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α-/β-Formylated Boron–Dipyrrin (BODIPY) Dyes: Regioselective Syntheses and Photophysical Properties

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Formylation has been performed on pyrrole-unsubstituted dipyrromethanes **1** and boron–dipyrrin (BODIPY) dyes **4** based on a Vilsmeier–Haack reaction. It is highly regioselective and complementary and occurs exclusively at the α- and β-position, respectively, for pyrrole-unsubstituted dipyrromethanes **1** and BODIPY dyes **4**. This regioselective formylation enables the syntheses of a variety of α- and β-substituted BODIPY dyes. The installation of formyl groups affects the electronic properties of the BODIPY chromophore, resulting in red- and blueshifts of the absorption and emission maxima, respectively, for the α- and β-formylated BODIPYs **3** and **5**.

Introduction

Boron–dipyrrin (BODIPY) dyes have been widely used as bright fluorescent dyes for cellular imaging due to their remarkable photophysical properties, such as photostability, large extinction coefficients and high fluorescent quantum yields.[1,2] Recent improvements in functionalization methods for BODIPY has allowed fine-tuning of the properties of the chromophore and brought renewed research interest in BODIPYs for diverse fields, such as chemosensors,[3,4] long-wavelength absorbing/emitting fluorescent dyes,[5–8] laser dyes,[9] photosensitizers,[10] sensitizers for solar cells,[11] energy-transfer cassettes,[12] light harvesters[13] and fluorescent organic devices.[14]

Post-modification methods on some ready-made BODIPY frameworks are convenient for preparing α- and β-functionalized BODIPYs (Figure 1). Of these compounds, α-functionalized BODIPYs are often achieved by Knoevenagel condensation,[3a,3b,6] Sonogashira/Suzuki coupling[3g,5] or oxidative formylation.[15] Functionalization at the β-position is mainly achieved by sulfonation,[16] nitration,[17] palladium-catalyzed C–H functionalization,[18] and halogenation reactions.[5e,10] Recently, our group has reported the efficient synthesis of a series of β-formylated BODIPYs,[19] which constitute a good platform for further functionalization of the BODIPY core at the β-position.[20] However, all of these β-functionalization methods face regioselectivity issues on the BODIPY core, such as the methyl groups in 1,3,5,7-tetramethyl-substituted BODYPYs, because the regiochemistry is predetermined by pyrrole-substituted BODIPYs **A** and **B** (Figure 1), which block the other positions from participating in these reactions.

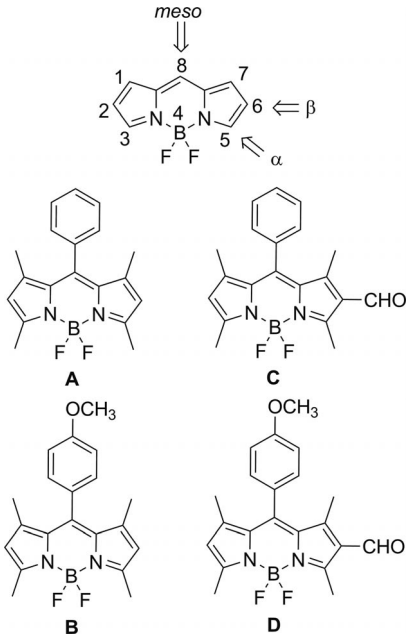

Figure 1. IUPAC numbering system for the BODIPY core, chemical structures for 1,3,5,7-tetramethyl-substituted BODIPYs **A** and **B**, and their β-formylated products **C** and **D**.[20]

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In this case, we envisioned the possibility of regioselective direct β-formylation on these pyrrole-unsubstituted BODIPYs **4** (Schemes 1 and 2). Formylation is an electrophilic substitution reaction and would prefer to occur at the least positively charged positions of the BODIPY core. Indeed, the Mulliken charge analysis of pyrrole-unsubstituted BODIPY **4a** (–0.37 for the β-carbon atom) shown in Figure 2, and Figure S1 in the Supporting Information, which is consistent with the ^{1}H NMR spectroscopy results (δ = 6.55 ppm for the β-proton), clearly shows that the β-position is the least positively charged site. Thus, by carefully controlling the reaction conditions, it would be possible to achieve regioselective β-formylation of pyrrole-unsubstituted BODIPYs.

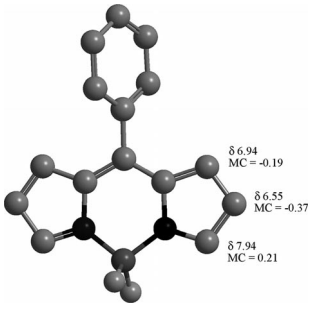


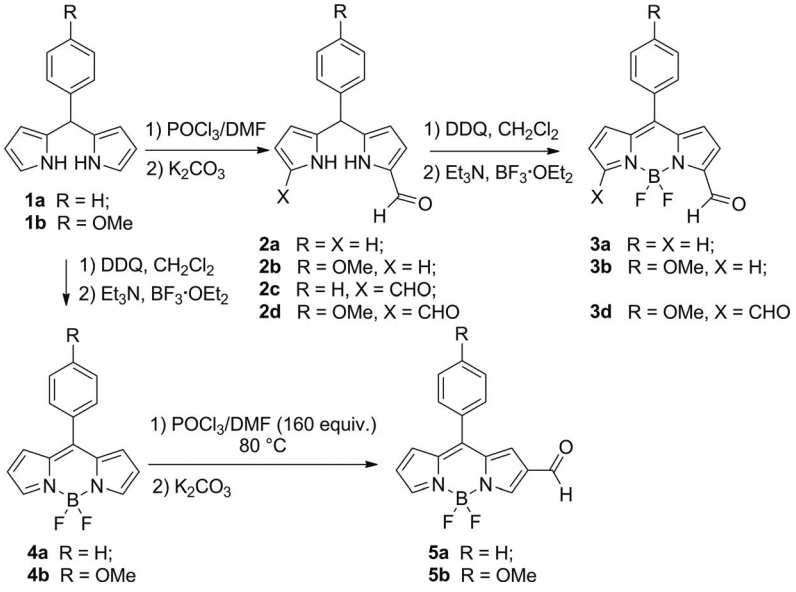
Figure 2. Top view of the calculated structure for *meso*-phenyl-substituted BODIPY **4a**, Mulliken charges (MC) of the three pyrrole carbon atoms and the relevant chemical shifts in the ^{1}H NMR spectrum for the corresponding hydrogen atoms on these carbon atoms in $CDCl_3$. H atoms are omitted for clarity.

While we designed this project, direct regioselective functionalization of pyrrole-unsubstituted BODIPYs, such as **4a**, was reported by Osuka and co-workers for iridium-catalyzed regioselective α- or β-borylation of BODIPY dyes,[21a] and by Dehaen and co-workers for regioselective nucleophilic substitution at the α-position of BODIPY.[21b,21c] These pioneering works further supported our above rationale. While we were preparing this manuscript, Ravikanth and co-workers reported the generation of several 3,5-diformyl-substituted BODIPYs through BF_3 complexation of the corresponding 3,5-diformyldipyrromethenes.[22] Herein, we report the regioselective syntheses of α- and β-formylated BODIPYs **3**, **5** and **6**, and their photophysical properties.

Results and Discussion

Syntheses of the BODIPY Dyes

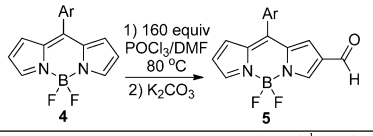
In contrast to their 1,3,5,7-tetramethyl-substituted BODIPY analogues **A** and **B** (Figure 1), pyrrole-unsubstituted BODIPYs **4** (Scheme 1) have attracted relatively little research interest until very recently due to synthetic difficulties. Traditionally, this type of BODIPY was prepared in modest overall yields (ca. 10%)[24b] by using Lindsey's method[23,24] of treating a large excess of pyrrole with aldehydes under acid-catalyzed conditions. Recent improvement has been made by using $InCl_3$ as the catalyst to reduce the amount of pyrrole used to only slightly more than a stoichiometric amount; however, two additional steps, the installation and removal of an α-thioalkyl group in the initial and final stages of the synthesis, are required.[24c] Thus, efficient synthesis of these pyrrole-unsubstituted BODIPYs has remained a challenge, until a recent report by Dehaen and co-workers regarding the water-phase synthesis of pyrrole-unsubstituted dipyrromethanes.[25] This has resulted in increased research interest in this type of molecule.[16,22,23,26] By using this method, a series of *meso*-substituted dipyrromethanes, such as **1a**,**b**, shown in Scheme 1, were efficiently generated on a multi-gram scale by condensation of aromatic aldehydes with pyrrole (3 equiv.) under



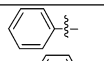
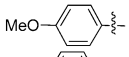
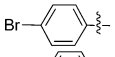
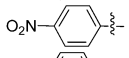
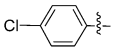
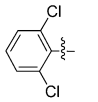
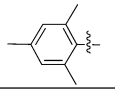
Scheme 1. Regioselective α- and β-formylation of dipyrromethanes **1a**,**b** and BODIPYs **4a**,**b**, respectively to generate α- and β-formylated BODIPY dyes **3a**,**b**,**d** and **5a**,**b**. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

HCl-catalyzed conditions at room temperature in water. The resulting dipyrromethanes were easily isolated from the reaction mixture as precipitates in an essentially pure state in high yields. Most of these dipyrromethanes were directly used for the DDQ oxidation and subsequent $BF_3{\cdot}OEt_2$ complexation reactions to generate the desired BODIPYs **4a**–**i** (see Schemes 1 and 2 and Table 1) in 21–62% isolated yields.

Table 1. Syntheses of BODIPYs **5**.



4 **5**

BODIPY	Ar-	Isolated yield	δ(^{1}H) of CHO
5a		75%	9.79 ppm
5b		75%	9.88 ppm
5c		71%	9.87 ppm
5d		54%	9.84 ppm
5e		69%	9.87 ppm
5f		72%	9.84 ppm
5g		68%	9.90 ppm
5h		81%	9.74 ppm

The reaction of *meso*-aryldipyrromethanes **1a**,**b** under standard Vilsmeier–Haack conditions with 1 or 2 equiv. of Vilsmeier reagent ($POCl_3$/DMF) generated the corresponding α-formylated dipyrromethanes **2a**,**b** and α,α-diformylated dipyrromethanes[27] **2c**,**d**, respectively, in around 50% isolated yield with perfect regioselectivity at the α-positions. The reaction of the resulting α-formylated dipyrromethanes **2a**,**b** in the DDQ oxidation under ice-cold conditions and subsequent treatment with Et_3N and $BF_3{\cdot}Et_2O$ smoothly generated the desired α-formylated BODIPYs **3a**,**b** in around 15% isolated yields. Under similar conditions, α,α-diformylated dipyrromethane **2d** was also smoothly converted into the corresponding α,α-diformylated BODIPY **3d**[22] in an overall yield of 21%, as shown in Scheme 1. In contrast, no α,α-diformylated BODIPY was obtained for α,α-diformylated *meso*-phenyldipyrromethane **2c** under these conditions. This may be attributed to the instability of dipyrromethene, which is the DDQ oxidization product of dipyrromethane **2c**, under these reaction conditions in the presence of a large excess of Et_3N. Changing the reaction conditions, such as temperature, solvent and the reagent ratio of $BF_3{\cdot}Et_2O/Et_3N$, still failed to convert dipyrromethane **2c** into the desired α,α-diformylated BODIPY.

On the other hand, treatment of **4a** or **4b** under modified Vilsmeier reaction conditions led to the isolation of β-formylated BODIPYs **5a** or **5b** in yields of 75% with high regioselectivity at the β-position. As expected, no α-formylated BODIPYs or other isomers were isolated from this reaction under various conditions. This highly regioselective β-formylation is in agreement with the MC analysis results described above, indicating that the β-position is the most reactive site under these reaction conditions. In comparison with the 1,3,5,7-tetramethyl-substituted BODIPY analogues **A** and **B**, the BODIPYs **4a**,**b** showed a reduced reactivity in this formylation reaction. The reaction required a higher temperature (80 °C), a large excess of the Vilsmeier reagents and a much longer reaction time (10 h). This different reactivity may be attributed to reduced electron density on the BODIPY core in BODIPYs **4a**,**b** due to the absence of electron-donating pyrrole substituents.

Mono-α- and -β-formylation was confirmed by ^{1}H and ^{13}C NMR spectroscopy and X-ray analysis results, which are shown in Figures 3 and 4. BODIPYs **3a** and **5a** showed molecular ion signals at 296.0936 and 296.0926, respectively, in HRMS (calcd. 296.0932) corresponding to the monoformylated BODIPY product. In the ^{1}H NMR spectra, BODIPYs **3a** and **5a** showed characteristic signals at δ = 10.39 and 9.79 ppm, respectively, for the monoformyl group. Crystals suitable for the X-ray analysis were obtained by the slow concentration of solutions of BODIPYs **3a** and **5a** in dichloromethane in air. Both α- and β-monoformylated BODIPYs **3a** and **5a** showed a planar BODIPY framework with dihedral angles of 54 and 56°, respectively, between the *meso*-phenyl substituent and the BODIPY core. The plane defined by the F–B–F atoms for these two BODIPY molecules is perpendicular to that of BODIPY core, similar to previously reported results.[23b] The average B–N distances for BODIPYs **3a** and **5a** are 1.548(2) and 1.540(3) Å, respectively, which implies typical delocalization of the positive charge. In **3a**, there is also an intramolecular hydrogen bond between the two fluorine atoms and the formyl proton[15b] in the α-position, with an average C–H···F distance of 2.74 Å. The formation of α,α-diformylated BODIPY **3d** was also confirmed by HRMS and NMR

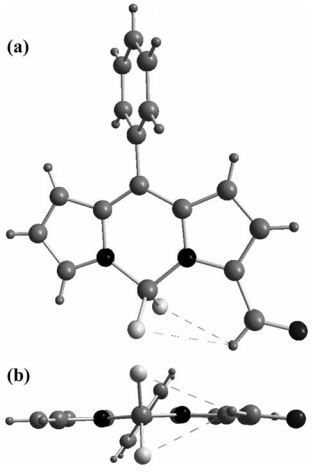


Figure 3. Top (a) and side views (b) of the X-ray structure of BODIPY **3a**. Hydrogen bonding between F atoms and the formyl proton is indicated by thin dashed lines for clarity.

spectroscopy. A molecular ion signal at 354.0985 in HRMS (calcd. 354.0987) corresponded to the diformylated BODIPY, and a characteristic signal at δ = 10.48 ppm was observed for the two formyl groups.

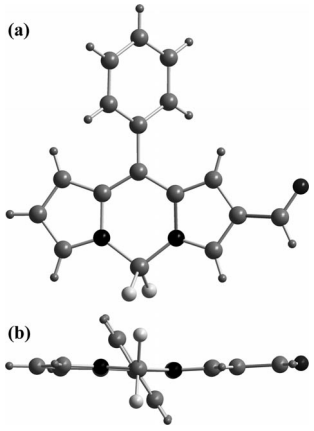
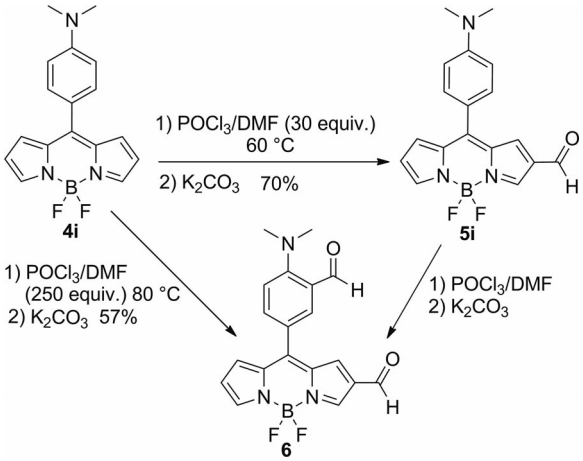


Figure 4. Top (a) and side views (b) of the X-ray structure of BODIPY **5a**.

The F atoms in BODIPY molecules are strongly electronegative and are able to form intermolecular hydrogen bonds (C–H···F) with hydrogen atoms.[28] In the solid state, each molecule of **5a** forms eight such C–H···F intermolecular hydrogen-bonding interactions (with the aldehyde proton, the hydrogen atom at the 3-position of the BODIPY core, and the *ortho*-/*meta*-hydrogen atoms of the *meso*-phenyl substituent); the H···F hydrogen-bond length is in the range of 2.409(3)–2.845(3) Å, as shown in Figure S6 in the Supporting Information. In this way, each molecule of **5a** is connected to three other neighbouring molecules of **5a**, which eventually leads to the formation of the crystal-packing structure observed for **5a**. In this crystal-packing structure, all molecules of **5a** are almost parallel to each other in a head-to-tail orientation.

To test the versatility of this regioselective β-formylation reaction, BODIPYs **4c**–**h** were also used for this optimized formylation reaction, as shown in Table 1. In comparison with **4a**, BODIPYs **4c**–**h** showed similar reactivities in this formylation reaction and generated exclusively β-formylated BODIPYs **5c**–**h** in 54–81% yields. In the ^{1}H NMR spectra, each of these BODIPYs **5c**–**h** gave a characteristic formyl proton signal as a singlet in the range δ = 9.74–9.90 ppm, as summarized in Table 1.

However, the treatment of *meso*-substituted *p*-(dimethylamino)phenyl-substituted BODIPY **4i** with 160 equiv. of Vilsmeier reagent at 80 °C gave mainly the *meso*,β-diformylated BODIPY **6** instead of the desired β-monoformylated BODIPY **5i**, as shown in Scheme 2. The formation of BODIPY **6** may be attributed to increased electron density at the *meso*-phenyl carbon atoms adjacent to the dimethylamine substituent, which facilitates further formylation at the *meso*-position for β-monoformylated BODIPY **5i**. The second formylation of BODIPY **4i** at the *p*-(dimethylamino)phenyl moiety is surprising, because no formylated product is obtained for *p*-substituted dimethylanilines under Vilsmeier reaction conditions. Instead, these *p*-substituted dimethylanilines are usually converted into the dibenzo[*b*,*f*][1,5]diazocines and tetrahydroquinazolinium salts under these conditions, according to the literature.[29]



Scheme 2. Syntheses of mono-β-formylated BODIPY **5i** and *meso*,β-diformylated BODIPY **6**.

This interesting result promoted us to investigate the optimized reaction conditions for the formylation of *meso*-[*p*-(dimethylamino)phenyl]-substituted BODIPY **4i**. Because diformylated BODIPY **6** resulted from further formylation of BODIPY **5i**, less Vilsmeier reagent (30 equiv.) and a lower reaction temperature (60 °C) were used for the formylation reaction to achieve the β-monoformylated BODIPY **5i**. Under these conditions, the desired β-monoformylated BODIPY **5i** was isolated as the major product in 70% yield. To improve the yield of *meso*,β-diformylated BODIPY **6**, various reaction conditions regarding solvent and temperature were investigated, but no clear improvement in the yield was obtained. On the other hand, increasing the amount of Vilsmeier reagent from 160 to 250 equiv. increased the yield to 57%. In contrast, no such *meso*,β-diformylated BODIPY was obtained for the other *meso*-aryl-substituted BODIPYs **4a**–**h** under various formylation conditions. Thus, the presence of a strongly electron-donating substituent at the *meso*-aryl group facilitates this formylation reaction.

Photophysical Characterization of BODIPYs 3

BODIPYs **4**, **5** and **6** are colourful to the eye, and most of them are brilliant upon irradiation. The photophysical properties of these molecules are summarized in Table 2. Pyrrole-unsubstituted BODIPYs **4** showed a strong absorption band at around (500 ± 15) nm, and most of them gave a weak fluorescence emission at (530 ± 15) nm with the exception of BODIPY **4g**, which gave an emission maximum at 626 nm. The longest-wavelength emission and the largest Stokes shift observed in BODIPY **4g** may be attributed to the presence of the 2-thiophene group at the *meso* position

of the BODIPY core, which participates in a twisted intramolecular charge transfer (TICT), as described in the literature.[26d,26e]

Table 2. Photophysical properties of BODIPYs **3**, **4**, **5** and **6** in dichloromethane at room temperature.

BODIPY	λ_{max} [nm]	$\log \varepsilon_{max}$	λ_{em} [nm]	Stokes shift [cm^{-1}]	Φ[a]
3a	519	4.11	542	818	0.29
3b	517	4.15	538	755	0.24
3d	544	4.43	590	1430	0.08
4a	500	4.52	527	1025	0.03
5a	496	4.39	521	967	0.03
4b	502	4.50	529	1017	0.02
5b	499	4.13	525	992	0.01
4c	498	4.68	529	1177	0.05
5c	493	4.25	519	1016	0.03
4d	508	4.13	545	1336	0.01
5d	505	4.61	540	1283	0.01
4e	502	4.73	528	981	0.02
5e	498	4.46	525	1033	0.03
4f	512	4.86	534	805	0.71
5f	508	4.39	532	888	0.71
4g	510	4.47	626	3633	0.01
5g	505	4.08	624	3776	0.01
4h	501	4.67	521	766	0.84
5h	497	4.49	518	816	0.87
4i	491	4.82	517	1024	0.01
5i	479	4.35	521	1683	0.01
6	494	4.21	518	900	0.02

[a] The fluorescence quantum yields were calculated by using fluorescein in a 0.1 N aqueous solution of NaOH (Φ = 0.90) as the standard.

In comparison with the 1,3,5,7-tetramethyl-substituted BODIPY analogues, the low fluorescence quantum yields observed for most of the BODIPYs **4** may be attributed to free rotation of the *meso* substituent around a carbon–carbon single bond,[24b,24c] which increased the non-radiative deactivation process in these BODIPYs. The high fluorescence emission observed in BODIPYs **4f** and **4h** was comparable to that of the 1,3,5,7-tetramethyl-substituted BODIPY analogues and may be attributed to the presence of methyl and chloro substituents at the 2,6-positions of the *meso*-aryl groups. The steric hindrance effect prevents free rotation of the *meso* group in these two BODIPYs.[23b,24b,24c]

The installation of formyl group(s) on the BODIPY core affected the photophysical properties of these molecules, as demonstrated in the normalized absorption and emission spectra of BODIPY dyes **3b**, **4b**, **5b** and **3d** shown in Figure 5. These formylated BODIPY dyes show good dispersion of UV/Vis absorbance and fluorescence emission characteristics for BODIPY dyes. α-Formylation leads to a redshift of absorption (around 15 and 40 nm for BODIPYs **3b** and **3d**, respectively) and emission maxima (around 10 and 60 nm for BODIPYs **3b** and **3d**, respectively), with the largest spectral shifts for the α,α-diformylated BODIPY **3d**. Several interesting shoulders on the signals of α-formylated BODIPYs **3b** and **3d** may be attributed to the intramolecular charger transfer due to the existence of formyl groups.[15b] On the other hand, β-formylation results in a slight blueshift of the spectrum for BODIPY **5b** (around 5 nm). Similarly, the installation of a formyl group at the β-position of the BODIPY core generally gave a blueshift in both the absorption (3–12 nm) and emission (3–10 nm) maxima for most of the β-formylated BODIPYs **5**, as summarized in Table 2. For the *meso*-substituted *p*-(dimethylamino)phenyl-substituted BODIPY **4i**, β-formylation resulted in a 12 nm blueshift of the absorption and a 4 nm redshift of the emission maxima in BODIPY **5i**, whereas the *meso*,β-diformylation gave absorption and emission spectra in BODIPY **6** similar to those of the starting BODIPY **4i**. In comparison with the starting BODIPYs **4**, formylation had little effect on the fluorescence quantum yields of the resulting formylated BODIPYs **3d**, **5** and **6**, except for the α-monoformylated BODIPYs **3a**,**b**, which gave enhanced fluorescence quantum yields, as summarized in Table 2.

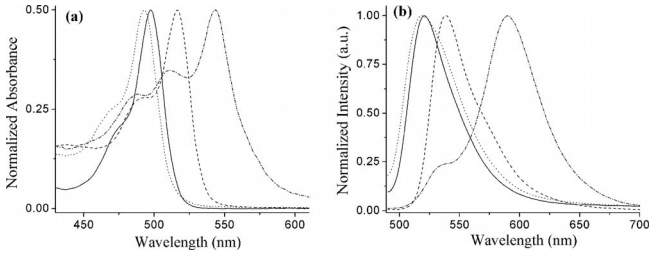


Figure 5. Normalized UV/Vis absorption (a) and normalized fluorescence emission (b) spectra of BODIPYs **4b** (solid line), **3b** (dashed line), **5b** (dotted line) and **3d** (dash-dotted line) in CH_2Cl_2.

Conclusions

We have developed a regioselective formylation of pyrrole-unsubstituted dipyrromethanes and BODIPY dyes at the α- and β-positions, as well as an interesting *meso*,β-diformylation reaction for the preparation of some *meso*,β-diformylated BODIPYs. The high regioselectivity of this formylation procedure offers a new way to synthesize different kinds of α- and β-substituted BODIPY dyes. This formylation affected the photophysical properties of the BODIPY chromophore, leading to a redshift in both the absorption and emission spectra in the resulting α-formylated and α,α-diformylated BODIPYs **3a**,**b** and **3d**, and a slight blueshift in the β-formylated BODIPYs **5**. Extending the high regioselectivity of this formylation reaction to the other electrophilic substitution reactions, such as the halogenation reaction, is currently underway in our laboratory.

Experimental Section

General Procedure for the Preparation of the Mono-α-formylated BODIPYs 3a–b: DDQ (150 mg, 0.66 mmol) was slowly added to a round-bottomed flask containing α-formyldipyrromethane **2a**,**b**[27] (0.6 mmol) in CH_2Cl_2 (20 mL) cooled on an ice bath. The reaction mixture was stirred at this temperature for 20 min before triethyl-

amine (0.6 mL) and BF_3·Et_2O (0.6 mL) were quickly added to the reaction mixture. The reaction was further stirred at room temperature for 15 min and extracted with CH_2Cl_2 (3× 40 mL). The organic layers were combined, washed with water (2× 100 mL), dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was further purified by column chromatography on silica gel using dichloromethane as the eluent to give the desired α-formylated BODIPYs as reddish powders.

BODIPY 3a: Compound **2a** (150 mg, 0.6 mmol) was used for this reaction to give BODIPY **3a** in 14% yield (25 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.39 (s, 1 H, CHO), 8.24 (s, 1 H, py), 7.64–7.52 (m, 5 H, ph), 7.16 (s, 1 H, py), 7.10 (s, 1 H, py), 6.87 (s, 1 H, py), 6.75 (s, 1 H, py) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 184.3, 150.1, 149.2, 147.7, 137.0, 136.7, 135.2, 133.2, 131.5, 130.6, 128.7, 121.8, 118.3 ppm. HRMS (EI): calcd. for $C_{16}H_{11}BF_2N_2O$ $[M]^+$ 296.0932; found 296.0936.

BODIPY 3b: Compound **2b** (168 mg, 0.6 mmol) was used for this reaction to give BODIPY **3b** in 16% yield (32 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.39 (s, 1 H, CHO), 8.19 (s, 1 H, py), 7.57 (d, J = 7.8 Hz, 2 H, ph), 7.19 (s, 1 H), 7.11–7.08 (m, 3 H, ph, py), 6.91 (s, 1 H, py), 6.74 (s, 1 H, py), 3.94 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 184.4, 162.8, 149.2, 149.0, 147.2, 136.7, 134.9, 132.8, 128.4, 125.8, 121.5, 118.1, 114.4, 55.7 ppm. HRMS (EI): calcd. for $C_{17}H_{13}BF_2N_2O_2$ $[M]^+$ 326.1038; found 326.1031.

Preparation of the α,α-Diformylated BODIPY 3d: The key synthetic precursor **2d** for **3d** was prepared according to the literature,[27] and was directly used for subsequent oxidation and complexation reactions. DDQ (250 mg, 1.1 mmol) in CH_2Cl_2 (10 mL) was added to a round-bottomed flask containing **2d** (308 mg, 1.0 mmol) in CH_2Cl_2 (60 mL) cooled in an ice bath. The reaction mixture was stirred at this temperature for 30 min, then triethylamine (2.0 mL) and BF_3·Et_2O (3.0 mL) were quickly added. The reaction mixture was further stirred at room temperature for an additional 30 min, poured into water (100 mL) and extracted with CH_2Cl_2 (3× 50 mL). The organic layers were combined, dried with anhydrous Na_2SO_4, and the solvent was removed under vacuum. The crude product was further purified by column chromatography (silica gel, CH_2Cl_2/hexane = 3:1, v/v) to give **3d** as a green powder (21%, 75 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.48 (s, 2 H, CHO), 7.63 (d, J = 8.1 Hz, 2 H, ph), 7.21 (s, 2 H, py), 7.14 (d, J = 5.4 Hz, 4 H, ph), 3.97 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 184.3, 163.7, 150.4, 137.6, 133.5, 132.4, 125.9, 119.9, 114.8, 55.8 ppm. HRMS (EI): calcd. for $C_{18}H_{13}BF_2N_2O_3$ $[M]^+$ 354.0987; found 354.0985.

General Procedure for the Preparation of Starting BODIPYs 4: BODIPYs **4** were prepared in a one-pot, two-step synthetic procedure from dipyrromethanes prepared according to the literature.[25] This involved DDQ oxidation of the dipyrromethanes and BF_3 complexation of the resultant dipyrromethenes. DDQ (454 mg, 2.0 mmol) in CH_2Cl_2 (10 mL) was added to a round-bottomed flask containing the dipyrromethane (2.0 mmol) in CH_2Cl_2 (40 mL) cooled in an ice bath. The reaction mixture was stirred at this temperature for 10 min, then triethylamine (4 mL) and BF_3·Et_2O (4 mL) were quickly added to the reaction mixture. The reaction mixture was further stirred at room temperature for 2 h, washed with water (50 mL), a 0.2 M aqueous solution of NaOH (100 mL), and water (50 mL). The organic layer was collected, dried with anhydrous $NaSO_4$, and the solvent was removed under vacuum. The crude product was further purified by column chromatography on silica gel using a mixture of dichloromethane and hexane as the eluent to give the desired BODIPYs **4** as powders.

BODIPY 4c: The general procedure was applied with 4-bromobenzaldehyde (368 mg, 2.0 mmol) as the aromatic aldehyde. Final purification was performed by column chromatography on silica gel (CH_2Cl_2/hexane = 1:2, v/v) to give BODIPY **4c** (430 mg, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (s, 2 H, py), 7.68 (s, 2 H, ph), 7.45 (s, 2 H, ph), 6.91 (s, 2 H, py), 6.56 (s, 2 H, py) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.8, 144.6, 134.7, 132.6, 131.8, 131.3, 125.5, 118.9 ppm. HRMS (EI): calcd. for $C_{15}H_{10}BBrF_2N_2$ $[M]^+$ 346.0088; found 346.0093.

BODIPY 4e: The general procedure was applied with 4-chlorobenzaldehyde (280 mg, 2.0 mmol) as the aromatic aldehyde. Final purification was performed by column chromatography on silica gel (CH_2Cl_2/hexane = 1:2, v/v) to give BODIPY **4e** as a greenish powder (364 mg, 60% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (s, 2 H, py), 7.53 (s, 4 H, ph), 6.92 (s, 2 H, py), 6.57 (s, 2 H, py) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.8, 143.5, 136.2, 133.7, 131.1, 130.7, 130.3, 127.9, 117.8 ppm. HRMS (EI): calcd. for $C_{15}H_{10}BClF_2N_2$ $[M]^+$ 302.0594; found 302.0590.

BODIPY 4f: The general procedure was applied with 2,6-dichlorobenzaldehyde (348 mg, 2.0 mmol) as the aromatic aldehyde. Final purification was performed by column chromatography on silica gel (CH_2Cl_2/hexane = 1:2, v/v) to give BODIPY **4f** (343 mg, 43%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (s, 2 H, py), 7.53–7.41 (m, 3 H, ph), 6.71 (d, J = 3.9 Hz, 2 H, py), 6.52 (d, J = 3.6 Hz, 2 H, py) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.4, 140.7, 135.1, 134.8, 131.3, 130.0, 128.3, 119.1 ppm. HRMS (EI): calcd. for $C_{15}H_9BCl_2F_2N_2$ $[M]^+$ 336.0204; found 336.0203.

BODIPY 4i: The general procedure was applied with *p*-(dimethylamino)benzaldehyde (298 mg, 2.0 mmol) as the aromatic aldehyde. Final purification was performed by column chromatography on silica gel (CH_2Cl_2/hexane = 1:1, v/v) to give BODIPY **4i** (131 mg, 21%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (s, 2 H, py), 7.57 (d, J = 7.8 Hz, 2 H, ph), 7.04 (s, 2 H, py), 6.81 (d, J = 7.8 Hz, 2 H, ph), 6.54 (s, 2 H, py), 3.11 (s, 6 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.6, 148.5, 141.7, 134.5, 133.1, 130.8, 121.8, 117.6, 111.5, 40.1 ppm. HRMS (EI): calcd. for $C_{17}H_{16}BF_2N_3$ $[M]^+$ 311.1405; found 311.1403.

General Procedure for the Preparation of BODIPYs 5: A mixture of DMF (3 mL, 39 mmol) and $POCl_3$ (3 mL, 32 mmol) was cooled in an ice bath and stirred under argon for 5 min. After warming to room temperature, the reaction mixture was further stirred for 30 min. Then, BODIPY **4** (0.2 mmol) in $ClCH_2CH_2Cl$ (10 mL) was added to the reaction mixture. After raising the temperature to 80 °C, the reaction mixture was further stirred for 10 h, cooled to room temperature and slowly poured into a saturated aqueous solution of K_2CO_3 (200 mL) cooled in an ice bath. After warming to room temperature, the reaction mixture was further stirred for 1 h and extracted with CH_2Cl_2 (3× 100 mL). The organic layers were combined, washed with water (2× 100 mL), dried with anhydrous $NaSO_4$, and the solvent was removed under reduced pressure. The crude product was further purified by gel column chromatography on silica gel using a mixture of dichloromethane (or ethyl acetate) and hexane as the eluent to give the β-formylated BODIPYs **5** as reddish-brown powders.

BODIPY 5a: BODIPY **4a** (65 mg, 0.24 mmol) was used as the starting material. Final purification was performed by column chromatography on silica gel (CH_2Cl_2/hexane = 1:1, v/v) to give BODIPY **5a** (54 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.79 (s, 1 H, CHO), 8.21 (s, 1 H, py), 8.11 (s, 1 H, py), 7.56–7.51 (m, 5 H, ph), 7.24 (s, 1 H, py), 7.09 (s, 1 H, py), 6.66 (s, 1 H, py) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 184.9, 149.5, 142.9, 137.0, 135.0,

134.7, 132.9, 131.8, 131.6, 130.5, 128.8, 128.7, 121.5 ppm. HRMS (EI): calcd. for $C_{16}H_{11}BF_2N_2O$ $[M]^+$ 296.0932; found 296.0926.

BODIPY 5b: BODIPY **4b** (60 mg, 0.20 mmol) was used as the starting material. Final purification was performed by column chromatography on silica gel (CH_2Cl_2/hexane = 3:2, v/v) to give BODIPY **5b** (49 mg, 75%). ^1H NMR (300 MHz, $CDCl_3$): δ = 9.88 (s, 1 H, CHO), 8.27 (s, 1 H, py), 8.15 (s, 1 H, py), 7.60 (d, J = 7.8 Hz, 2 H, ph), 7.37 (s, 1 H, py), 7.20 (s, 1 H, py), 7.11 (d, J = 8.1 Hz, 2 H, ph), 6.73 (s, 1 H, py), 3.94 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.9, 148.6, 147.4, 141.5, 135.7, 133.6, 131.7, 130.7, 129.5, 127.8, 127.3, 124.5, 120.1, 113.5, 54.6 ppm. HRMS (EI): calcd. for $C_{17}H_{13}BF_2N_2O_2$ $[M]^+$ 326.1038; found 326.1034.

BODIPY 5c: BODIPY **4c** (60 mg, 0.17 mmol) was used as the starting material. Final purification was performed by column chromatography on silica gel (CH_2Cl_2/hexane = 1:1, v/v) to give BODIPY **5b** (46 mg, 71%). ^1H NMR (300 MHz, $CDCl_3$): δ = 9.87 (s, 1 H, CHO), 8.30 (s, 1 H, py), 8.20 (s, 1 H, py), 7.75 (d, J = 8.4 Hz, 2 H, ph), 7.49 (d, J = 8.4 Hz, 2 H, ph), 7.29 (s, 1 H, py), 7.15 (d, J = 4.5 Hz, 1 H, py), 6.76 (d, J = 4.2 Hz, 1 H, py) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 183.8, 148.9, 146.9, 142.2, 135.7, 133.6, 133.2, 131.2, 130.8, 130.6, 127.4, 125.5, 120.8, 113.7 ppm. HRMS (EI): calcd. for $C_{16}H_{11}BBrF_2N_2O$ $[M + H]^+$ 374.0038; found 374.0032.

BODIPY 5d: BODIPY **4d** (60 mg, 0.19 mmol) was used as the starting material. Final purification was performed by column chromatography on silica gel (CH_2Cl_2/hexane = 3:2, v/v) to give BODIPY **5d** (35 mg, 54%). ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 9.84 (s, 1 H, CHO), 8.63 (s, 2 H, py), 8.44 (s, 2 H, ph), 8.02 (s, 2 H, ph), 7.32 (s, 2 H, py), 6.96 (s, 1 H, py) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 186.3, 153.0, 149.5, 146.3, 144.3, 138.7, 137.0, 136.0, 134.0, 132.6, 128.6, 124.3, 123.7, 110.4 ppm. HRMS (EI): calcd. for $C_{16}H_{10}BF_2N_3O_3$ $[M]^+$ 341.0783; found 341.0775.

BODIPY 5e: BODIPY **4e** (60 mg, 0.20 mmol) was used as the starting material. Final purification was performed by column chromatography on silica gel (CH_2Cl_2/hexane = 1:1, v/v) to give BODIPY **5e** (45 mg, 69%). ^1H NMR (300 MHz, $CDCl_3$): δ = 9.87 (s, 1 H, CHO), 8.30 (s, 1 H, py), 8.20 (s, 1 H, py), 7.60–7.53 (m, 4 H, ph), 7.29 (s, 1 H, py), 7.15 (d, J = 4.4 Hz, 1 H, py), 6.75 (d, J = 4.4 Hz, 1 H, py) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 184.8, 149.9, 147.9, 143.2, 138.2, 136.8, 134.7, 134.3, 131.8, 131.7, 131.2, 129.3, 128.5, 121.9 ppm. HRMS (EI): calcd. for $C_{16}H_{10}BClF_2N_2O$ $[M]^+$ 330.0455; found 330.0437.

BODIPY 5f: BODIPY **4f** (60 mg, 0.18 mmol) was used as the starting material. Final purification was performed by column chromatography on silica gel (CH_2Cl_2/hexane = 3:2, v/v) to give BODIPY **5f** (47 mg, 72%). ^1H NMR (300 MHz, $CDCl_3$): δ = 9.84 (s, 1 H, CHO), 8.29 (s, 1 H, py), 8.23 (s, 1 H, py), 7.53–7.49 (m, 3 H, ph), 7.06 (s, 1 H, py), 6.95 (d, J = 4.5 Hz, 1 H, py), 6.72 (d, J = 4.5 Hz, 1 H, py) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 184.7, 151.4, 143.6, 142.9, 137.5, 134.9, 133.9, 133.4, 131.8, 130.2, 128.4, 126.8, 122.3 ppm. HRMS (EI): calcd. for $C_{16}H_9BCl_2F_2N_2O$ $[M]^+$ 364.0153; found 364.0156.

BODIPY 5g: BODIPY **4g** (60 mg, 0.22 mmol) was used as the starting material. Final purification was performed by column chromatography on silica gel (CH_2Cl_2/hexane = 3:2, v/v) to give BODIPY **5g** (45 mg, 68%). ^1H NMR (300 MHz, $CDCl_3$): δ = 9.90 (s, 1 H, CHO), 8.28 (s, 1 H, py), 8.16 (s, 1 H, py), 7.84 (d, J = 4.1 Hz, 1 H, th), 7.66 (s, 2 H, py), 7.49 (s, 1 H, th), 7.34 (s, 1 H, th), 6.77 (s, 1 H, py) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 185.0, 148.9, 142.7, 141.6, 136.2, 134.8, 134.2, 133.9, 133.7, 133.2, 131.7, 128.9, 128.6, 121.5 ppm. HRMS (EI): calcd. for $C_{14}H_9BF_2N_2OS$ $[M]^+$ 302.0497; found 302.0490.

BODIPY 5h: BODIPY **4h** (50 mg, 0.16 mmol) was used as the starting material. Final purification was performed by column chromatography on silica gel (CH_2Cl_2/hexane = 1:2, v/v) to give BODIPY **5h** (44 mg, 81%). ^1H NMR (300 MHz, $CDCl_3$): δ = 9.74 (s, 1 H, CHO), 8.18 (s, 1 H, py), 8.09 (s, 1 H, py), 6.96–6.85 (m, 4 H, ph and py), 6.59 (s, 1 H, py), 2.30 (s, 3 H, CH_3), 2.02 (s, 6 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 183.8, 148.9, 141.9, 138.6, 136.8, 136.7, 135.1, 132.6, 130.8, 130.7, 127.6, 127.4, 126.2, 120.6, 20.1, 18.9 ppm. HRMS (EI): calcd. for $C_{19}H_{17}BF_2N_2O$ $[M]^+$ 338.1402; found 338.1408.

BODIPY 5i: A mixture of DMF (0.5 mL, 6.5 mmol) and $POCl_3$ (0.45 mL, 4.8 mmol) was cooled in an ice bath and stirred under argon for 5 min. After warming to room temperature, the reaction mixture was further stirred for 30 min. BODIPY **4i** (50 mg, 0.16 mmol) in $ClCH_2CH_2Cl$ (10 mL) was added to this reaction mixture. After the temperature had been raised to 60 °C, the reaction mixture was further stirred for 10 h. Workup was performed by applying the general procedure described for the preparation of BODIPYs **5**. The crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:2, v/v) to give BODIPY **5i** as a reddish-brown powder (38 mg, 70%). ^1H NMR (300 MHz, $CDCl_3$): δ = 9.87 (s, 1 H, CHO), 8.21 (s, 1 H, py), 8.04 (s, 1 H, py), 7.60–7.57 (m, 2 H, ph), 7.41 (s, 1 H, py), 7.23 (s, 1 H, py), 6.84 (d, J = 8.2 Hz, 2 H, ph), 6.69 (s, 1 H, py), 3.14 (s, 6 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 185.2, 153.3, 150.2, 145.6, 141.3, 135.8, 134.5, 133.7, 131.4, 127.3, 121.3, 120.0, 111.9, 40.2 ppm. HRMS (EI): calcd. for $C_{18}H_{16}BF_2N_3O$ $[M]^+$ 339.1354; found 339.1345.

BODIPY 6: The general procedure was applied with the requirement for an excess amount of the Vilsmeier reagents: a mixture of DMF (3 mL, 39 mmol) and $POCl_3$ (3 mL, 32 mmol) was used for the formylation of BODIPY **4i** (40 mg, 0.13 mmol). Final purification was performed by column chromatography on silica gel (EtOAc/hexane = 4:3, v/v) to give BODIPY **6** as a reddish-brown powder (27 mg, 57% yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 10.11 (s, 1 H, CHO), 9.89 (s, 1 H, CHO), 8.27 (s, 1 H, py), 8.14 (s, 1 H, py), 7.99 (d, J = 2.4 Hz, 1 H, py), 7.73 (dd, J = 8.7 Hz, 1 H, ph), 7.36 (s, 1 H, ph), 7.22 (d, J = 4.5 Hz, 1 H, py), 7.16 (d, J = 8.7 Hz, 1 H, ph), 6.75 (d, J = 3.9 Hz, 1 H, py), 3.16 (s, 6 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.0, 185.0, 156.2, 148.5, 148.0, 142.4, 136.7, 136.6 (7), 136.4, 134.1, 131.6, 127.6, 124.4, 124.3 (8), 123.0, 121.2, 121.1, 116.9, 44.7 ppm. HRMS (EI): calcd. for $C_{19}H_{16}BN_3O_2$ $[M]^+$ 367.1304; found 367.1309.

Supporting Information (see footnote on the first page of this article): General methods, molecular modeling, X-ray analysis, copies of ^1H and ^{13}C NMR and HR mass spectra for all new compounds.

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[1] a) A. Loudet, K. Burgess, *Chem. Rev.* **2007**, *107*, 4891; b) G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem.* **2008**, *120*,

1202; *Angew. Chem. Int. Ed.* **2008**, *47*, 1184; c) R. Ziessel, G. Ulrich, A. Harriman, *New J. Chem.* **2007**, *31*, 496.

[2] a) Q. Zheng, G. Xu, P. N. Prasad, *Chem. Eur. J.* **2010**, *16*, 5812; b) E. Y. Schmidt, B. A. Trofimov, A. I. Mikhaleva, N. V. Zorina, N. I. Protzuk, K. B. Petrushenko, I. A. Ushakov, M. Y. Dvorko, R. Méallet-Renault, G. Clavier, T. T. Vu, H. T. T. Tran, R. B. Pansu, *Chem. Eur. J.* **2009**, *15*, 5823; c) C. Peters, A. Billich, M. Ghobrial, K. Hoegenauer, T. Ullrich, P. Nussbaumer, *J. Org. Chem.* **2007**, *72*, 1842; d) Z. Li, R. Bittman, *J. Org. Chem.* **2007**, *72*, 8376; e) R. West, C. Panagabko, J. Atkinson, *J. Org. Chem.* **2010**, *75*, 2883.

[3] a) O. A. Bozdemir, R. Guliyev, O. Buyukcakir, S. Selcuk, S. Kolemen, G. Gulseren, T. Nalbantoglu, H. Boyaci, E. U. Akkaya, *J. Am. Chem. Soc.* **2010**, *132*, 8029; b) A. O. Bozdemir, F. Sozmen, O. Buyukcakir, R. Guliyev, Y. Cakmak, E. U. Akkaya, *Org. Lett.* **2010**, *12*, 1400; c) H. Sunahara, Y. Urano, H. Kojima, T. Nagano, *J. Am. Chem. Soc.* **2007**, *129*, 5597; d) L. Zeng, E. W. Miller, A. Pralle, E. Y. Isacoff, C. J. Chang, *J. Am. Chem. Soc.* **2006**, *128*, 10; e) K. Yamada, Y. Nomura, D. Citterio, N. Iwasawa, K. Suzuki, *J. Am. Chem. Soc.* **2005**, *127*, 6956; f) M. Baruah, W. Qin, N. Basarić, W. M. Borggraeve, N. Boëns, *J. Org. Chem.* **2005**, *70*, 4152; g) S. Yin, V. Leen, S. V. Snick, N. Boëns, W. Dehaen, *Chem. Commun.* **2010**, *46*, 6329; h) T. W. Hudnall, F. P. Gabbai, *Chem. Commun.* **2008**, 4596; i) K. Krumova, P. Oleynik, P. Karam, G. Cosa, *J. Org. Chem.* **2009**, *74*, 3641; j) R. Ziessel, L. Bonardi, P. Retailleau, G. Ulrich, *J. Org. Chem.* **2006**, *71*, 3093.

[4] a) M. Yuan, W. Zhou, X. Liu, M. Zhu, J. Li, X. Yin, H. Zheng, Z. Zuo, C. Ouyang, H. Liu, Y. Li, D. Zhu, *J. Org. Chem.* **2008**, *73*, 5008; b) T. Cheng, Y. Xu, S. Zhang, W. Zhu, X. Qian, L. Duan, *J. Am. Chem. Soc.* **2008**, *130*, 16160; c) J. Wang, X. Qian, *Org. Lett.* **2006**, *8*, 3721; d) X. Peng, J. Du, J. Fan, J. Wang, Y. Wu, J. Zhao, S. Sun, T. Xu, *J. Am. Chem. Soc.* **2007**, *129*, 1500; e) L. Jiao, J. Li, S. Zhang, C. Wei, E. Hao, M. G. H. Vicente, *New J. Chem.* **2009**, *33*, 1888.

[5] For examples of modifications of the BODIPY core with aryl, vinyl, styryl and arylethynyl substituents, see: a) T. Rohand, M. Baruah, W. Qin, N. Boëns, W. Dehaen, *Chem. Commun.* **2006**, 266; b) T. Rohand, W. Qin, N. Boëns, W. Dehaen, *Eur. J. Org. Chem.* **2006**, 4658; c) V. Leen, E. Braeken, K. Luckermans, C. Jackers, M. Auweraer, N. Boëns, W. Dehaen, *Chem. Commun.* **2009**, 4515; d) L. Li, B. Nguyen, K. Burgess, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 3112; e) D. Zhang, Y. Wen, Y. Xiao, G. Yu, Y. Liu, X. Qian, *Chem. Commun.* **2008**, 4777; f) J. Han, O. Gonzalez, A. Aguilar-Aguilar, E. Peña-Cabrera, K. Burgess, *Org. Biomol. Chem.* **2009**, *7*, 34; g) L. Jiao, C. Yu, T. Uppal, M. Liu, Y. Li, Y. Zhou, E. Hao, X. Hu, M. G. H. Vicente, *Org. Biomol. Chem.* **2010**, *8*, 2517.

[6] For examples of modifications of the BODIPY core by means of Knoevenagel condensation reactions, see: a) K. Rurack, M. Kollmannsberger, J. Daub, *Angew. Chem.* **2001**, *113*, 396; *Angew. Chem. Int. Ed.* **2001**, *40*, 385; b) O. Buyukcakir, O. A. Bozdemir, S. Kolemen, S. Erbas, E. U. Akkaya, *Org. Lett.* **2009**, *11*, 4644; c) M. Baruah, W. Qin, C. Flors, J. Hofkens, R. A. L. Vallée, D. Beljonne, M. van der Auweraer, W. M. D. Borggraeve, N. Boëns, *J. Phys. Chem. A* **2006**, *110*, 5998.

[7] For examples of modifications of the BODIPY core with a rigid ring system, see: a) Y.-W. Wang, A. B. Descalzo, Z. Shen, X.-Z. You, K. Rurack, *Chem. Eur. J.* **2010**, *16*, 2887; b) A. B. Descalzo, H.-J. Xu, Z.-L. Xue, K. Hoffmann, Z. Shen, M. G. Weller, X.-Z. You, K. Rurack, *Org. Lett.* **2008**, *10*, 1581; c) Z. Shen, H. Röhr, K. Rurack, H. Uno, M. Spieles, B. Schulz, G. Reck, N. Ono, *Chem. Eur. J.* **2004**, *10*, 4853; d) J. Chen, A. Burghart, A. Derecskei-Kovacs, K. Burgess, *J. Org. Chem.* **2000**, *65*, 2900; e) K. Tan, L. Jaquinod, R. Paolesse, S. Nardis, C. Natale, A. Carlo, L. Prodi, M. Montalti, N. Zaccheroni, K. M. Smith, *Tetrahedron* **2004**, *60*, 1099; f) L. Jiao, C. Yu, J. Li, Z. Wang, M. Wu, E. Hao, *J. Org. Chem.* **2010**, *75*, 6035.

[8] a) W. Zhao, E. M. Carreira, *Angew. Chem.* **2005**, *117*, 1705; *Angew. Chem. Int. Ed.* **2005**, *44*, 1677; b) S. Goeb, R. Ziessel, *Org. Lett.* **2007**, *9*, 737; c) K. Umezawa, Y. Nakamura, H. Makino, D. Citterio, K. Suzuki, *J. Am. Chem. Soc.* **2008**, *130*, 1550; d) K. Umezawa, A. Matsui, Y. Nakamura, D. Citterio, K. Suzuki, *Chem. Eur. J.* **2009**, *15*, 1096.

[9] a) J. Bañuelos-Prieto1, A. R. Agarrabeitia, I. Garcia-Moreno, I. Lopez-Arbeloa1, A. Costela, L. Infantes, M. E. Perez-Ojeda, M. Palacios-Cuesta, M. J. Ortiz, *Chem. Eur. J.* **2010**, *16*, 140964; b) S. Mula, A. K. Ray, M. Banerjee, T. Chaudhuri, K. Dasgupta, S. Chattopadhyay, *J. Org. Chem.* **2008**, *73*, 2146.

[10] a) T. Yogo, Y. Urano, Y. Ishitsuka, F. Maniwa, T. Nagano, *J. Am. Chem. Soc.* **2005**, *127*, 12162; b) A. Gorman, J. Killoran, C. O'Shea, T. Kenna, W. M. Gallagher, D. F. O'Shea, *J. Am. Chem. Soc.* **2004**, *126*, 10619; c) S. Atilgan, Z. Ekmekci, A. L. Dogan, D. Guc, E. U. Akkaya, *Chem. Commun.* **2006**, 4398; d) S. H. Lim, C. Thivierge, P. Nowak-Sliwinska, J. Han, H. Bergh, G. Wagnieres, K. Burgess, H. B. Lee, *J. Med. Chem.* **2010**, *53*, 2865.

[11] a) S. Ertan-Ela, M. D. Yilmaz, B. Icli, Y. Dede, S. Icli, E. U. Akkaya, *Org. Lett.* **2008**, *10*, 3299; b) T. Rousseau, A. Cravino, T. Bura, G. Ulrich, R. Ziessel, J. Roncali, *Chem. Commun.* **2009**, 1673; c) D. Collado, J. Casado, S. R. González, J. T. L. Navarrete, R. Suau, E. Perez-Inestrosa, T. M. Pappenfus, M. M. M. Raposo, *Chem. Eur. J.* **2011**, *17*, 498.

[12] a) A. Harriman, R. Ziessel, *Chem. Commun.* **2011**, *47*, 611; b) Z. Gu, D. Guo, M. Sun, Y. Liu, *J. Org. Chem.* **2010**, *75*, 3600; c) A. C. Benniston, G. Copley, A. Harriman, D. Howgego, R. W. Harrington, W. Clegg, *J. Org. Chem.* **2010**, *75*, 2018; d) J.-Y. Shin, T. Tanaka, A. Osuka, Q. Miao, D. Dolphin, *Chem. Eur. J.* **2009**, *15*, 12955.

[13] a) M. D. Yilmaz, O. A. Bozdemir, E. U. Akkaya, *Org. Lett.* **2006**, *8*, 2871; b) M. Yuan, X. Yin, H. Zheng, C. Ouyang, Z. Zuo, H. Liu, Y. Li, *Chem. Asian J.* **2009**, *4*, 707; c) S. Zrig, P. Rémy, B. Andrioletti, E. Rose, I. Asselberghs, K. Clays, *J. Org. Chem.* **2008**, *73*, 1563; d) I. Pochorovski, B. Breiten, W. B. Schweizer, F. Diederich, *Chem. Eur. J.* **2010**, *16*, 12590.

[14] G. Ulrich, C. Goeze, M. Guardigli, A. Roda, R. Ziessel, *Angew. Chem.* **2005**, *117*, 3760; *Angew. Chem. Int. Ed.* **2005**, *44*, 3694.

[15] a) G. Sathyamoorthi, L. T. Wolford, A. M. Haag, J. H. Boyer, *Heteroat. Chem.* **1994**, *5*, 245; b) A. Haefele, C. Zedde, P. Retailleau, G. Ulrich, R. Ziessel, *Org. Lett.* **2010**, *12*, 1672.

[16] L. Li, J. Han, B. Nguyen, K. Burgess, *J. Org. Chem.* **2008**, *73*, 1963.

[17] M. Shah, K. Thangaraj, M.-L. Soong, L. T. Wolford, J. H. Boyer, I. R. Politzer, T. G. Pavlopoulos, *Heteroat. Chem.* **1993**, *4*, 39.

[18] C. Thivierge, R. Bandichhor, K. Burgess, *Org. Lett.* **2007**, *9*, 2135.

[19] L. Jiao, C. Yu, J. Li, Z. Wang, M. Wu, E. Hao, *J. Org. Chem.* **2009**, *74*, 7525.

[20] S. Kolemen, Y. Cakmak, S. Erten-Ela, Y. Altay, J. Brendel, M. Thelakkat, E. U. Akkaya, *Org. Lett.* **2010**, *12*, 3812.

[21] a) J. Chen, M. Mizumura, H. Shinokubo, A. Osuka, *Chem. Eur. J.* **2009**, *15*, 5942; b) V. Leen, V. Zaragozi Gonzalvo, W. M. Deborggraeve, N. Boëns, W. Dehaen, *Chem. Commun.* **2010**, *46*, 4908; c) V. Leen, M. V. Auweraer, N. Boëns, W. Dehaen, *Org. Lett.* **2011**, *13*, 1470.

[22] S. Madhu, M. R. Rao, M. S. Shaikh, M. Ravikanth, *Inorg. Chem.* **2011**, DOI: 10.1021/ic102499h.

[23] a) D. Wang, J. Fan, X. Gao, B. Wang, S. Sun, X. Peng, *J. Org. Chem.* **2009**, *74*, 7675; b) A. Cui, X. Peng, J. Fan, X. Chen, Y. Wu, B. Guo, *J. Photochem. Photobiol. A: Chem.* **2007**, *186*, 85.

[24] a) B. J. Littler, M. A. Miller, C.-H. Hung, R. W. Wagner, D. F. O'Shea, P. D. Boyle, J. S. Lindsey, *J. Org. Chem.* **1999**, *64*, 1391; b) H. L. Kee, C. Kirmaier, L. Yu, P. Thamyongkit, W. J. Youngblood, M. E. Calder, L. Ramos, B. C. Noll, D. F. Bocian, R. Scheidt, R. R. Birge, J. S. Lindsey, D. Holten, *J. Phys. Chem. B* **2005**, *109*, 20433; c) P. Thamyongkit, A. D. Bhise, M. Taniguchi, J. S. Lindsey, *J. Org. Chem.* **2006**, *71*, 903.

[25] T. Rohand, E. Dolusic, T. H. Ngo, W. Maes, W. Dehaen, *ARKIVOC* **2007**, *x*, 307.

[26] a) I. J. Arroyo, R. Hu, G. Merino, B. Z. Tang, E. Peña-Cabrera, *J. Org. Chem.* **2009**, *74*, 5719; b) E. Lager, J. Liu, A. Aguilar-Aguilar, B. Z. Tang, E. Peña-Cabrera, *J. Org. Chem.* **2009**, *74*, 2053; c) E. Peña-Cabrera, A. Aguilar-Aguilar, M. Gonzalez-Dominguez, E. Lager, R. Zamudio-Vazquez, J. Godoy-Vargas, F. Villanueva-Garcia, *Org. Lett.* **2007**, *9*, 3985; d) A. C. F. Gómez-Durán, I. García-Moreno, A. Costela, V. Martin, R. Sastre, J. Bañuelos, F. L. Arbeloa, I. L. Arbeloa, E. Peña-Cabrera, *Chem. Commun.* **2010**, *46*, 5103; e) K. Kim, C. Jo, S. Easwaramoorthi, J. Sung, D. H. Kim, D. G. Churchill, *Inorg. Chem.* **2010**, *49*, 4881.

[27] a) R. G. Khoury, L. Jaquinod, K. Aoyagi, M. M. Olmstead, A. J. Fisher, K. M. Smith, *Angew. Chem.* **1997**, *109*, 2604; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2497; b) A. Wickramasinghe, L. Jaquinod, D. J. Nocera, K. M. Smith, *Tetrahedron* **2001**, *57*, 426; c) C. Bruckner, J. J. Posakony, C. K. Johnson, R. S. Boyle, B. R. James, D. Dolphin, *J. Porphyrins Phthalocyanines* **1998**, *2*, 455.

[28] Y. Zhou, Y. Xiao, D. Li, M. Fu, X. Qian, *J. Org. Chem.* **2008**, *73*, 1571.

[29] a) O. Meth-Cohn, D. Taylor, *J. Chem. Soc., Chem. Commun.* **1995**, 1463; b) Y. Cheng, O. Meth-Cohn, D. Taylor, *J. Chem. Soc. Perkin Trans. 1* **1998**, 1257; c) Y. Cheng, B. Wang, O. Meth-Cohn, *Synthesis* **2003**, 2839.

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