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ORIGINAL ARTICLE

Methylated Unsymmetric BODIPY Compounds: Synthesis, High Fluorescence Quantum Yield and Long Fluorescence Time

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Abstract

We show that unsymmetric BODIPY compounds with one, two, and three methyl groups can be synthesized easily and efficiently by the unsymmetric reaction method. Their steady state and time-resolved fluorescence properties are examined in solvents of different polarity. These compounds show high fluorescence quantum yields (0.87 to 1.0), long fluorescence lifetimes (5.89 to 7.40 ns), and small Stokes shift (199 to 443 cm^{-1}). The methyl substitution exhibits influence on the UV-Vis absorption and fluorescence properties, such as the blue shift in emission and absorption spectra. It is the number rather than the position of methyls that play major roles. Except for 3 M-BDP, the increase in the number of methyls on BODIPY core leads to the increase in both fluorescence quantum yield and radiative rate constant, but causes the decrease in fluorescence lifetime. H-bonding solvents increase both the fluorescence lifetime and quantum yields. The methylated BODIPYs show the ability to generate singlet oxygen ($^1\Delta_g$) which is evidenced by near-IR luminescence and DPBF chemical trapping techniques. The formation quantum yield of singlet oxygen ($^1\Delta_g$) for the compounds is up to 0.15 ± 0.05.

Keywords Unsymmetric BODIPY · Fluorescence · Synthesis · Absorption · Methyl substitution

Introduction

BODIPY compounds are widely studied and have been applied in chemistry, biology, medical and materials sciences [1–7]. A large number of substituted BODIPYs, mainly symmetrical ones, have been synthesized and extensively explored [1–3], after they were first discovered by Treibs and Kreuzer in 1968 [8]. In spite of this, the core BODIPY (BDP in Scheme 1) was not reported until 2009 due to the difficulty in its synthesis [9–11]. The mono-, di-, and tri-methyl substituted BODIPYs (Scheme 1) are among the most similar to BDP and could be considered as the references to those containing BODIPY core as a whole or sub-functional unit. Only a few of methyl substituted BODIPYs has been reported so far due to their unsymmetric nature [1–3, 12]. The synthetic method for unsymmetric BODIPYs is different from that of symmetric ones (Scheme 1) and presents more challenges. On the other hand, the methyl substituted BODIPYs have some particular applications, such as the starting materials of Knoevenagel condensation to attach an alkenyl unit and selective lateral lithiation for linking an electrophile (Scheme 2) [13–15].

The unsymmetric synthetic method for BODIPYs needs two different pyrroles and one of them must have a –CHO or a –COCl group (Scheme 1). The symmetric method, however, requires only one pyrrole (Scheme 1). Compound BDP and 8 M-BDP can be prepared by either an unsymmetric or a symmetric method. The usage of the symmetric method in BODIPY synthesis is enormous in literature [3, 12] but that of the unsymmetric method is rare and still not well developed. Compound 3 M-BDP, 38DM-BDP, and 138TM-BDP are unsymmetric and have not been reported in literature. Due to the reasons mentioned above, we report hereby the

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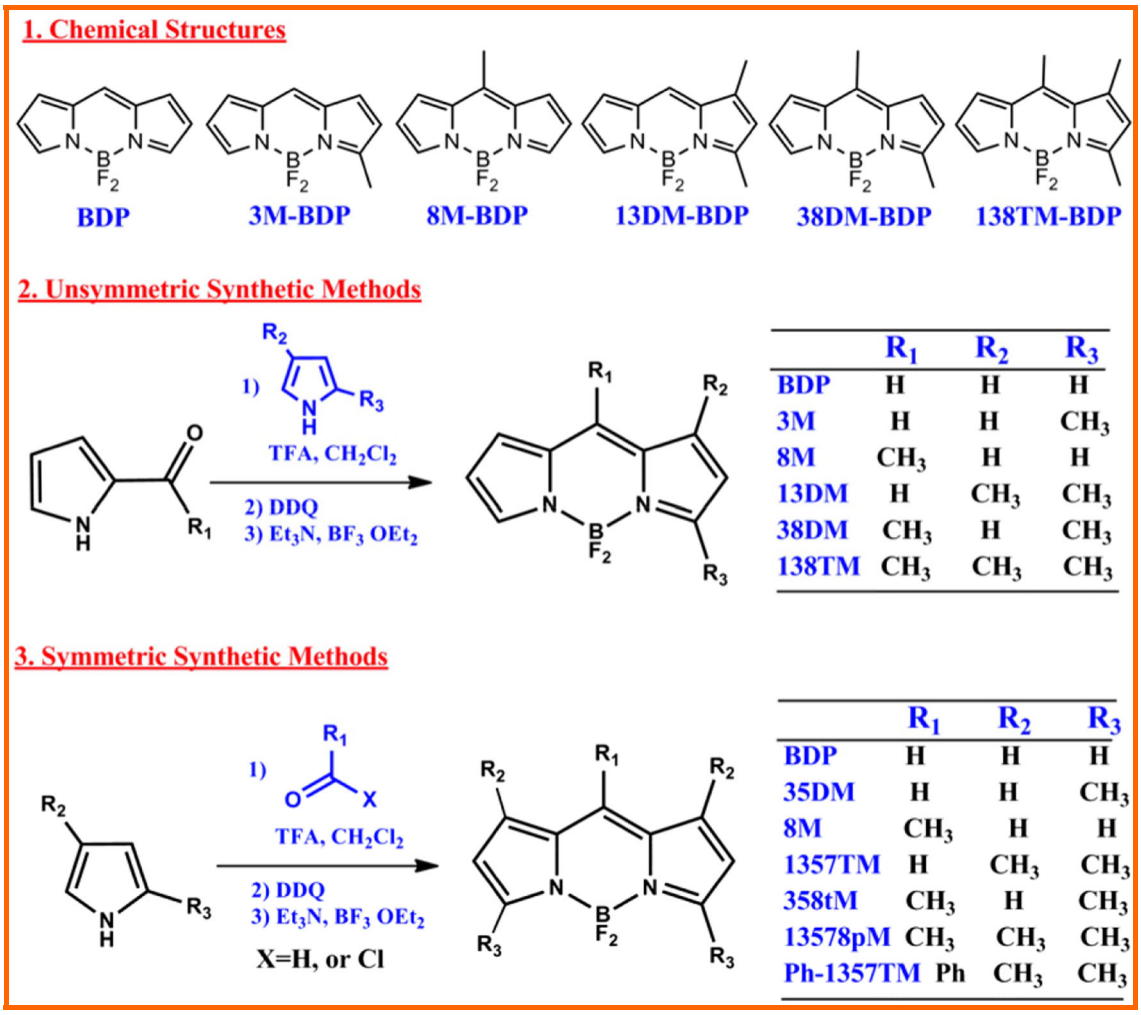


	R_1	R_2	R_3
BDP	H	H	H
3M	H	H	CH_3
8M	CH_3	H	H
13DM	H	CH_3	CH_3
38DM	CH_3	H	CH_3
138TM	CH_3	CH_3	CH_3

	R_1	R_2	R_3
BDP	H	H	H
35DM	H	H	CH_3
8M	CH_3	H	H
1357TM	H	CH_3	CH_3
358tM	CH_3	H	CH_3
13578pM	CH_3	CH_3	CH_3
Ph-1357TM	Ph	CH_3	CH_3

Scheme 1 Chemical structures and synthetic methods of BODIPYs

synthesis of BDP, 3 M-BDP, 8 M-BDP, 13DM-BDP, 38DM-BDP, and 138TM-BDP using the unsymmetric method. We have also measured and analyzed their fluorescence and singlet oxygen photosensitizing properties according to our experience in this area [16–21].

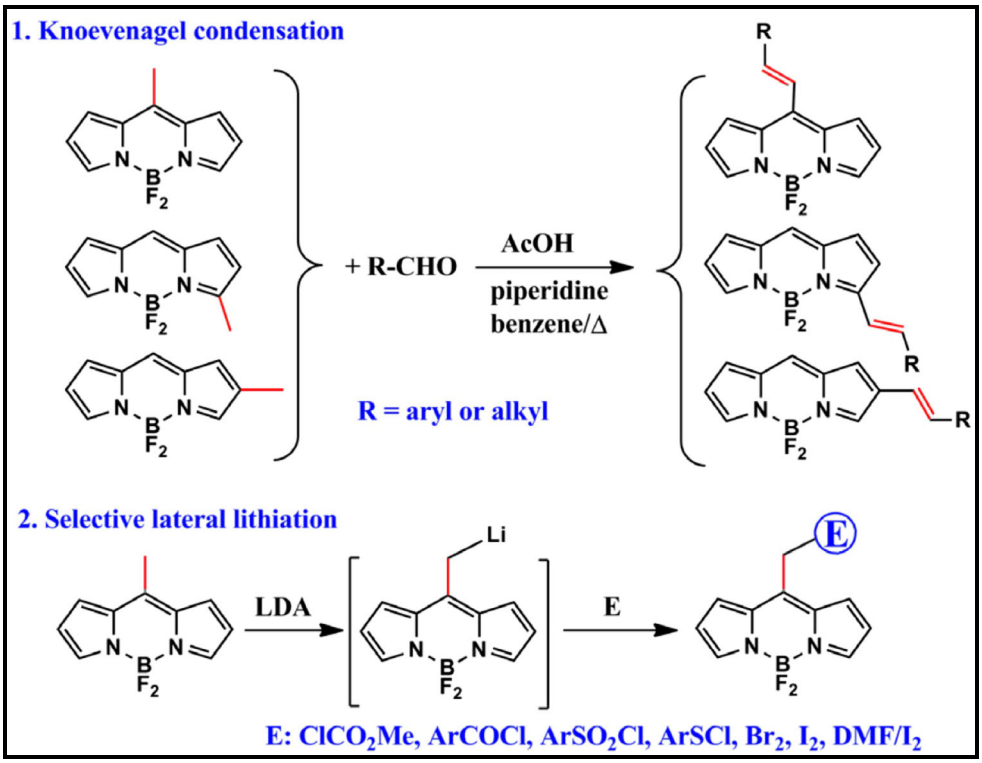
Experimental

Materials and Instruments

All solvents for spectrum studies were dried and redistilled before use. All reagents for synthesis were analytical grade and used as received. ^{1}H and ^{13}C NMR spectra were obtained at room temperature on a Bruker AVANCE III HD 600 MHz NMR spectrometer. Chemical shifts (δ) are given in ppm relative to $CDCl_3$ (7.26 ppm for ^{1}H and 77 ppm for ^{13}C) or to internal TMS (0 ppm for ^{1}H). High resolution MS spectra were measured with a Thermal Fisher LCQ Fleet™ mass spectrometer using ESI in positive mode. UV-vis spectra were measured on an Agilent 8454 spectrophotometer using 1 cm matched quartz cuvettes. Fluorescence spectra were measured by FLS920 steady-state/time-resolved fluorescence spectrometer (UK Edinburgh Instruments Ltd.).

Synthesis

The general procedure for the synthesis and purification of methyl substituted BODIPYs is as following. Dichloromethane (50 mL) containing methyl substituted pyrrole (2 mmol) and a drop of trifluoroacetic acid were stirred at room temperature. Then 2-formylpyrrole or 2-carbonylpyrrole (2.3 mmol) dissolved in dichloromethane (25 ml) was added dropwisely. The resulting mixture was stirred until TLC showed the complete consumption of 2-formylpyrrole or 2-carbonylpyrrole. After that triethylamine (7 mL) in dichloromethane (20 mL) was added to the reaction mixture, which was followed by the slow addition of borontrifluoride-etherate (10 mL) in dichloromethane (20 mL) to the reaction mixture. Ice cooling was applied during these additions. Solvent was removed by vacuum distillation.



Scheme 2 Application of methyl BODIPYs in synthesis

Purification was carried out by column chromatography with silica gel (200–300 mesh) and the eluent solvent is *n*-hexane/CH_2Cl_2 (90:10 *v*/v). Column chromatography was repeated twice or more to completely purify the product.

BDP The yield was 9.5%. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.90 (s, 2H), 7.43 (s, 1H), 7.16 (d, J = 3.9 Hz, 2H), 6.56 (d, J = 3.6 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-d) δ 145.08, 141.42, 135.17, 131.38, 118.81. HRMS: $[M + Na]^+$ cald. 215.0563, found: 215.0554.

3 M-BDP The yield was 11.3%. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.26 (s, 1H), 7.06 (s, 1H), 6.94 (d, J = 4.0 Hz, 2H), 6.27 (d, J = 4.0 Hz, 2H), 2.62 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 158.28, 134.72, 130.07, 126.78, 119.58, 14.94. HRMS (ESI): $[M + Na]^+$ cald. 229.0719, found: 229.0710.

8 M-BDP The yield was 12.4%. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.85 (s, 2H), 7.31 (s, 2H), 6.55 (s, 2H), 2.64 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 145.88, 143.42,135.55, 128.04, 117.99, 16.19. HRMS (ESI): $[M + Na]^+$ cald. 229.0719, found: 229.0709.

13DM-BDP The yield was 10.2%. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.64 (s, 1H), 7.20 (s, 1H), 6.93 (d, J = 3.7 Hz, 1H), 6.43 (s, 1H), 6.16 (s, 1H), 2.59 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 163.11, 145.78, 139.20, 136.48, 132.60, 126.49, 124.72, 121.23, 116.30, 15.19, 11.41. HRMS (ESI): $[M + Na]^+$ cald. 243.0876, found: 243.0866; $[2\ M + Na]^+$ cald. 463.1859; found: 463.1840.

38DM-BDP The yield was 22.6%. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.67 (s, 1H), 7.25–7.23 (m, 1H), 7.13 (d, J = 3.8 Hz, 1H), 6.46 (dd, J = 4.3, 2.0 Hz, 1H), 6.34 (d, J = 4.3 Hz, 1H), 2.62 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 160.39, 142.49, 139.74, 136.17, 134.32, 129.60, 125.11, 120.44, 116.47, 15.62, 15.06. HRMS (ESI): $[M + Na]^+$ cald. 243.0876, found: 243.0865.

138TM-BDP The yield was 17.6%. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.60 (s, 1H), 7.07 (d, J = 4.0 Hz, 1H), 6.42 (dd, J = 4.1, 2.1 Hz, 1H), 6.14 (s, 1H), 2.56 (s, 3H), 2.52 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 159.97, 145.48, 142.00, 137.84, 134.20, 134.13, 123.84, 122.74, 115.57, 16.86, 16.42, 14.89. HRMS (ESI): $[M + Na]^+$ cald. 257.1032, found: 257.1020; $[2\ M + Na]^+$ cald. 491.2172; found:491.2149.

Sample Solution Preparation for Measurements

For each solvent, parent BODIPY solid was first dissolved in a small vial to make a concentrated stock solution (1 mL). It was then diluted in another vial until the absorbance was ~0.80 at the peak maximum for absorption spectra. For fluorescence measurements, the fluorescence quantum yield is very sensitive

to the sample concentration and excitation wavelength due to the self-absorption effect. Therefore the dye concentration in any solvent was adjusted low enough to yielding an absorbance of ~ 0.090 at the excitation wavelength (480 nm) in 1 cm path cuvettes to avoid self-absorption effect.

Methods for Spectral Measurements and Data Processing

The procedure is similar to that in our previous report [22, 23]. Fluorescence measurements were performed by using a FLS 920 fluorospectrometer of Edinburgh Instruments with cuvettes of 1 cm and excitation at 480 nm (22 °C). Both the emission and excitation slits were 0.5 nm. The fluorescence was measured at 90° to the incident excitation beam. The fluorescence intensity at a wavelength was calibrated against the detector response and the excitation light intensity. The fluorescence quantum yield was computed by using Eq. (1).

$$\Phi_f = \Phi_f^0 \bullet \frac{F_s}{F_0} \bullet \frac{A_0}{A_s} \bullet \frac{n_s^2}{n_0^2}, \quad (1)$$

in which **F** is the integrated fluorescence intensity, **A** is the absorbance at excitation wavelength, n is the refractive index of the solvent used, the subscript 0 stands for a reference compound and s represents samples. Fluorescein in ethanol containing 1×10^{-3} mol/L NaOH was used as the reference ($\Phi_f^0 = 0.92$) [23]. Φ_f values of Eosin Y, Eosin B thus obtained in ethanol also match the reported values. Several measurements for a Φ_f value were performed and averaged by choosing different concentrations and excitation wavelengths.

Measurements of the fluorescence lifetimes were performed with standard time-correlated single-photon counting method. The excitation light was a portable diode laser (EPL-515, Edinburgh Instruments), the 509 nm (80 ps, 0.10 mW) laser beam was guided into the samples, and emission at 520 nm was detected with a PMT (Hamamatsu R928) cooled to −21 °C. The repetition rate is 10 MHz whilst the count rate did not exceed 20 kHz (0.2%) in order to avoid pile-up effects. The bandwidth for excitation as well as for emission was <2 nm. The prompt response function of the system had an fwhm between 500 and 700 ps.

The convolution method supplied with the instrument was used to fit the $I(t) = A + B \times e^{(-t/\tau_f)}$ to obtain the fluorescence lifetime τ_f. The chi-squared value is less than 1.25 for fitting data. R6G in ethanol was used as the reference to test the lifetime measurement ($\tau_f = 3.97$ ns), which is in excellent agreement with the measured value of 3.96 ns [22]. The fluorescence lifetimes of the BODIPY dyes showed no dependence on the emission wavelength and sample concentration in the test range from 0.01 to 0.1 mmol/L. The lifetime value of a fluorescein dye was easily reproducible regardless of the change on emission wavelength and the dye concentration.

Computational Simulation

The calculations were carried out using density functional theory (DFT) method as implemented in the Gaussian 09 package. The B3LYP exchange-correlation functional was chosen together with a 6-311G++ basis set for structural optimization. The solvent effect was modeled using the Polarizable Continuum Model (CPCM) method. In all the cases frequency analysis was made after geometry optimization to ensure the convergence to an energy minimum.

Results and Discussion

Synthesis

In our case, the unsymmetric reaction of two different pyrroles gives the desired products, in which 3 M-BDP, 38DM-BDP, and 138TM-BDP have not been reported in literature. It is essentially a facile one-pot reaction. The experimental procedure is significantly easier than that of the symmetric procedure. On the other hand, the pyrrole molecule containing a C=O group can have self-reaction (i.e. it reacts with another such a molecule) and leads to the by-products. To avoid such side reactions, the titration of 2-formylpyrrole (or 2-carbonylpyrrole) into methyl-pyrrole under fast stirring was used. The reaction temperature was maintained at 22 °C or lower to prevent the side reaction. Low polarity solvent as eluent gives good purification results. HRMS, ^{1}H NMR, ^{13}C NMR, and UV-Vis spectra all well consistent with the product structure.

The Absorption, Fluorescence Properties and the Effect of Methyl Substitution

The UV-Vis absorption and fluorescence spectra were measured in three solvents: n-hexane, DCM and methanol. Table 1 summarizes the results. Fig. 1 shows the spectra in methanol. The shape and main band position of these BODIPYs are consistent with those for BODIPYs in literature [10, 11, 14, 24]. Comparing the spectra of these compounds, the difference in peak positions but similarity in spectral shape is obviously existent between them. This is because both the number and position of methyls on the BDP core affect the spectra, as shown in Fig. 2. In comparison to the unsubstituted BDP, only 3 M-BDP is red shifted in emission and absorption maximum (λ_{em} and λ_{abs} in Fig. 2), while λ_{em} and λ_{abs} of all other compounds are blue shifted. This indicates that 3-methyl is dominated by the position effect. For compounds other than 3 M-BDP, it is the number of methyls that determines the λ_{em} and λ_{abs} for mono-, di-, and tri-methyl substituted BODIPYs. From Fig. 2, we conclude that the more the methyls on BDP core, the shorter the λ_{em} and λ_{abs} in each solvent (except 3 M-

Table 1 The photophysical data in air saturated n-hexane, DCM and methanol

	Solvent	λ_{abs}/ nm	λ_{ex}/ nm	λ_{em}/ nm	$\Delta\nu$/ cm^{-1}	Φ_f	τ_f/ ns	k_{nr}/ 10^8 s^{-1}	k_f/ 10^9 s^{-1}
BDP	n-hexane	502	501	509	274	0.92	6.79	0.12	0.14
	DCM	503	502	510	273	0.88	6.78	0.18	0.13
	MeOH	497	497	505	319	0.96	7.35	0.054	0.13
3 M-BDP	n-hexane	510	509	515	190	0.96	6.75	0.059	0.14
	DCM	511	510	517	227	0.92	6.20	0.13	0.14
	MeOH	506	505	512	232	1.00	6.96	~0.00	0.14
8 M-BDP	n-hexane	500	499	506	237	0.96	6.62	0.060	0.15
	DCM	499	498	507	316	0.88	6.14	0.20	0.14
	MeOH	494	493	503	362	1.00	6.69	~0.00	0.15
13DM-BDP	n-hexane	493	499	504	443	0.93	6.21	0.11	0.15
	DCM	498	497	507	356	0.87	5.89	0.22	0.15
	MeOH	493	492	503	403	0.99	6.34	0.016	0.16
38DM-BDP	n-hexane	499	499	504	199	0.96	6.61	0.061	0.15
	DCM	498	497	506	317	0.89	6.23	0.18	0.14
	MeOH	494	492	502	323	1.00	6.76	~0.00	0.15
138TM-BDP	n-hexane	492	491	498	245	0.98	6.10	0.033	0.16
	DCM	488	488	500	492	0.95	5.93	0.084	0.16
	MeOH	486	484	497	455	1.01	6.31	~0.00	0.16
1357TM-BDP	c-hexane	508	508	514	230	0.96	5.85	0.068	0.16
	DCM	506	505	513	270	0.92	5.73	0.14	0.16
	ethanol	503	503	510	273	0.99	5.95	0.017	0.17
Ph-1357TM-BDP	n-hexane	501	501	511	391	0.56	3.37	1.31	0.17
	DCM	501	501	513	467	0.63	3.97	0.93	0.16
	MeOH	498	498	510	473	0.58	3.90	1.08	0.15

BDP). A methyl is considered an electron donating group, when a hydrogen atom on an aromatic ring (such as benzene and naphthalene) is replaced by a methyl, the λ_{em} and λ_{abs} of the aromatic compound is expected to show red shift due to the hyperconjugative effect. The hyperconjugative effect occurs when the electrons in a σ orbital (C–H of CH_3) are delocalized into an adjacent empty π orbital (of the benzene ring) to give an extended molecular orbital. The CH_3 makes the π-system extended and therefore causes the red shift of absorption and emission maximum. However, it is clearly not the case (no hyperconjugative effect for these CH_3 substituted BODIPYs) for the methyl substituted BODIPYs except 3 M-BDP. BDP π-system is different from that of benzene and naphthalene. BF_2 is very strong electron withdrawing but B

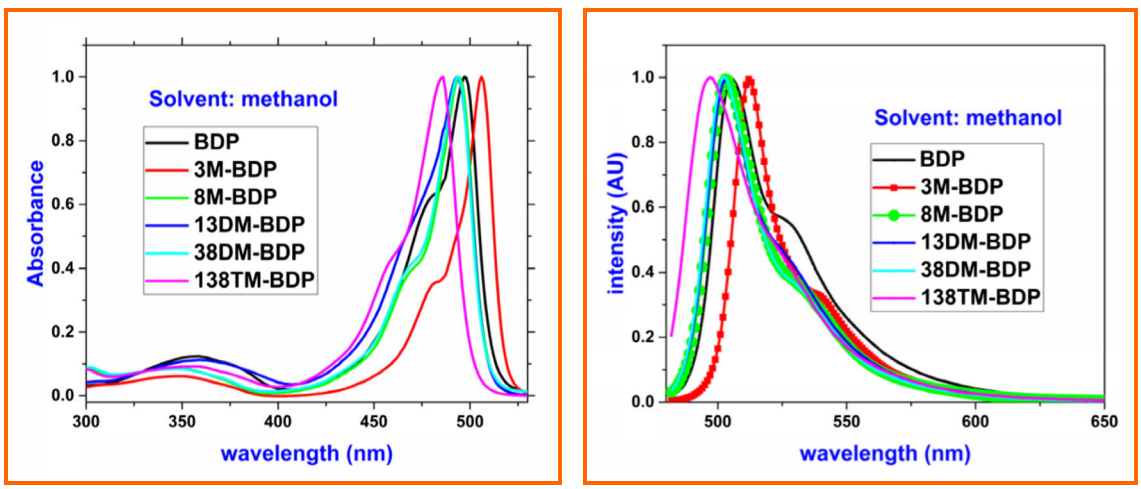


Fig. 1 The UV-Vis absorption and fluorescence spectra in methanol. For fluorescence spectra, the excitation is 470 nm with absorbance 0.090 at 470 nm

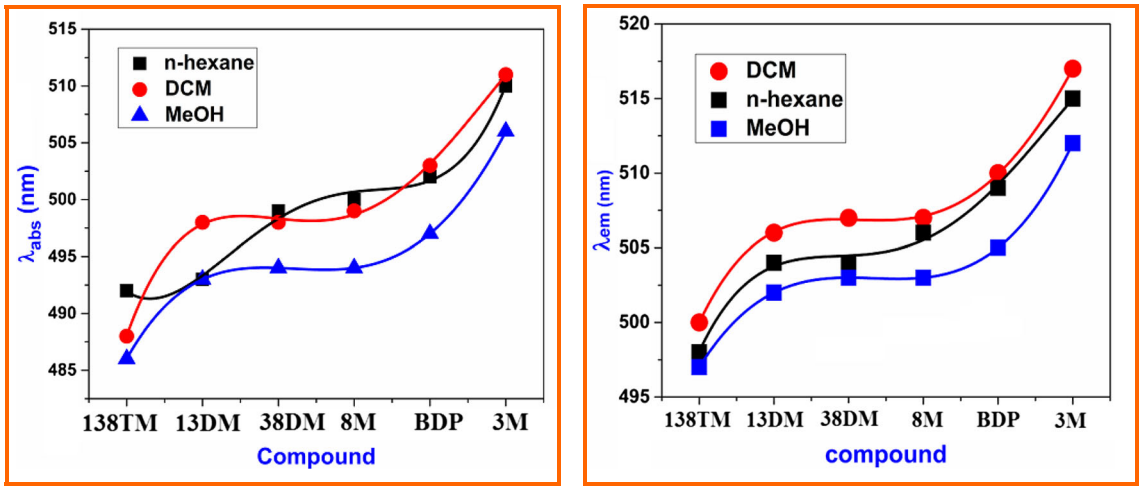


Fig. 2 Effects of methyl substitution (number and position of methyls) and solvent on the emission maxima λ_{em}, absorption maxima λ_{abs}

atom in BDP is not part of the π-system although B atom is coplanar with other BDP carbon atoms. In fact, 8-NH_2 substitution causes a much larger blue shift (90–100 nm) since it significantly alters the electronic and geometrical properties of the molecule [25]. 3-C of BDP is significantly more positively charged than other carbon atoms, so that 3-methyl is able to donate electrons and show hyperconjugative effect. The blue shift of 13DM-BDP is likely due to that 1-methyl causes dominant blue shift which cancels the small red shift of 3-methyl.

Fig. 3 compares the normalized absorption, excitation and emission spectra. The excitation spectrum of a compound is basically the same as its absorption spectrum, while the emission spectrum is mirror symmetric to its maximum absorption band, indicating that S_1 is the only state which emits fluorescence.

Comparing emission maximum (λ_{em}) of each compound in three solvents (Fig. 2 right, the red line of DCM is higher than the black line of n-hexane, while the black line of n-hexane is higher than the blue line of methanol), we can see that λ_{em} of each compound shows the same solvent effect, in other words this relation holds for each compound: λ_{em} (DCM) > λ_{em} (n-hexane) > λ_{em} (MeOH). Methanol H can form strong Hydrogen-bonding MeO···H···F···BF, so that methanol shows much smaller solvent polarity effect.

Effects of Methyl Substitution on Fluorescence Quantum Yield and Lifetime Values

The fluorescence lifetime value is an important parameter for a fluorophore to be used in fluorescence lifetime imaging. The fluorescence quantum yield (Φ_f) and lifetime values for these compounds were also measured in the three solvents (Table 1), the data for symmetric **1357TM-BDP** and **Ph-1357TM-BDP** are also included for comparison. All fluorescence decays are monoexponential (Fig. 4). **Ph-1357TM-BDP** is a symmetric BODIPY compound which is very often used in literature due to its easy synthesis and good solubility, its Φ_f is 0.59 ± 0.04 and τ_f is 3.75 ± 0.38 ns in the solvents. Compared to that of **Ph-1357TM-BDP**, Φ_f of any other

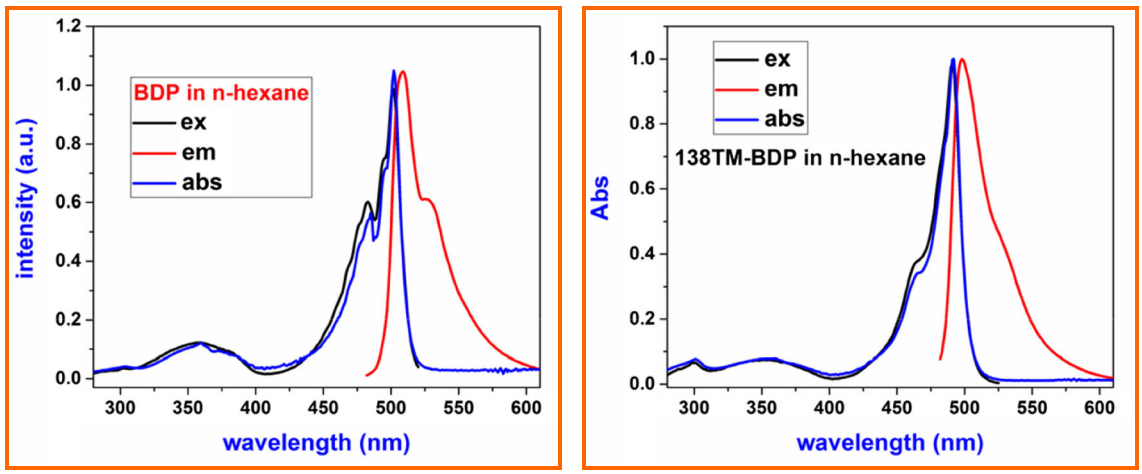


Fig. 3 Comparison of the normalized absorption, excitation and emission spectra

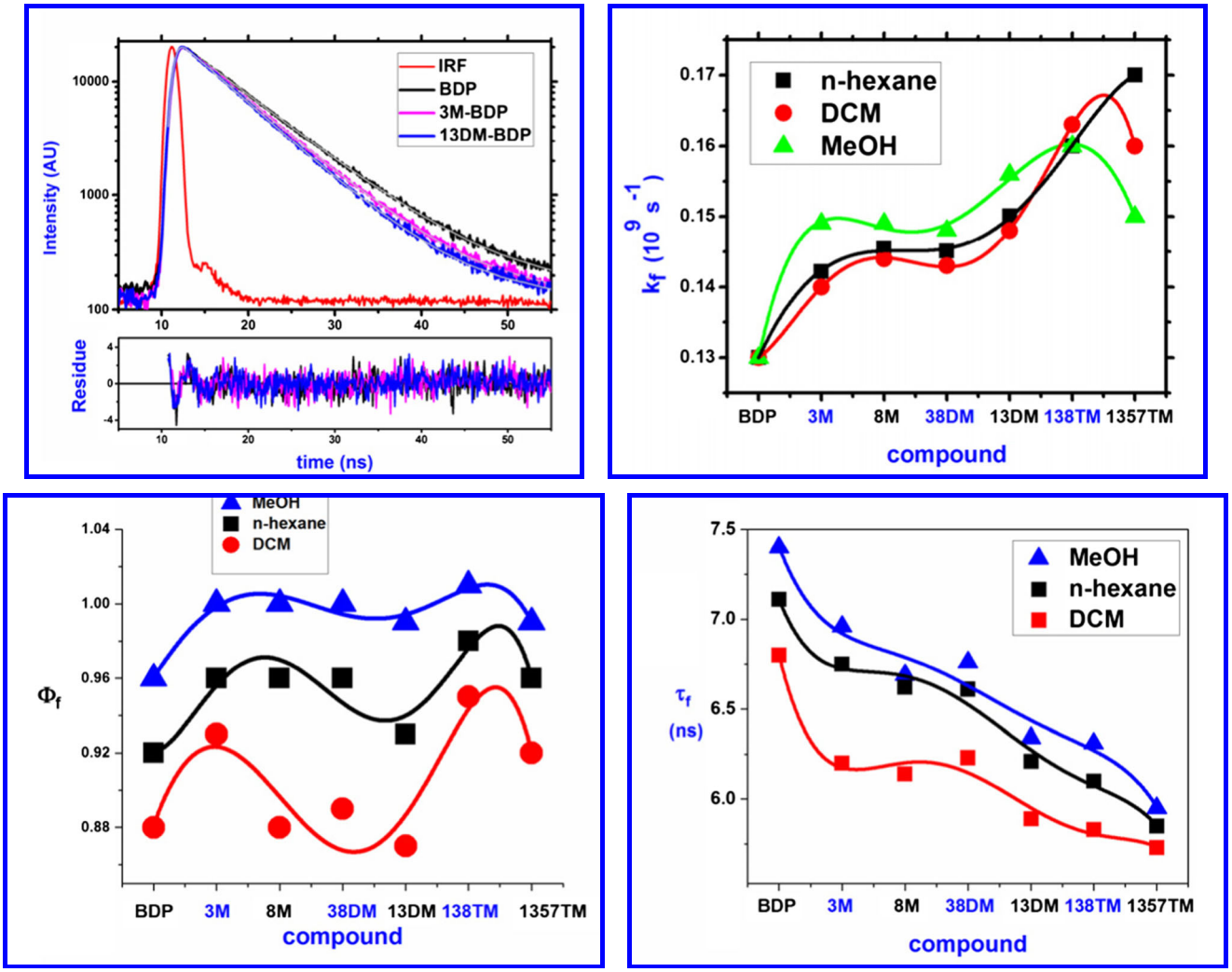


Fig. 4 **Top left:** fluorescence decays at 520 nm with laser excitation at 509 nm in n-hexane. **Top right:** Effects of methyl substitution (number and position) on k_f. **Bottom**: Effects of methyl substitution and solvent on the fluorescence quantum yield Φ_f and fluorescence lifetime τ_f

compound containing no 8-phenyl is significantly higher in each solvent, and the value is in the range from 0.87 to 1.00 (Table 1). τ_f for these compounds is also much longer than that of **Ph-1357TM-BDP** in each solvent, ranging from 5.83 to 7.40 ns (Table 1). Due to the rotation of 8-phenyl (its mass is much larger than a methyl and the rotation causes energy loss of S_1), **Ph-1357TM-BDP** exhibits much lower Φ_f and τ_f values. The lifetime values except that of **Ph-1357TM-BDP** are remarkably longer than that of xanthene dyes (4 ns or less for fluorescein, rhodamine and their derivatives) and phthalocyanines [22, 23].

For each compound, it shows the same solvent effect (Fig. 4): Φ_f (MeOH) > Φ_f (n-hexane) > Φ_f (DCM), τ_f (MeOH) > τ_f (n-hexane) > τ_f (DCM). Because of the H-bonding (MeO···H···F···BF), the S_1 state of a BODIPY molecule is more stabilized in methanol, so that the τ_f and Φ_f value of a BODIPY compound in methanol is the highest. To confirm the H-bonding effect, we also measured τ_f and Φ_f in ethanol and water for BDP, and the value is indeed ranked by the H-bonding intensity: Φ_f (0.98 in water) > Φ_f (0.96 in methanol) > Φ_f (0.92 in ethanol), τ_f (7.42 ns in water) > τ_f (7.35 ns in methanol) > τ_f (6.98 ns in ethanol).

The Cl atoms in CH_2Cl_2 have external heavy atom effect on the S_1 state of BODIPY, which quenches the S_1 state of a BODIPY molecule. Therefore τ_f and Φ_f value of a BODIPY compound in DCM shows the smallest value compared to that in n-hexane and methanol.

Fig. 4 shows how the methyl substitution (number and position) affects these values in different solvents. The lifetime τ_f clearly decreases with the increase of methyl numbers, but Φ_f change is complicated with the increase of methyl numbers. Among the unsymmetric compounds, 138TM-BDP shows the highest Φ_f but shortest τ_f in all three solvents, therefore the largest k_f (fluorescence emission constant $k_f = \Phi_f/\tau_f$). BDP, on the other hand, exhibits the lowest Φ_f but longest τ_f in all three solvents, therefore the smallest k_f.

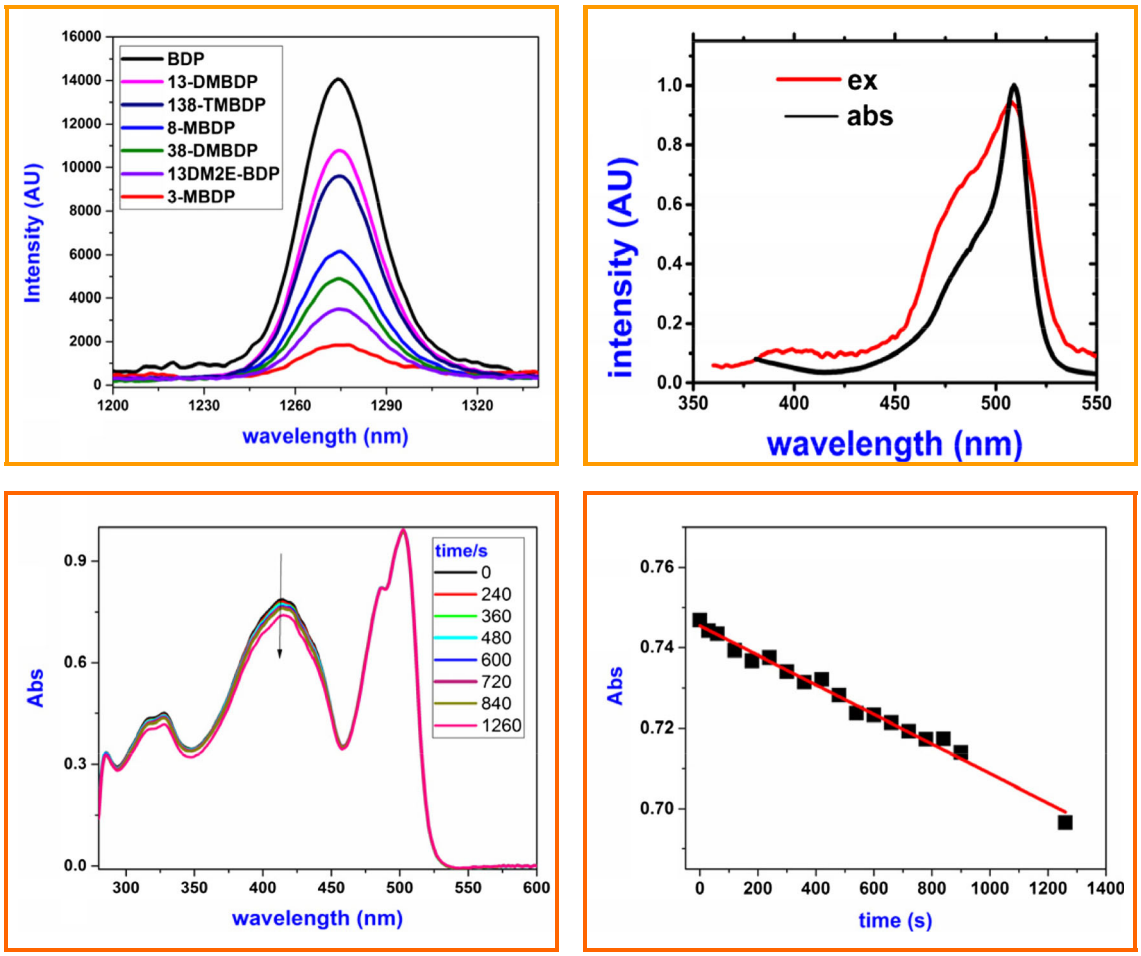


Fig. 5 **Top left:** NIR luminescence of parent BDP and its methyl substituted derivatives in air saturated CS_2 solutions (excitation at 500 nm, absorbance at 500 nm was all adjusted as 1.0). **Top right:** Excitation spectrum of NIR emission of 13DM-BDP (emission was set as 1275 nm). **Bottom Left:** The absorption spectra of photosensitized oxidation of DPBF in the presence of BDP as the photosensitizer (air saturated toluene as solvent). The irradiation wavelength is 509 nm, BODIPY concentration is ca. 15 μM, the initial DPBF concentration is ca. 30 μM. **Bottom Right:** Chemical kinetic curves of DPBF decomposition

The trend is that increasing the number of methyl leads to a higher k_f except 3 M-BDP in DCM (Fig. 4 top right) and symmetric 1357TM-BDP. The nonradiative rate constant ($k_{nr} = (1-\Phi_f)/\tau_f$) values are also included in Table 1. For each new compound, k_{nr} is much smaller than k_f, and the solvent effect on k_{nr} is that k_{nr} (in DCM) > k_{nr} (in hexane) > k_{nr} (in Methanol). The number of methyl plays more important role in tuning the Φ_f and τ_f values than the position of a methyl.

Table 2 Φ_Δ values

	CS_2	Toluene
BDP	0.15	0.12
3 M-BDP	0.040	0.032
8 M-BDP	0.070	0.20
13DM-BDP	0.12	0.078
38DM-BDP	0.055	0.083
138TM-BDP	0.14	0.067

Singlet Oxygen Detection from NIR Luminescence and DPBF Chemical Trapping

We then identified singlet oxygen formed by the BODIPYs using NIR emission technique. Fig. 5 shows the NIR photoluminescence for these compounds. The emission band was observed at 1275 nm. The band was disappeared when oxygen in the solutions was purged by argon gas bubbling. The NIR spectral shape and peak position are all consistent with that of singlet oxygen ($^1\Delta_g$) reported. Further more, the excitation spectrum of 1275 nm band (Fig. 5 top right) matches its UV-Vis absorption, also indicating that singlet oxygen is originated from the BODIPYs.

The photosensitized singlet oxygen formation of these compounds was also examined by DPBF (diphenylisobenzofuran) chemical trapping with light irradiation at 509 nm in air saturated toluene solution of each compound. The green fluorescent DPBF specifically reacts with singlet oxygen quantitatively and then decomposes to colorless product. As shown in Fig.

5 bottom, the BDP absorption band (500 nm) shows no change during light irradiation while DPBF absorption (410 nm) is decreased (Fig. 5 bottom left). When any one of oxygen, light, and a methyl BDP was absent, the DPBF decomposition did not occur. This demonstrates that the singlet oxygen is formed by the photosensitizing process of the BODIPYs.

The change of DPBF absorbance upon time is linear (Fig. 5 bottom right as an example), indicating it is zero order kinetics for DPBF decomposition, $[DPBF]_t = [DPBF]_0 - kt$, in which k is the reaction constant, t is time in second. According to Lamber-Beer law, $A(t) = \varepsilon[DPBF]_t l$, in which ε is the molar absorption coefficiency, l is the path length, we then have $A(t) = A(0) - k\varepsilon lt = A(0) - k't$ (k' is a constant). From the obtained slope the formation quantum yield of singlet oxygen (Φ_Δ) can be obtained (Table 2). In CS_2 and toluene BDP, 13DM-BDP, and 138TM-BDP show remarkable Φ_Δ value up to 0.20. As shown in our previous paper [21], this unexpected good Φ_Δ values are due to that the excited triplet state T_1 of a methylated BDP formed by two paths: 1) the conventional intersystem crossing from S_1 state with a low efficiency; 2) the interaction of molecular oxygen with S_1 state of BODIPY induces both T_1 and singlet oxygen formation, from which one quenched S_1 leads to two singlet oxygen formation ($S_1 + O_2 \rightarrow T_1 + {}^1\mathbf{O_2}$, then $T_1 + O_2 \rightarrow S_0 + {}^1\mathbf{O_2}$) [21]. To confirm the processes, T_1 energy (E_T) for the BODIPYs was computed using TD-DFT method with a 6-311G++ basis set. The calculated E_T is in the range from 1.20 to 1.30 eV, while experimental S_1 energy is in the range from 2.41 to 2.52 eV (Table 1, taking the mid point between absorption and emission maximum). The energy difference between S_1 and T_1 ($\mathbf{\Delta E_{ST}}$) of a methylated BDP is then in the range 1.11–1.32 eV, both $\mathbf{\Delta E_{ST}}$ and E_T are all larger than the excitation energy of singlet oxygen (0.97 eV).

Conclusions

Using the facile one pot unsymmetric reaction procedure, we have synthesized and characterized five methyl substituted BODIPY compounds, three of them (3 M-BDP, 38DM-BDP, and 138TM-BDP) are not reported previously. These compounds show high fluorescence quantum yield, long fluorescence lifetime, and small Stokes shift. The number of methyl groups on BDP plays more important role than the position in determining the fluorescence properties. Except for 3 M-BDP, the presence of methyl leads to the blue shift of emission and absorption. The increase in the number of methyls on BDP core enhances the spectral blue shift, increases Φ_f and k_f but decreases τ_f values. H-bonding solvents lead to the increase in both Φ_f and τ_f values. These compounds also exhibit the ability to photosensitize the generation of singlet oxygen ($^1\Delta_g$) in some solvents (with quantum yield up to 0.20).

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