPYs **1b**: selected bond distances (Å): N2–B, 1.55; N1–B, 1.52; N3H–F, 2.45 and 2.09; selected torsional angles (deg):C4–C5–C6–C7, 52; N2–C16–C17–N3, 2.8. BODIPYs **1e**: selected bond distances (Å): N2–B, 1.56; N1–B, 1.55; N3H–F, 2.66 and 2.01; selected torsional angles (deg):C4–C5–C14–C19, 83; N2–C9–C10–N3, −16. C grey, N blue, B yellow, F bright-green.

(Supporting information†) which are similar with the well-known absorption pattern for BODIPY derivatives.[1,37] The main absorption bands are attributed to the 0–0 vibrational band of a strong S_0–S_1 transition and the shoulder at its short wavelength side is assigned to the 0–1 vibrational band of the same transition.[37]

In addition, most of these BODIPYs showed a strong fluorescence emission at wavelengths over 600 nm with fluorescence quantum yields in the range of 0.15–0.68 in the various solvents studied (Supporting information†). In comparison with their starting BODIPYs **2a–2h**, there is a 70–80 nm red shift in their absorption and emission spectra.[33,37] This red shift indicated the extended π-conjugation of the system due to the participation of the conjugation pathway of the uncoordinated pyrrole. BODIPY **1d** showed a longer wavelength emission in polar solvents with a low fluorescence intensity, which is similar to that of the starting BODIPY **2d**[38] (Table S1, Supporting information†).

The starting BODIPYs **2a–2d** and **2f** showed low fluorescence due to the free rotation of the *meso*-substituents which is consistent with the literature.[39–40] Interestingly, the installation of pyrrole at the 3-position of the BODIPY core generally lead to the increase of the fluorescence quantum yield in these BODIPYs. For example, BODIPY **1a** showed an almost four times increase of the fluorescence quantum yield in comparison with that of BODIPY **2a** (Φ = 0.05 in dichloromethane). This fluorescence enhancement may be attributed to the enhanced rigidity of BODIPY **1a** as a result of the intramolecular hydrogen bonding between hydrogen attached to the uncoordinated pyrrolic nitrogen and the fluorines. Among these, BODIPYs **1e** and **1g** gave the strongest fluorescence emission. This may be attributed to steric hindrance effects from methyl and chlorine substituents at the 2,6-positions on the *meso*-phenyl group on these two BODIPYs, which prevent the free rotation of the *meso*-phenyl group, and reduced the number of nonradiative decay pathways in these two BODIPYs. Our data here are in agreement with Ravikanth's results[29] and BODIPYs **1** also have similar absorption and emission spectra to that of commercial BODIPY 576/589.

The time-resolved emissions of these BODIPYs were studied (Supporting information†) and the fluorescence lifetimes (τ) *via* TCSPC (Time-Correlated-Single-Photon-Counting) were determined in dichloromethane (Table 1). Most of those dyes gave a monoexponential decay function except **1c** and **1d** having electron donating methoxy or dimethylamine *para*-substituent groups on the *meso*-phenyl groups. The latter two, especially **1d**, can be described by a biexponential decay function and gave low lifetime values due to existences of charge transfer (CT) states as described earlier.[37a]

Consistent with steady state fluorescence data, BODIPYs **1e**, **1g** and **1h** which have higher fluorescent quantum yields due to internal steric constraints or in the absence of a *meso*-aryl substituent have longer fluorescence lifetime. While the radiative rate

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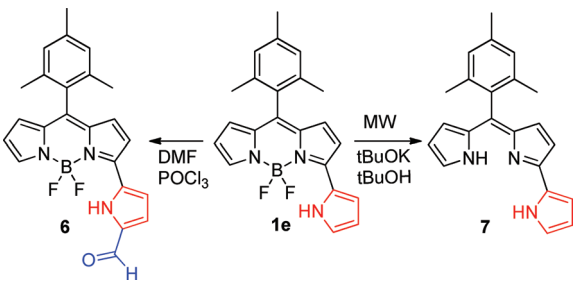
Table 1 Photophysical properties of BODIPYs **1a–h** in non-degassed dichloromethane at room temperature

BODIPY	λ_{abs} (nm)	λ_{em} (nm)	Φ^a	Stokes-shift (nm)	τ^b (ns)	k_f (10^9 s^{-1})	k_{nr} (10^9 s^{-1})
1a	576	609	0.24	33	3.90	0.06	0.19
1b	575	607	0.29	32	3.19	0.09	0.22
1c	575	606	0.28	31	2.84(τ_1), 931.50 (τ_2)[c]	—	—
1d	585	636	0.05	51	1.34(τ_1), 4.87(τ_2)[c]	—	—
1e	573	600	0.60	27	5.84	0.10	0.07
1f	578	612	0.27	34	3.04	0.09	0.24
1g	584	612	0.56	28	6.07	0.09	0.08
1h	567	593	0.34	26	6.56	0.05	0.10

[a] The fluorescence quantum yields (Φ) were calculated using Rhodamine B in anhydrous ethanol (Φ = 0.49) as standard. [b] The fluorescence lifetime. [c] The fluorescence decays measured as a function of emission wavelength described globally by a bi-exponential decay law.



Scheme 3 Syntheses of BODIPY **6** and pyrrolyldipyrrin **7**.

constants (k_f) for those BODIPYs are similar, the nonradiative rate constants (k_{nr}), however, dramatically decrease for **1e**, **1g** and **1h**, comparing with those of **1a**, **1b** and **1f**. Thus, these lower emission yields found in these aryl-substituted BODIPYs bearing no internal steric hindrance may be attributed to a facile S_1-excited-state nonradiative decay channel that is restricted when internal steric constraints are imposed or in the absence of a *meso*-aryl substituent.

The resultant BODIPYs can be easily applied for further functionalizations as demonstrated in Scheme 3. Treatment of BODIPY **1e** with 3 equiv of Vilsmeier reagent in the classic Vilsmeier–Haack conditions installed a formyl group at the α-position on the uncoordinated pyrrole and generated compound **6** in 94% isolated yield. The regioselectivity of this formylation reaction was confirmed by X-ray structure (Scheme S1, Supporting information†). This formyl group can be used for the further introduction of various functionalities on BODIPY for various applications.[41] Meanwhile, the removal of the BF_2 group from BODIPY **1e** using a modified literature procedure[42] under microwave irradiation (600 W) provided pyrrolyldipyrrin **7** in 83% isolated yield. Our synthesis of pyrrolyldipyrrin **7** opens a new way for the efficient synthesis of analogs of the nature product prodigiosin, without the need for expensive catalyst and tedious synthetic routes.

Pyrrolyldipyrrin **7** crystallized from dichloromethane to form a dimer in the asymmetric unit, which was held together by a

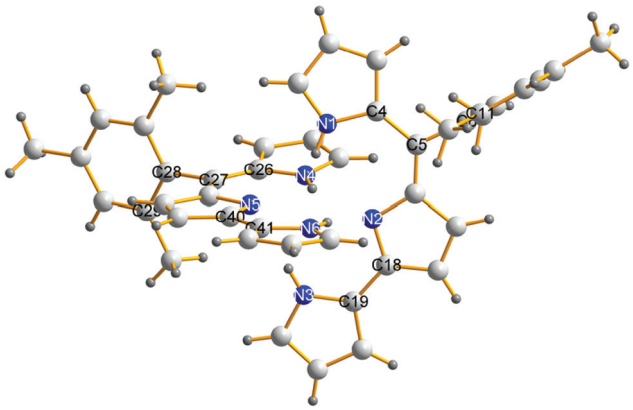


Fig. 3 X-Ray structure of pyrrolyldipyrrin **7** dimer. Selected bond distances (Å): N1H–N2, 2.39; N1H–N5, 2.28; N3H–N2, 2.71; N3H–N5, 2.19; N4H–N5, 2.37; N4H–N2, 2.29; N6H–N5, 2.65; N6H–N2, 2.16. Selected torsional angles (deg): C28–C29–C27–C26, 89; N6–C41–C40–N5, −0.9; C4–C5–C6–C11, 82; N3–C19–C18–N2, −4.6. C grey, N blue.

network of intermolecular hydrogen bonding between the pyrrolic hydrogens and the azafulvene nitrogen as shown in Fig. 3. Two similar dimers of natural prodigiosin derivatives have been reported by Parr,[43] Manderville[44] and their coworkers. The two pyrrolyldipyrrin **7** molecules showed slightly different dihedral-angles (82° and 89° respectively) between the *meso*-aryl substituents and the dipyrrin core, and between pyrrole and the dipyrrin core (−0.9° and −4.6° respectively). The lengths of intermolecular and intramolecular hydrogen bonding are in the range of 2.16–2.71 Å.

Conclusions

In summary, we have developed an alternative route for the efficient synthesis of pyrrolyldipyrrinato BF_2 complexes based on the oxidative nucleophilic substitution of the 3-hydrogen on the BODIPY core with pyrrole, from which a series of extended BODIPYs **1a–h** were obtained in good yields. Most of these resultant BODIPYs showed strong fluorescence emission at wavelengths over 600 nm, and can be easily applied for further functionalization as demonstrated here for the preparation of pyrrolyldipyrrin **7**, an analog of the natural product prodigiosin in high yield through a simple removal of the BF_2 group from the molecule.

Experimental section

General Experimental

Reagents and solvents were used as received from commercial suppliers unless noted otherwise. BODIPYs **2a–h** were synthesized by following the procedures described in our previous paper.[33] All reactions were performed in oven-dried or flame-dried glassware unless otherwise stated, and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254). ^1H and ^{13}C NMR are obtained on a 300 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given

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in ppm relative to $CDCl_3$ (7.26 ppm for ^1H and 77 ppm for ^{13}C) or to internal TMS. High-resolution mass spectra (HRMS) were obtained using EI-TOF in positive mode.

UV-visible absorption spectra and fluorescence emission spectra were recorded on a commercial spectrophotometer (190–1100 nm scan range). Relative fluorescence quantum efficiencies of BODIPY derivatives were obtained by comparing the areas under the corrected emission spectrum of the test sample in various solvents with Rhodamin B (0.49 in EtOH).[45] Non-degassed, spectroscopic grade solvents and a 10 mm quartz cuvette were used. Dilute solutions ($0.01 < A < 0.05$) were used to minimize the reabsorption effects. Quantum yields were determined using the following equation:[40]

$$\Phi_X = \Phi_S(I_X/I_S)(A_S/A_X)(\eta_X/\eta_S)^2$$

Where Φ_S stands for the reported quantum yield of the standard, I stands for the integrated emission spectra, A stands for the absorbance at the excitation wavelength and η stands for the refractive index of the solvent being used ($\eta = 1$ when the same solvent was used for both the test sample and the standard). X subscript stands for the test sample, and S subscript stands for the standard. Fluorescence lifetimes were measured on a combined steady-state lifetime fluorescence spectrometer and the fluorescence lifetimes were obtained from deconvolution and distribution lifetime analysis. Details of the instrumentation and experimental procedures used have been described elsewhere.[37a] When the fluorescence decays were monoexponential, the rate constants of radiative (k_f) and nonradiative (k_{nr}) deactivation were calculated from the measured fluorescence quantum yield and fluorescence lifetime according to the following equations: $k_f = \Phi/\tau$ and $k_{nr} = (1 - \Phi)/\tau$.

Crystals of BODIPYs **1b**, **1e**, **6** and **7** suitable for X-ray analysis were obtained by slow evaporation of their dichloromethane solutions. The vial containing this solution was placed, loosely capped, to promote the crystallization. The structure was solved by the direct method using the SHELXS-974 program and refined by the least-squares method on F^2, SHELXL-97,[46] incorporated in SHELXTL V5.10.[47]

General procedure for synthesis BODIPY 1. To a 10 mL dry Schlenk flask was added BODIPY **2** (0.2 mmol) in 0.5 mL freshly distilled pyrrole. The mixture was heated to reflux for 10–36 h under oxygen atmosphere. After the mixture was cooled to room temperature, excess amount of pyrrole was removed under vacuum and the crude product was purified using a short pad of silica gel column chromatography (petroleum ether/EtOAc = 25/1, v/v) and afforded BODIPY **1** as a purple powder product.

BODIPY 1a. BODIPY **2a** (54 mg, 0.2 mmol) was used for the reaction to afford BODIPY **1a** in 31% isolated yield (21 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 10.57 (s, 1H), 7.70 (s, 1H), 7.53 (br, 5H), 7.22 (s, 1H), 7.04 (s, 1H), 6.93 (d, J = 7.5 Hz, 2H), 6.67 (s, 1H), 6.47 (s, 1H), 6.41 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6, 144.1, 139.7, 136.7, 134.5, 133.4, 133.2, 130.4, 129.9, 128.3, 126.5, 125.1, 123.6, 121.1, 118.6, 116.0, 111.7. HRMS calcd. for $C_{19}H_{15}BF_2N_3$ $[M + H]^+$: 334.1327, found 334.1326.

BODIPY 1b. BODIPY **2b** (56 mg, 0.2 mmol) was used for the reaction to afford BODIPY **1b** in 28% isolated yield (19 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.68 (s, 1H), 7.42 (s, 2H), 7.29 (s, 2H), 7.19 (s, 1H), 7.00 (s, 2H), 6.89 (s, 1H), 6.67 (s, 1H), 6.44 (s, 1H), 6.38 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 140.2, 140.1, 137.7, 136.6, 133.4, 133.1, 131.7, 130.5, 129.1, 126.3, 125.2, 123.7, 120.9, 118.3, 115.9, 111.6, 21.4. HRMS calcd. for $C_{20}H_{17}BF_2N_3$ $[M + H]^+$: 348.1484, found 348.1484.

BODIPY 1c. BODIPY **2c** (60 mg, 0.2 mmol) was used for the reaction to afford BODIPY **1c** in 26% isolated yield (19 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 10.54 (s, 1H), 7.68 (s, 1H), 7.50 (s, 2H), 7.20 (s, 1H), 7.02 (br, 4H), 6.92(s, 1H), 6.71 (s, 1H), 6.47 (s, 1H), 6.40 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 151.2, 139.9, 137.6, 136.5, 133.4, 133.05, 132.0, 127.0, 126.1, 125.1, 123.7, 120.8, 118.1, 115.9, 113.9, 111.5, 55.5. HRMS calcd. for $C_{20}H_{17}BF_2N_3O$ $[M + H]^+$: 364.1433, found 364.1432.

BODIPY 1d. BODIPY **2d** (62 mg, 0.2 mmol) was used for the reaction to afford BODIPY **1d** in 27% isolated yield (20 mg).^1H NMR (300 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.67 (s, 1H), 7.51 (s, 1H), 7.48 (s, 1H), 7.16 (s, 1H), 7.08 (d, J = 3.0 Hz, 1H), 6.97 (s, 1H), 6.90 (d, J = 6.0 Hz, 1H), 6.81 (s, 2H), 6.78 (s, 1H), 6.47 (s, 1H), 6.38 (s, 1H), 3.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8, 150.1, 141.5, 137.1, 135.9, 133.3, 132.9, 132.4, 125.3, 125.2, 123.9, 122.3, 120.0, 117.1, 115.7, 111.5, 111.2, 40.2. HRMS calcd. for $C_{21}H_{20}BF_2N_4$ $[M + H]^+$: 377.1749, found 377.1747.

BODIPY 1e. BODIPY **2e** (62 mg, 0.2 mmol) was used for the reaction to afford BODIPY **1e** in 37% isolated yield (28 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.65 (s, 1H), 7.20 (s, 1H), 7.01–6.95 (br, 3H), 6.84 (s, 1H), 6.67 (s, 1H), 6.39 (s, 3H), 2.36 (s, 3H), 2.11 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 139.3, 138.4, 138.0, 136.8, 136.7, 133.4, 131.8, 130.3, 128.1, 126.4, 123.8, 123.7, 121.1, 118.5, 116.0, 111.7, 21.2, 20.0. HRMS calcd. for $C_{22}H_{21}BF_2N_3$ $[M + H]^+$: 376.1797, found 376.1795.

BODIPY 1f. BODIPY **2f** (69 mg, 0.2 mmol) was used for the reaction to afford BODIPY **1f** in 24% isolated yield (20 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.67 (d, J = 6.0 Hz, 2H), 7.64 (s, 1H), 7.42 (d, J = 9.0 Hz, 2H), 7.23 (s, 1H), 7.05 (s, 1H), 6.92 (s, 2H), 6.62 (s, 1H), 6.47 (s, 1H), 6.41 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9, 137.9, 137.5, 136.9, 133.4, 133.0, 132.7, 131.9, 131.7, 126.9, 124.7, 124.4, 123.6, 121.5, 119.0, 116.1, 111.9. HRMS calcd. for $C_{19}H_{14}BBrF_2N_3$ $[M + H]^+$: 412.0432, found 412.0430.

BODIPY 1g. BODIPY **2g** (67 mg, 0.2 mmol) was used for the reaction to afford BODIPY **1g** in 22% isolated yield (18 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 10.60 (s, 1H), 7.67 (s, 1H), 7.48 (d, J = 9.0 Hz, 2H), 7.42–7.36 (m, 1H), 7.26 (s, 1H), 7.08 (s, 1H), 6.91 (s, 1H), 6.69 (s, 1H), 6.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 142.8, 137.9, 137.0, 135.8, 132.1, 131.5, 130.8, 128.4, 128.2, 127.4, 123.7, 123.0, 122.1, 119.7, 116.1, 112.1. HRMS calcd. for $C_{19}H_{13}BCl_2F_2N_3$ $[M + H]^+$: 402.0548, found 402.0549.

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BODIPY 1h. BODIPY **2h** (50 mg, 0.2 mmol) was used for the reaction to afford BODIPY **1h** in 34% isolated yield (21 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.60 (s, 1H), 7.31 (s, 1H), 7.16 (s, 1H), 7.00 (s, 2H), 6.90 (d, J = 3.0 Hz, 1H), 6.47 (s, 1H), 6.38 (s, 1H), 2.84 (t, J = 6.0 Hz, 2H), 1.78–1.85 (m, 2H), 1.04 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 142.1, 137.8, 136.2, 133.5, 129.9, 125.9, 123.6, 121.8, 120.4, 118.0, 115.5, 111.4, 32.5, 26.6, 14.5. HRMS calcd. for $C_{16}H_{17}BF_2N_3$ $[M + H]^+$: 300.1484, found 300.1487.

BODIPY 6. A mixture of DMF (0.14 mL, 1.8 mmol) and $POCl_3$ (0.17 mL, 1.8 mmol) was stirred under ice-cold conditions for 5 min under argon. After warming up to room temperature, it was further stirred for 30 min before adding BODIPY **1e** (224 mg, 0.6 mmol) in $ClCH_2CH_2Cl$ (5 mL). The reaction mixture was stirred for 2 h at room temperature, and was slowly poured into a saturated aqueous solution of K_2CO_3 (100 mL) under the ice-cold conditions. After warming up to room temperature, the reaction mixture was further stirred for 20 min, extracted with dichloromethane (3 × 50 mL). The organic layers were combined and washed with water, dried over anhydrous Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified using column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) to give **6** as a purple powder in 94% isolated yield (228 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.04 (s, 1H), 9.69(s, 1H), 7.88 (s, 1H), 7.01 (s, 1H), 6.96 (s, 2H), 6.94 (s, 1H), 6.86 (d, J = 3.0 Hz, 1H), 6.70 (s, 1H), 6.62 (s, 1H), 6.50 (s, 1H), 2.37 (s, 3H), 2.11 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.3, 148.1, 144.1, 142.4, 138.9, 137.8, 136.9, 135.7, 134.9, 130.9, 129.8, 129.6, 128.4, 128.3, 120.6, 120.1, 118.4, 116.6, 21.1, 20.0. HRMS calcd. for $C_{23}H_{21}BF_2N_3O$ $[M + H]^+$: 404.1746, found 404.1745.

Pyrrolyldipyrrin 7. To a Schlenk tube were added potassium *tert*-butoxide (134 mg, 1.2 mmol) and BODIPY **1e** (75.0 mg, 0.2 mmol) in *tert*-butanol (15 mL). The mixture was heated in a microwave oven for 40 min under argon (power = 600 W, ramp to T = 92 °C, hold time = 40 min, stirring = medium). Then the reaction mixture was allowed to cool down to room temperature, diluted with dichloromethane (30 mL) and poured into a saturated aqueous solution of sodium bicarbonate (50 mL) in an ice bath. The organic layer was collected and the aqueous layer was extracted with dichloromethane (3 × 30 mL). The organic layers were combined and washed with water, dried over anhydrous Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified using silica gel column chromatography (petroleum ether/EtOAc = 15/1, v/v) to give **7** as a purple powder in 83% isolated yield (54 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.78 (s, 1H), 9.56 (s, 1H), 6.94 (s, 2H), 6.90 (d, J = 6.0 Hz, 1H), 6.83 (s, 1H), 6.80 (s, 2H), 6.75 (d, J = 3.0 Hz, 1H), 6.26 (s, 1H), 6.06 (s, 1H), 6.03 (s, 1H), 2.37 (s, 3H), 2.13 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9, 148.9, 137.3, 136.9, 136.1, 134.3, 131.7, 128.2, 127.8, 127.3, 126.6, 123.1, 122.6, 119.5, 113.2, 110.8, 110.6, 21.13, 19.88. HRMS calcd. for $C_{22}H_{21}N_3$ $[M + H]^+$: 328.1814, found 328.1810.

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