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PII: S0143-7208(13)00052-1

DOI: 10.1016/j.dyepig.2013.02.004

Reference: DYPI 3849

To appear in: Dyes and Pigments

Received Date: 25 December 2012

Revised Date: 30 January 2013

Accepted Date: 2 February 2013

Please cite this article as: Shandura MP, Yakubovskyi VP, Zatsikha YV, Kachkovsky OD, Poronik YM, Kovtun YP, Anionic, cationic and merocyanine polymethine dyes based on dipyrromethene core, *Dyes and Pigments* (2013), doi: 10.1016/j.dyepig.2013.02.004.

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#### Anionic, cationic and merocyanine polymethine dyes based on dipyrromethene core

Both symmetrical anionic polymethine dye which is derived from the boron difluoride form of the dipyrromethene (BODIPY) and the corresponding symmetrical cationic dye derived from the cationic form of the dipyrromethene have been obtained on the identical atomic framework. Their spectral properties and  $\pi$ -electronic structure suggest that these long-wavelength absorbing dyes are closely related. On the contrary, the non-symmetrical compounds belong to the different types of dyes, namely merocyanines in the case of boron dipyrromethene complexes, and non-symmetrical cationic dyes for salt-like compounds. Each of these types possesses a distinct complex of spectral properties.

Keywords: BODIPY compounds, Polymethine dyes, Dipyrromethene compounds, Longwavelength dyes, Merocyanine

#### **1. Introduction**

Dyes derived from boron dipyrromethene (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene, BODIPY, BDP) have been attracting considerable attention over the past two decades. The everincreasing interest in this type of compound stems from their excellent thermal, chemical, and photochemical stability, high molar absorption coefficients, high fluorescence quantum yields, general insensitivity to both solvent polarity and pH, large two-photon cross-section for multiphoton excitation, the lack of ionic charge and good solubility [1-6].



Scheme 1. A number of possible forms of dipyrromethenes

The fundamentals of BODIPY chemistry were established by Alfred Treibs in the 50's and 60's of the 20th century [7-10]. In spite of facilities available 60 years ago, notably those works (though sometimes not clear enough) showed a large variety of possible dipyrromethene forms, such as free bases (A), salts (B-type cations), boron dipyrromethenes (C) and its derivatives anionic (D) and cationic (E) forms (Scheme 1). In our recent reports we were able to enhance the concept of

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- ► The symmetrical anionic dye derived from BODIPY core was synthesized.
- Symmetrical cationic dye derived from the cationic form of dipyrromethene was obtained.
- ▶ Both dyes have absorption maxima around 800 nm.

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#### **1. Introduction**

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Scheme 1. A number of possible forms of dipyrromethenes

The fundamentals of BODIPY chemistry were established by Alfred Treibs in the 50's and 60's of the 20th century [7-10]. In spite of facilities available 60 years ago, notably those works (though sometimes not clear enough) showed a large variety of possible dipyrromethene forms, such as free bases (**A**), salts (**B**-type cations), boron dipyrromethenes (**C**) and its derivatives anionic (**D**) and cationic (**E**) forms (Scheme 1). In our recent reports we were able to enhance the concept of

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possible dipyrromethene forms. A number of *meso-* [11,12] and  $\alpha$ -BODIPY-derived [13] polymethine dyes of merocyanine type were obtained. In these cases, BODIPY core behaves as electron-withdrawing end group in the donor-acceptor merocyanine chromophore system, i.e. brings partial negative charge, whereas in classical dipyrromethene dyes partial positive charge is delocalized within BODIPY chromophore. There is a set of indirect evidences in favor of this claim, but only synthesis can clearly prove the existence of the anionic form of BODIPY. This work is addressed to the synthetic corroboration of the above-mentioned hypothesis. Moreover, compounds of this family could be long-wavelength dyes that are of interest for various applications ranging from materials science to biology and medicine [14-21].

#### 2. Results and Discussion

In our previous work [11] we failed to synthesize dye a **2a**, particularly under conditions mentioned in Scheme 2 (acetic anhydride in the presence of triethylamine). The reason appears to be the following: the reaction was carried out at the increased temperature (the usual conditions for cyanine condensations) [22-26]. Probably, during the heating in acetic anhydride the fluorine atoms of BODIPY undergo the substitution with the acetate anion, exemplified in the report [27]. Acetyloxy groups decrease the stability of the BODIPY, resulting in the cleavage of the complex that was demonstrated on the other examples [11]. While carrying out the condensation of compound **1a** with its anilidovinyl derivative at room temperature, it gave rise to dye **2a** in a high yield (Scheme 2). The merocyanine dyes **3a-6a** described in our previous report [11] are also shown in Scheme 2.

2



Scheme 2. Synthetic route to dyes 2a–6a.

Evidently, the most general form of dye **2a** representation is the form shown in Scheme 2. Nevertheless, the anionic part of this dye can be described with a set of mesomeric forms; some of them are shown in Scheme 3. The last resulting form, though roughly, depicts the end nucleus which is typical for cyanine dyes chemistry. In this sense, the latter helps to consider the boron dipyrromethene fragment as the entire terminal group of the polymethine chromophore system.



In addition, the alternative series of dyes **2b-6b** were obtained from dipyrromethene salt **1b** (Scheme 4). The symmetrical dye **2b** was synthesized analogously to the work of Treibs [10] by the condensation of the dipyrromethene **1b** with triethylorthoformate. Other non-symmetrical cationic dyes **3b-6b** have been obtained by the reaction of compound **1b** with corresponding hemicyanines in the conditions typical for cyanine condensations [22-26]. The absorption spectra of the dyes **2a-5a** are shown in Fig. 1, dyes **2b-5b** in Fig. 2, and their spectral characteristics in Tab. 1, respectively. It is worth mentioning that the dyes **2b-6b** undergo the dissociation in dilute solutions and

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subsequently decompose. By this reason, quantitative spectra of these dyes were measured with the addition of 5% acetic acid.

Some of the cationic dyes can be transformed into to the corresponding merocyanines. For example, the formation of free base **3c** can be observed on treating salt **3b** solutions with bases, however, the compound **3c** cannot be isolated due to its instability. On the other hand, the treating with the base in the presence of borontrifluoride etherate gives rise to the formation of merocyanine. The stability of free bases tends to decrease on the increase of electron-donor properties of the second end moiety, making it more difficult to undergo such a reaction. Most of all, this is related to the symmetrical dyes. There were no traces of dye **2a** observed on treating the compound **2b** with bases in the presence of boron trifluoride etherate due to the decomposition of the free base.



### Figure 1. Absorption spectra of compounds 2a - 5a in acetonitrile (C = 1 x 10<sup>-5</sup> M)

One can see the similarity of the absorption spectra of the dyes **2a** and **2b**. Both have quite intense long-wavelength bands with the absorption maxima around 800 nm and the weak absorption bands with maxima around 600 nm. The quantum-chemical analysis was carried out in order to estimate their spectral properties. The quantum-chemical calculations were performed with the Gaussian 03 program package [28]. The ground state geometry was optimized by the DFT/6-31(d,p)/B3LYP method. The TD-SCF-AM1 method was employed to obtain the characteristics of the electron transitions. We could not use the "spectroscopic" ZINDO method owing to the absence of the boron atom parameters.



Figure 2. Absorption spectra of compounds 2b - 5b in acetonitrile containing 5% of acetic acid (C = 1 x  $10^{-5}$  M)

As shown by the optimized geometry of the symmetrical anionic dye 2a and the cationic dye 2b, both molecules are not planar due to spatial hindrances. The calculations show that atoms of the polymethine chain in both cases are set approximately at 5° torsion angles. Phenyl substituents in the cationic dye 2b are turned out of the dipyrromethene framework plane at an angle of  $20^\circ$ , but in the anionic dye 2a they are set at  $32^\circ$  angle due to the additional spatial hindrance of the BF<sub>2</sub> bridge. The end groups as the entire molecular fragment in the dye 2b are turned out of the plane of  $16^\circ$ .

The performed calculations show that the transition from the cationic dye 2b to its anionic analogue 2a hardly alters the C-C bond length in the chromophores of symmetrical dyes The optimized C-C bond lengths ( $l_v$ ) along the conjugated system ranging from the *meso*-position atom of the polymethine chain, through C-atoms of the pyrrole and benzene rings to the atom at the *p*-

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position of the phenyl substituent are shown in Figure 3a (for convenience, an average value of  $l_v$  was taken for the equivalent positions in the branched part of end groups). As one can see, the alteration of the average charge hardly changes C-C bond lengths in the polymethine chain or in the end moieties, namely in the  $\pi$ -electronic system of the dye chromophore. Analogously, in the chromophore systems of the dyes **2a** and **2b** charges of the atoms  $q_{\mu}$  appeared to be almost equal, although they differ in total charge. The calculated charges of C-atoms are presented in Fig. 3b. The analysis of calculations suggests the significant alternation of the electron density along the chromophore chain which is typical for polymethine dyes not being affected by the sign of the total charge. The amplitude of the alternation is almost equal. The additional information about the similarity of the electron density redistribution upon the transition to the excited state. The diagram of the change of electron density upon the excitation is shown in Fig. 3c:  $\Delta q_{\mu} = q_{\mu}^* - q_{\mu}^0$ , where the superscripts \* and <sup>0</sup> denote the excited and the ground states respectively. The analysis shows that the values of the parameter  $\Delta q_{\mu}$  are really close, especially for atoms of the polymethine chain.

Dye	CH <sub>3</sub> CN			
	$\lambda_{abs},$	$\epsilon, \mathrm{M}^{-1} \cdot \mathrm{cm}^{-1}$	fwhm <sup>*</sup> , cm <sup>-1</sup>	
2a	810	138 000	1348	
2b	805	94 000	1074	
3a ([11])	671	111 000	1656	
3b	663	82 000	2575	
4a ([11])	683	116 000	1595	
4b	606	49 000	4065	
5a ([11])	705	117 000	1403	
5b	607	52 000	3833	
6a ([11])	752	74 000	2184	
6b	768	115 000	1099	

Table 1 Optical	properties	of the prepared	compounds
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fwhm = full width at half-maximum height.





**Figure 3.** Bond CC-lengths (a), charges in ground state (b) and charge changes upon excitation (c) at carbon atoms in chromophore of dyes 2a(---) and 2b(--).

It is worth saying that signs of alteration of the electron density also match, and this means that the transition occurs between the orbitals of the same symmetry. Fig. 4 shows, that the shapes of the frontier and adjacent to them molecular orbitals of the cationic and anionic dyes **2b** and **2a** are also in good agreement. In particular, the HOMO-1 and HOMO orbitals are practically degenerated and can be considered as local orbitals extended only within the terminal groups. They have their nodes at the carbon atoms connected with open polymethine chain. As the result, these local MOs of both terminal groups cannot interact with each other in symmetrical molecules **2a** and **2b**.



Figure 4 Positions of electron levels and electron transitions in symmetrical cationic (2b) and anionic (2a) dyes

Fig. 4 clearly demonstrates that the main difference between symmetrical dyes 2a and 2b is the dramatic shift of molecular levels upwards during the change of the total charge from positive to negative. The peculiar localization of molecular levels on an energy scale of the anionic polymethine dyes has already been noticed by us for dioxaborines [29]. Meanwhile, the abovementioned shift of the frontier and adjacent to them levels does not affect the nature of the highest electronic transitions (Fig. 4). For the pair of symmetrical dyes the calculations demonstrate comparable values of wavelengths and dipole moments for the corresponding electronic transitions, which are in good agreement with the spectral data. Therefore, the highest transitions in cationic and anionic dyes involve the same MOs, and the calculated absorption spectra well match with the experimental spectra. Evidently,  $\pi$ -systems of the cationic and anionic dyes 2b and 2a possess the similar electronic structure and differ only in total charge.

Thus, the long-wavelength absorption bands in the spectra of both cationic and anionic symmetrical dyes are connected with the first electron transitions involved frontier orbitals:  $| \text{HOMO}\rightarrow\text{LUMO} \rangle$ . These MOs have the opposite symmetry, the  $| S_0 \rightarrow S_1 \rangle$  transition is polarized along the polymethine chromophore; its oscillator strength is quite large, that is in agreement with high intensity of the first spectral band. The next spectral band, weakly intense for both symmetric dyes, corresponds to two practically degenerated electron transitions from two local orbitals to LUMO. The splitting of the  $| S_0 \rightarrow S_2 \rangle$  and  $| S_0 \rightarrow S_3 \rangle$  is negligible (3-5 nm) although the oscillator strengths  $f_2$  and  $f_3$  differ significantly. Also, the fourth transition involves the delocalized highest

occupied level and the next vacant level; these orbitals have equal symmetry and, as the result, this transition has very low dipole moment that explains weak absorption in the spectral region around 400 nm.



Figure 5. Absorption spectra of compounds 5a - 6a in acetonitrile and of compounds 5b - 6b in acetonitrile containing 5% of acetic acid (C = 1 x  $10^{-5}$  M)

In contrast to symmetrical dyes, each type of non-symmetrical derivatives possesses a distinct complex of spectral properties. In the first case, there is a set of merocyanines with BODIPY as the weak electron-withdrawing end nucleus, which gives rise to certain spectral consequences, thoroughly analyzed [11-13]. The derivatives of **b**-type are non-symmetrical cationic polymethine dyes with the dipyrromethene fragment acting as the weak electron-donor end nucleus. Therefore, dye **3b**, containing the weak electron-donor indoline end nucleus exhibits the most intense and the narrowest long-wavelength band (Figure 2). This means that the structure of this dye is the most electron-symmetrical within **3b-5b** series.

The difference between the dyes of **a** and **b** series can be well illustrated by spectral properties of dyes consisting of end nuclei of distinct electron donor-acceptor ability (Fig. 5). In the case of dye **6a**, a derivative of the weak electron-donor benz[c,d]indole end nucleus, the broad and weak absorption band is observed, hence, the structure somewhat loses the cyanine character and gains that of polyene, while dye **6b** demonstrates the narrow and intense long-wavelength absorption, suggesting its electron-symmetrical state. In the case of dyes with the electron rich quinoline nucleus, the opposite spectral effects are observed. The merocyanine **5a** shows narrow and intense absorption, whereas the absorption of the cationic dye **5b** is broad and weak which suggests the significant electronic asymmetry.

#### **3.** Conclusions

In conclusion, for the first time we have obtained a very unusual structure – the symmetrical anionic dye derived from BODIPY core. The possibility of existence of the anionic dipyrromethene form has been predicted in the basic works of Treibs, but later this idea was not further developed. The symmetrical cationic dye derived from the cationic form of dipyrromethene also has been obtained. The spectral properties and parameters resulted from the quantum-chemical analysis suggest that this dye is closely related to the anionic analogue, based on the same framework. The only difference between the symmetrical dyes of both types is the energy of the molecular orbitals which is higher for the anionic dye. This case is of theoretical interest, as first cationic and anionic polymethine dyes on the same framework were compared. Moreover, these compounds are intensive long-wavelength dyes.

Unsymmetrical dyes synthesized belong to completely different types merocyanines in the case of boron dipyrromethene complexes, and non-symmetrical cationic dyes for salt-like compounds. The dipyrromethene end moiety in the former case behaves as the weak electron-acceptor fragment, while in the latter case as the weak electron-donor which in both cases gives rise to its own set of spectral properties and regularities.

All dyes synthesized are practically not fluorescent.

#### 4. Experimental

**General:** The absorption spectra were recorded with a Shimadzu UV-3100 spectrophotometer. <sup>1</sup>H spectra were recorded with a Varian VXR-300 spectrometer and <sup>13</sup>C NMR spectra were obtained on a Bruker Avance 500 spectrometer. Chemical shifts are given in ppm and were referenced using residual signals of the solvent as internal standard (<sup>1</sup>H: CHCl<sub>3</sub>, 7.26 ppm and [D5]DMSO, 2.50 ppm. <sup>13</sup>C: [D6]-DMSO, 39.5 ppm). LC–MS measurements were performed with a liquid chromatography–mass spectrometric system consisting of an Agilent 1100 Series HPLC instrument equipped with a diode matrix detector and an Agilent LC/MSD SL mass-selective detector. The atmospheric pressure chemical ionization (APCI) technique with detection of positive ions was used.

#### Dye 2a

Compound **1a** (0.18 g, 0.5 mmol) and 4,4-difluoro-3,5-diphenyl-8-(2-N-phenylaminoethen-1-yl)- 4bora-3a,4a-diaza-s-indacene [11] (0.23 g, 0.5 mmol) was added to mixture of  $Ac_2O$  (1 mL) and triethylamine (1 mL). The reaction mixture was stirred for 2 h at room temperature. Then reaction mixture was diluted with i-PrOH and stirred additionally 15 min. Crude product was filtered, washed with i-PrOH and recrystallized from i-PrOH. Yield 0.23 g, 56%; m.p. > 250 °C. <sup>1</sup>H NMR ([D6]DMSO):  $\delta$  = 8.83 (br. s, 1 H, <sup>+</sup>NH), 8.43 (t, *J* = 13.2 Hz, 1 H, CH), 7.69 (d, *J* = 6.8 Hz, 8 H, ArH), 7.42 (d, *J* = 13.2 Hz, 2 H, CH), 7.36 (t, *J* = 6.8 Hz, 8 H, ArH), 7.28 (t, *J* = 6.8 Hz, 4 H, ArH), 7.18 (d, *J* = 3.6 Hz, 4 H, pyrrole H), 6.53 (d, *J* = 3.6 Hz, 4 H, pyrrole H), 3.08 (q, *J* = 7.6 Hz, 6 H, CH<sub>2</sub>), 1.16 (t, *J* = 7.6 Hz, 9 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR ([D6]DMSO):  $\delta$  = 9.2, 46.3, 116.6, 119.4, 119.5, 120.2, 120.3, 127.7, 128.2, 129.0, 133.9, 135.1, 139.9, 147.0, 148.1 ppm. Anal. calcd. for C<sub>51</sub>H<sub>47</sub>B<sub>2</sub>F<sub>4</sub>N<sub>5</sub>. C, 74.02; H, 5.72; N, 8.46. Found C, 74.21; H, 5.79; N, 8.51.

#### Dye 2b

Triethyl orthoformate (0.25 g, 1.69 mmol) was added to suspension of compound **1b** (0.25 g, 0.5 mmol) in Ac<sub>2</sub>O (2 mL) and the reaction mixture was heated at 100 °C for 30 min. After cooling to room temperature, the product was filtered and washed with Ac<sub>2</sub>O. Yield 0.11 g, 52 %; m.p. > 250 °C. <sup>1</sup>H NMR ([D6]DMSO):  $\delta$  = 12.24 (s, 4 H, NH), 8.05 (t, *J* = 13.2 Hz, 1 H, CH), 7.92 (d, *J* = 6.6 Hz, 8 H, ArH), 7.60 (d, *J* = 13.2 Hz, 2 H, CH), 7.35-7.53 (m, 18 H, 14 ArH, 4 pyrrole H), 6.99-7.13 (m, 6 H, 2 ArH, 4 pyrrole H), 2.28 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR ([D6]DMSO):  $\delta$  = 21.3, 112.3, 126.0, 128.7, 129.0, 129.4, 130.5, 130.8, 131.1, 133.2, 134.5, 135.1, 136.7, 138.6, 142.3, 145.5 ppm. Anal. calcd. for C<sub>52</sub>H<sub>42</sub>N<sub>4</sub>O<sub>3</sub>S. C, 77.78; H, 5.27; N, 6.98. Found C, 77.89; H, 5.35; N, 7.07

#### Dye 3a

To the suspension of dye **3b** (0.22 g, 0.33 mmol) in  $BF_3 \cdot Et_2O$  (2 mL)  $Et_3N$  (0.33 g, 3.3 mmol) was added, the reaction mixture was refluxed for 5 min and then was cooled to room temperature, diluted with EtOH and precipitate was filtered. Yield 0.04 g, 23 %. All characteristics are identical to those from ref. [11].

#### General Procedure for the Synthesis of Dyes 3b – 6b:

Compound **1b** (0.5 mmol) was added to the corresponding hemicyanine (0.55 mmol) in  $Ac_2O$  (2 mL) and the reaction mixture was heated at reflux for 2–3 min. After cooling to room temperature, the crude product was filtered and washed with HOAc.

#### Dye 3b

Yield 0.18 g, 54 %; m.p. > 250 °C. <sup>1</sup>H NMR ([D6]DMSO):  $\delta$  = 12.09 (s, 2 H, NH), 8.26 (t, *J* = 13 Hz, 1 H, CH), 7.95 (d, *J* = 6.6 Hz, 4 H, ArH), 7.34-7.64 (m, 13H), 7.11 (d, *J* = 3.8 Hz, 2 H, pyrrole H), 6.94-6.6.99 (m, 3 H, 2 ArH, 1 CH), 6.81 (d, *J* = 3.8 Hz, 2 H, pyrrole H), 3.83 (s, 3 H, NCH<sub>3</sub>), 2.29 (s, 3 H, CH<sub>3</sub>), 1.60 (s, 6 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR ([D6]DMSO):  $\delta$  = 21.3, 27.1, 32.8, 50.3, 109.8, 113.3, 119.8, 120.9, 121.2, 123.0, 125.2, 126.0, 127.2, 128.6, 129.4, 132.5, 138.1, 139.6, 140.6, 141.9, 142.0, 142.9, 146.2, 153.5, 177.3 ppm.

#### Dye 4b

Yield 0.17 g, 53 %; m.p. > 250 °C. <sup>1</sup>H NMR ([D6]DMSO):  $\delta$  = 11.95 (s, 2 H, NH), 8.18 (d, *J* = 8.1 Hz, 1 H, ArH), 8.04 (d, *J* = 8.4 Hz, 1 H, ArH), 7.85-7.98 (m, 5 H, 4 H, ArH, 1 CH), 7.75 (t, *J* = 8.1 Hz, 1 H, ArH), 7.62 (t, *J* = 8.4 Hz, 1 H, ArH), 7.42-7.50 (m, 4 H, ArH), 7.25-7.36 (m, 3 H, 2 ArH, 1 CH), 7.16 (d, *J* = 11.7 Hz, 1 H, CH), 6.88 (d, *J* = 3.8 Hz, 2 H, pyrrole H), 6.65 (d, *J* = 3.8 Hz, 2 H, pyrrole H), 4.12 (s, 3 H, NCH<sub>3</sub>) ppm. <sup>13</sup>C NMR ([D6]DMSO):  $\delta$  = 35.4, 109.4, 110.4, 110.9, 116.0,

118.8, 119.5, 120.5, 125.3, 126.2, 127.5, 128.2, 129.4, 131.7, 132.2, 137.7, 139.2, 142.5, 149.4, 169.8 ppm.

#### Dye 5b

Yield 0.18 g, 53 %; m.p. > 250 °C. <sup>1</sup>H NMR ([D6]DMSO):  $\delta$  = 11.83 (s, 2 H, NH), 8.63 (d, *J* = 9.3 Hz, 1 H, ArH), 8.35 (d, *J* = 8.7 Hz, 1 H, ArH), 8.13 (d, *J* = 8.1 Hz, 2 H, ArH), 8.08 (t, *J* = 8.1 Hz, 1 H, ArH) 7.78-7.92 (m, 5 H), 7.40-7.50 (m, 6 H), 7.24-7.34 (m, 5 H), 7.10 (d, *J* = 8.1 Hz, 2 H, ArH), 6.87 (d, *J* = 3.7 Hz, 2 H, pyrrole H), 6.54 (d, *J* = 3.7 Hz, 2 H, pyrrole H), 4.36 (s, 3 H, NCH<sub>3</sub>), 2.29 (s, 3 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR ([D6]DMSO):  $\delta$  = 21.3, 44.4, 108.6, 109.7, 114.3, 116.7, 117.7, 119.5, 120.1, 122.0, 125.3, 126.0, 127.5, 128.5, 129.1, 130.0, 132.2, 134.6, 135.3, 135.8, 137.5, 138.1, 139.3, 143.9, 146.3, 147.0, 152.4 ppm.

#### Dye 6b

Yield 0.26 g, 73 %; m.p. > 250 °C. <sup>1</sup>H NMR ([D6]DMSO):  $\delta$  = 12.32 (s, 2 H, NH), 8.61 (t, *J* = 13.2 Hz, 1 H, CH), 8.30 (d, *J* = 8.1 Hz, 1 H, ArH), 8.12 (d, *J* = 7.5 Hz, 1 H, ArH), 8.00 (d, *J* = 4.5 Hz, 4 H, ArH), 7.89-7.93 (m, 2 H, ArH), 7.74-7.82 (m, 3 H, ArH, 1 CH), 7.39-7.60 (m, 6 H), 7.24 (d, *J* = 13.2 Hz, 1 H, CH), 7.14 (*J* = 3.7 Hz, 2 H, pyrrole H), 7.03 (d, *J* = 3.7 Hz, 2 H, pyrrole H), 4.50 (q, *J* = 7.8 Hz, 2 H, CH<sub>2</sub>), 1.87 (q, *J* = 7.8 Hz, 2 H, CH<sub>2</sub>), 1.47 (q, *J* = 7.8 Hz, 2 H, CH<sub>2</sub>), 0.98 (t, *J* = 7.8 Hz, 2 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR ([D6]DMSO):  $\delta$  = 14.2, 21.3, 31.5, 44.6, 112.2, 112.4, 123.5, 124.7, 126.2, 127.7, 128.3, 129.5, 129.9, 130.2, 130.3, 131.2, 132.1, 132.9,133.5, 134.2, 136.0, 137.7, 139.1, 141.2, 142.5, 152.5, 156.2 ppm.

#### Acknowledgment

This work was partially financially supported by the NATO "Science for Peace" program, project NUKR.SFPP 984189.

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12

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► The symmetrical anionic dye derived from BODIPY core was synthesized.

Symmetrical cationic dye derived from the cationic form of dipyrromethene also has been obtained.

► Both dyes have quite intense long-wavelength bands with the absorption maxima around 800 nm.

► The only difference between the symmetrical dyes of both types is the energy of the molecular orbitals, which is higher for the anionic dye.