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# Exciton coupling and energy transfer in oxygen-bridged unsymmetrical BODIPY dyads

dyads.



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ARTICLE INFO	A B S T R A C T
Keywords: BODIPY	Herein, we report the synthesis of unsymmetrical BODIPY dyads through the reaction of phenol oxygen on BODIPYs with $\alpha$ -carbon atoms on bromoBODIPYs. Excited state interactions were observed for the dyads
Unsymmetrical dyad Exciton coupling	composed of components having similar absorption wavelengths. When dissimilar components were used to construct the dyad, exciton coupling disappeared and an energy transfer causing a large pseudo-Stokes shift was

## 1. Introduction

Energy transfer

BODIPY fluorophore has gained great fame in the last 30 years thanks to its favorable photophysical properties and diverse functionalization possibilities. The compounds based on this fluorophore have found place in numerous studies on photophysics and dye-based application fields [1-7]. Various BODIPY dyads have been synthesized during the heavy researches on the photophysics of BODIPY. These dyads were synthesized by integrating the same fluorophores directly [8-14] or by using alkenyl/alkyne [15], phenyl [16], sulfur [17] and other [18-21] linkers. In most of these dyads, the components interacted with each other in their excited states as evidenced by the splitting of their absorption bands. Some dvads composed of dissimilar BODIPY components were also synthesized [22-26]. However no exciton coupling has been reported in such systems. Interestingly, no BODIPY dyad of which components absorb light at similar energies has been investigated. In present work, we report the synthesis of such dyads and our first photophysical findings of these systems (Scheme 1). We also managed to control the photophysical processes in these dyads by simple substitutions on the core.

## 2. Results and discussion

The BODIPY dyads composed of dissimilar BODIPY components had been achieved only by the connection of the monomers through *meso*position. The connection of different BODIPY units through other positions has remained a challenge. Recently, Savoldelli et al. reported the first synthesis of unsymmetrical BODIPYs which were connected to each other through pyrrolic  $\alpha$  positions [22]. The method we introduced here to construct unsymmetrical BODIPY dyads is based on the substitution of the  $\alpha$ -bromine on a BODIPY molecule with the phenol oxygen at another BODIPY (Scheme 1).

observed. The reported structures are the first examples of oxygen-bridged unsymmetrical BODIPY-BODIPY

*meso*-Phenyl substituted BODIPY **1** was synthesized according to the literature [27]. To obtain  $\alpha$ -phenol substituted BODIPYs, the radical coupling reaction of BODIPY with diazonium salts was used [28]. The reaction of **1** with the diazonium salts of *p*- and *m*-aminophenols gave the compounds **2** and **3** with 26% and 17% yields, respectively. Then compound **4** was obtained quantitatively by reacting compound **1** with 6 equivalents of bromine [29]. Halogen atoms on  $\alpha$ -positions of the BODIPY core have already been shown to substitute with various nucleophiles [30,31]. Thus, heating the compound **4** with excess pyrrole furnished structure **5** with excellent yield. To obtain the dyads, phenolbearing monomers (**2** or **3**) and bromine-bearing monomers (**4** or **5**) were stirred for 10 min in acetonitrile in the presence of K<sub>2</sub>CO<sub>3</sub>. With this method Dyad **1**, **2** and **3** were synthesized by 46, 43, 72% yields, respectively.

Absorption and emission spectra of the synthesized compounds were collected in chloroform. The obtained data were summarized in Table 1. The absorption maxima of compounds 2 and 3 were at 541 and 531 nm, respectively. They had similar Stokes' shift (23 nm for 2, 22 nm for 3) and fluorescence quantum yield values (0.06 for 2, 0.08 for 3). Maximum absorption of the brominated BODIPY derivative 4 was at 558 nm. This compound exhibited maximum fluorescence at 570 nm with a quantum yield near to unity (0.98). The observed high fluorescence quantum yield for 4 is highly interesting as bromine was expected to decrease this value by facilitating intersystem crossing. Substitution

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Scheme 1. Synthesis of BODIPY monomers and dyads.

Table 1				
Steady s	state photophysical	properties of	the synthesized	compounds.

Compound	$\lambda_{abs, max}$ (nm)	log (ɛ)	$\lambda_{flo, max}$ (nm)	$\phi_{flo}{}^a$
2 3 4 5 Dyad 1 Dyad 2	541 531 558 626 562 556	4.82 4.81 4.99 4.76 5.16 5.28	564 553 570 642 574 568	0.06 0.08 0.98 $0.47^{b}$ 0.01 0.28
Dyad 3	627	5.02	644	0.18 <sup>b</sup>

<sup>a</sup> Fluorescence quantum yield was calculated by using the cresy violet [27] as standart material.

<sup>b</sup> Excited at 570 nm.

of one of the bromines on **4** with pyrrole caused a dramatic bathochromic shift ( $\lambda_{abs} = 626$  nm,  $\lambda_{flo} = 642$  nm) with a concomitant twofold decrease in fluorescence quantum yield.

The absorption spectra of **Dyad 1**, **Dyad 2** and their monomers were shown in Fig. 1. Absorption spectra of both **Dyad 1** and **Dyad 2** didn't match the sum of its components' spectra. In the absorption spectrum of **Dyad 1**, maximum of component **4** red shifted by 4 nm while that

of component **2** blue shifted by 22 nm (Fig. 1a). In **Dyad 2** the absorption maxima of **4** and **2** shifted to blue by 2 and 7 nm, respectively (Fig. 1b). Shifts in absorption wavelengths had been reported for only symmetric BODIPY dimers so far and was explained by the exciton coupling of the excited states of the components [8,11,18]. Herein we report the first observation of this phenomenon in asymmetric BODIPY dyads.

**Dyad 1** and **Dyad 2** emitted light at 574 and 568 nm, with the fluorescence quantum yields of 0.01 and 0.28, respectively. The obtained fluorescence spectra (Table 1 and Fig. S20) pointed out that the fluorescence of the dyads caused mostly (or completely) from component **4**. The emission maxima of both dyads were also observed to be

independent of the excitation wavelength. All these findings were parallel with the observations made for symmetrical BODIPY dyads.

According to the molecular exciton theory, exciton coupling weakens as the lowest energy levels of the components diverge [31]. To investigate this phenomenon on an unsymmetrical BODIPY dyad, we synthesized **Dyad 3** of which components have very different absorption maxima. As predicted, we saw that the absorption spectrum of **Dyad 3** was nearly the exact sum of its monomers **3** and **5** (Fig. 2a). When the dyad was excited at 520 no emission was observed from component **3** and the dyad emitted light at a similar wavelength as the component **5** does (644 nm) (Fig. 2b). Emission from monomer **5** was very low when excited at this wavelength. These results indicated an energy transfer from component **3** to component **5** in Dyad **3**. When the excitation spectrum was scanned for the emission wavelength at 670 nm, the excitation and absorption spectra were observed to match well. This observation further confirmed the fluorescence at 670 nm arose from both components of the dyad.

#### 3. Conclusion

In conclusion, we constructed the first oxygen-bridged unsymmetrical BODIPY-BODIPY dyads. When the components of the dyads had similar absorption maxima, an exciton coupling was observed. In the case of the dyad of which monomers absorb at different wavelengths, no excited state interaction between the components was observed. Instead, there was an energy transfer from one component to another. These results showed that bridging the BODIPY monomers through ether linkers allows the straightforward and manifested manipulation of the photophysical processes taking place in the dyad. The route we described in this paper provides a novel method to construct unsymmetrical BODIPY dyads and also beat a path for the integration of BODIPY with any other fluorophore having phenolic hydroxyl group on its structure.



Fig. 1. Normalized absorption spectra of (a) Dyad 1 and its monomers (b) Dyad 2 and its monomers.

## 4. Experimental section

#### 4.1. Materials and instrumentation

Chemicals were obtained from Acros Organics or J.T. Baker, Fisher Scientific and were used without further purification. The reactions were monitored by thin layer chromatography (Kiesegel 60, F254, E. Merck). The products were purified by flash column chromatography using silica gel 60 (0.063-0.200 mm, 70-230 mesh, ASTM, Merck) as the stationary phase. NMR spectra were recorded on Bruker DPX-400, ultra shield, high performance digital FT-NMR spectrometer (400 MHz for <sup>1</sup>H NMR, 100 MHz for <sup>13</sup>C NMR, 376 MHz for <sup>19</sup>F NMR). Chemical shifts ( $\delta$ ) were given as ppm and coupling constants (J) as Hz. Spin multiplicities were given as s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublets), t (triplet) and m (multiplet). Mass spectra were recorded on Agilent TOF LC/MS 1200/6210. UV-vis spectra were recorded on MAPADA Instruments, UV-3100PC Spectrophotometer. Fluorescence spectra were recorded on Thermo Scientific, Lumina Fluorescence Spectrometer. Fluorescence quantum yield of the compounds were calculated by comparative method using Cresyl Violet [27] as standard material.

Compounds 1 [32] and 4 [16] were synthesized according to literature methods.

### 4.2. General method for the coupling of 1 with diazonium salts

The method of Verbelen et al. [28] was used with some

modifications for the synthesis of compounds 2 and 3. To a cold solution of aminophenol (42 mg, 0.6 mmol) in 3 M HCl (0.88 mL) was added a solution of NaNO<sub>2</sub> (22.2 mg, 0.6 mmol) in cold water (0.6 mL) and was stirred for 5 min at room temperature. A solution of BODIPY 1 (161 mg, 0.6 mmol) in acetone (3 mL) was added to this mixture and was stirred under room temperature for 5 min. Finally, a solution of ferrocene (0.12 mmol) in acetone (1.2 mL) was (80 µL each minutes) added to the diazonium solution. After the TLC analysis showed the total consumption of 1 (about 1.5 h), the crude product was extracted to dichloromethane  $(3 \times 5 \text{ mL})$  and then the solvent was evaporated under vacuum. The mixture corresponding to red-pink spot (the most intense spot on TLC) was separated on column chromatography using ethyl acetate/hexane (1:8) as eluent. The pure product was isolated by a second column chromatography using chloroform/triethylamine (20:1) for 2 or dichloromethane/acetic acid (10:1) for 3 as eluent. At the last step triethylamine and acetic acid were removed by washing a solution of phenol-BODIPY with water.

Compound 2; Yield: 26%. Black iridescent solid, red in solution. <sup>1</sup>H NMR (400 MHz, d-DMSO)  $\delta$  10.29 (s, 1H), 7.97 (d, J = 8.3 Hz, 2H), 7.91 (s, 1H), 7.65-7.60 (m, 5H), 7.05-7.00 (m, 2H), 6.93 (d, J = 8.3 Hz, 2H), 6.81 (d, J = 2.9 Hz, 1H), 6.60 (s, 1H).<sup>13</sup>C NMR (100 MHz, d-DMSO)  $\delta$  161.1, 160.6, 143.7, 141.2, 137.3, 134.0, 133.9, 133.3, 132.1, 131.0, 130.9, 129.0, 128.3, 122.3, 118.3, 116.0. <sup>19</sup>F NMR (376 MHz, d-DMSO)  $\delta$  -137.0 (dd, J = 62.5, 30.2 Hz). HRMS (APCI): m/z calcd. for C<sub>21</sub>H<sub>9</sub>BF<sub>2</sub>N<sub>2</sub>O [M-H]<sup>-</sup>: 358.1209; found: 358.1232.

Compound 3; Yield: 17%. Black iridescent solid, red in solution.  $^{1}$ H NMR (400 MHz, d-DMSO)  $\delta$  9.73 (s, 1H), 8.01 (s, 1H), 7.70-7.61 (m,



Fig. 2. (a) Normalized absorption and (b) fluorescence spectra of Dyad 3 (purple) and its monomers 3 (blue) and 5 (red) in chloroform. (Excitation wavelength for straight lines: 520 nm, for dashed lines: 575 nm).

5H), 7.40–7.37 (m, 2H) 7.32 (t, J = 7.8 Hz, 1H), 7.06–7.05 (d, J = 4.3 Hz, 1H), 6.94–6.91 (m, 3H), 6.67 (d, J = 2.2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, d-DMSO)  $\delta$  159.5, 157.2, 145.3, 142.9, 136.3, 133.3, 133.2, 133.0, 132.7, 130.8, 130.5, 129.8, 129.4, 128.6, 121.6, 120.2, 118.9, 117.22, 115.98. <sup>19</sup>F NMR (376 MHz, d-DMSO)  $\delta$  – 136.2 (dd, J = 61.4, 30.3 Hz). HRMS (APCI): m/z calcd. for C<sub>21</sub>H<sub>9</sub>BF<sub>2</sub>N<sub>2</sub>O [M-H]<sup>-:</sup> 358.1209; found: 358.1221.

## 4.3. Synthesis of compound 5

A mixture of BODIPY **2** (40.3 mg, 0.07 mmol) and pyrrole (0.5 mL) were stirred at 40 °C until the UV analysis showed the total consumption of **2**. Crude product was purified on column chromatography using ethyl acetate/hexane (1:10) as eluent. Yield: 90%. Black iridescent solid, blue in solution. <sup>1</sup>H NMR (400 MHz, d-DMSO)  $\delta$  11.03 (s, 1H), 7.74–7.52 (m, 5H), 7.45 (s, 2H), 7.28 (s, 1H), 6.84 (s, 1H), 6.44 (s, 1H). <sup>13</sup>C NMR (100 MHz, d-DMSO)  $\delta$  149.50, 138.77, 136.12, 135.59, 133.65, 132.54, 131.28, 131.05, 129.25, 128.78, 126.98, 125.71, 120.73, 120.60, 111.90, 111.20, 108.65. <sup>19</sup>F NMR (376 MHz, d-DMSO)  $\delta$  –139.43 (dd, *J* = 63.7, 31.8 Hz). HRMS (APCI): *m/z* calcd. for C<sub>19</sub>H<sub>11</sub>BBr<sub>3</sub>F<sub>2</sub>N<sub>3</sub> [M – H]<sup>---</sup> 564.8528; found: 564.8492.

#### 4.4. General procedure for the synthesis of the dyads

To BromoBODIPY (4 or 5) (0.2 mmol) in acetonitrile (25 mL) was added  $K_2CO_3$  and phenol-BODIPY (2 or 3) (0.1 mmol in 10 mL acetonitrile). The reaction mixture was stirred at room temperature until TLC analysis showed the complete consumption of phenol-BODIPY. Then the mixture was filtrated to remove excess  $K_2CO_3$ . After removing the solvent under vacuum, the product was isolated by column chromatography on silica gel using ethyl acetate/hexane (1:10) as eluent.

**Dyad 1**; Black iridescent solid, red in solution. Yield: 46%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, J = 8.5 Hz, 2H), 7.79 (s, 1H), 7.59–7.41 (m, 10H), 7.19 (d, 2H, J = 8.3), 6.97 (s, 1H), 6.91 (d, J = 4.2 Hz, 1H), 6.80 (d, J = 3.3 Hz, 1H), 6.75 (s, 1H), 6.63 (d, J = 4.2 Hz, 1H), 6.46 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.9, 158.9, 156.3, 145.6, 142.5, 142.3, 137.3, 134.5, 134.2, 134.1, 134.0, 132.8, 131.9, 131.4, 131.2, 130.5, 130.5, 130.3, 129.9, 129.4, 129.1, 128.9, 128.7, 128.4, 120.9, 118.3, 118.1, 109.8, 98.9. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ – 139.2 (dd, J = 61.6, 30.0 Hz), -147.8 (dd, J = 54.4, 25.8 Hz). HRMS (APCI): (the molecule fragmented through ether bridge during ionization) m/z calcd. for C<sub>21</sub>H<sub>9</sub>BF<sub>2</sub>N<sub>2</sub>O [M – H]<sup>-:</sup> 358.1209; found: 358.1192. m/z calcd. for C<sub>15</sub>H<sub>8</sub>BBr<sub>3</sub>F<sub>2</sub>N<sub>2</sub>O [M – H]<sup>-:</sup> 515.8242; found: 515.8211.

**Dyad 2**; Black iridescent solid, red in solution. Yield: 43%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, J = 7.7 Hz, 1H), 7.89 (s, 1H), 7.70 (s, 1H), 7.64–7.49 (m, 11H), 7.31 (s, 1H), 7.06 (s, 1H), 6.97 (d, J = 4.0 Hz, 1H), 6.91 (d, J = 3.3 Hz, 1H), 6.82 (s, 1H), 6.69 (d, J = 4.0 Hz, 1H), 6.56 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.5, 158.1, 154.7, 146.2, 143.3, 141.9, 137.1, 134.9, 134.9, 134.1, 133.9, 133.8, 132.5, 131.9, 131.1, 130.6, 130.5, 130.4, 130.3, 129.8, 129.5, 129.0, 128.8, 128.7, 128.4, 126.48, 120.8, 119.7, 119.6, 118.6, 109.4, 98.9. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -138.7 (dd, J = 61.1, 30.2 Hz), -147.7 (dd, J = 54.2, 26.0 Hz). HRMS (APCI): (the molecule fragmented through ether bridge during ionization) m/z calcd. for C<sub>15</sub>H<sub>8</sub>BBr<sub>3</sub>F<sub>2</sub>N<sub>2</sub>O [M – H]<sup>-:</sup> 515.8242; found: 515.8143.

**Dyad 3**; Black iridescent solid, purple in solution. Yield: 72%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.43 (s, 1H), 7.88–7.72 (m, 2H), 7.61 – 7.36 (m, 13H), 7.17 (d, J = 8.6 Hz, 1H), 7.09 (s, 1H), 6.94 (s, 1H), 6.88 (d, J = 4.1 Hz, 1H), 6.81 (d, J = 3.5 Hz, 1H), 6.73 (s, 1H), 6.61 (d, J = 4.0 Hz, 1H), 6.46 (s, 1H), 6.33 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.7, 155.9, 155.4, 154.54, 146.0, 143.1, 139.4, 138.8, 137.1, 135.8, 134.6, 134.0, 133.8, 133.0, 132.5, 130.5, 130.4, 130.2, 130.2, 129.7, 128.9, 128.6, 128.4, 127.1, 126.6, 125.6, 125.5, 125.5, 121.6, 120.9, 119.3, 118.9, 118.8, 118.4, 111.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  – 138.9 (dd, J = 60.9, 29.9 Hz), –140.7 (dd, J = 65.9, 33.2 Hz).

HRMS (APCI): m/z calcd. for  $C_{40}H_{25}B_2Br_2F_4N_5O [M-H]^{-1}$  844.0548; found: 844.0583.

#### **Declaration of Competing Interest**

The authors declare no conflict of interest.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2019. 112073.

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