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Oxidative C-H/C-H Coupling of Dipyrromethanes with Azines by TiO$_2$-Based Photocatalytic System. Synthesis of New BODIPY Dyes and Their Photophysical and Electrochemical Properties

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Abstract: Oxidative C-H/C-H coupling reactions of dipyrromethanes with azines in the presence of a heterophase oxidative photocatalytic system (O$_2$/TiO$_2$/visible light irradiation) were carried out. As a result of cyclization of obtained compounds with boron trifluoride etherate, new hetaryl-containing derivatives of 4,4-difluoro-4-boron-3a,4a-diaza-s-indacene were synthesized. For the obtained compounds, absorption and luminescence spectra, quantum yields of luminescence as well as cyclic volt-amperograms were measured.

Keywords: dipyrromethane; BODIPY; azine; TiO$_2$; C-H/C-H couplings; ONSH; photocatalysis

1. Introduction

4,4-Difluoro-4-boron-3a,4a-diaza-s-indacene derivatives (I, Figure 1) represent an important class of organic luminophores. The first publication on the synthesis of some derivatives of the presented series appeared in 1968 [1]. Further, it was shown that various 1,2,3- and 5,6,7-methyl- and ethyl-substituted derivatives of compound I have high quantum yields of luminescence in various solvents [2].

Figure 1. 4,4-difluoro-4-boron-3a,4a-diaza-s-indacene (I), 4,4-difluoro-1,3,5,7-tetramethyl-4-boron-3a,4a-diaza-s-indacene (II).
It was later found that derivatives of compound I can be useful for biological applications [3], as dyes for lasers [4], including as fluorescent labels in biology [5]. Currently, the name given to this class of compounds is BODIPY [6,7]. Most often, the term BODIPY refers to compound I [8–12] and sometimes to its 1,3,5,7-tetramethyl-substituted derivative (II, Figure 1) [6,13,14]. These dyes have similar optical properties. However, their meso-phenyl-substituted derivatives can have very different photoluminescence quantum yields because the methyl substituents at the positions 1 and 7 sterically block the rotation of the phenyl ring [15]. It should be noted that compound I was synthesized only in 2009 [8,9,16]. In derivative I, all atoms except for the fluorines lie almost in the same plane [8,9]. The optical properties of this compound are weakly dependent on solvent [8,17]. The introduction of various substituents into structure I allows varying these properties and make them dependent on the medium, which is in demand in various applications [10]. BODIPY derivatives are currently widely used as fluorescent dyes [18], chemosensors [19,20], fluorescent probes [21,22], laser dyes [23,24] and as compounds for photodynamic therapy [25–27].

BODIPY dyes with aromatic and heteroaromatic substituents, which are used for in vivo imaging, are promising for practical applications since they reduce the harmful effect of radiation on living systems, allow it to penetrate deeper into organic tissues and reduce autofluorescence of biological objects [28]. Therefore, new methods of obtaining and studying properties of various derivatives of BODIPY fluorophores are being actively developed [28–30].

Methods for the synthesis of heteroaryl derivatives of BODIPY in most cases are based on the one hand on multistep methods for the construction of heteroaryl-substituted pyrrole synthons [31,32] and on the other hand on the use of transition metal-catalyzed cross-coupling reactions of halogen derivatives of BODIPY with nitrogen-containing heterocycles [33–37]. These transformations require the use of metal-based catalysts and additional functionalization of starting reagents. In addition, a significant disadvantage is a mandatory additional purification of the target product. A more atom-economical method of incorporating functional groups into the BODIPY nucleus at positions 3,5 is an oxidative substitution of \( \alpha \)-hydrogen by fragments of C-, N-nucleophiles [38]. In addition, examples of radical C-H arylation/heteroarylation of BODIPY dyes using aryldiazonium salts are known [39,40], ferrocene is used to generate aryl radical species in these transformations.

In our previous works, we proposed the oxidative C-H/C-H couplings of azines with aromatic and heteroaromatic nucleophiles, including pyrrole, in the presence of the heterogeneous air \( \text{O}_2/\text{TiO}_2 \) catalyst/light irradiation photocatalytic system [41–43]. The method allows one to selectively perform direct C-H functionalization of various substituted and unsubstituted mono-, di- and triazines as well as benzoannulated analogs. This work reports for the first time a new synthetic technique for modifying dipyrromethanes as the main starting material for BODIPY dyes via direct oxidative C-H functionalization. It was found that dipyrromethanes undergo direct C-H/C-H coupling reactions with azines under aerobic conditions in the presence of a heterogeneous TiO\(_2\) photocatalyst. As a result of further cyclization of obtained compounds, new mono- and diazirinyl-substituted BODIPY dyes were obtained, absorption and luminescence spectra, and quantum yields of luminescence in tetrachlorethylene and benzene, as well as cyclic voltamperograms in dichloromethane were measured.

2. Results
2.1. Synthesis

Starting dipyrromethanes 3a–e were synthesized according to previously published procedures [44–47] by condensation of aldehydes 1a–e with an excess of pyrrole 2 at room temperature upon activation with trifluoroacetic acid (Scheme 1).
It was found that, similar to the interaction of azines with pyrroles and indoles [41–43], reactions of oxidative photocatalyzed C-H/C-H coupling of azines with dipyrromethanes under aerobic conditions can be successfully carried out. TiO$_2$ obtained by a sol-gel method followed by annealing at 800 °C for 1 h in a hydrogen atmosphere was used as a photocatalyst. This catalyst was previously studied in the reaction of oxidative coupling of acridine with indole [48]. It was found that in its presence the reaction proceeds upon irradiation in the visible light range (Xe lamp, 5000 K, 35 W, using a yellow light filter, λ > 480 nm). Moreover, the synthesized TiO$_2$ afforded the target product with a high yield compared to the commercially available TiO$_2$ catalysts, Degussa P25 and Hombifine N. Optimization of the synthesis conditions was carried out using acridine 4a having one reaction center and 5-(4-bromophenyl)dipyrromethane 3a as an appropriate (simple and convenient) model (Table 1). Experiments were initially carried out in acetic acid upon irradiation with light in the visible range (EvoluChem™ LED, Beverly, MA, USA, 18 W, 425 nm) under aerobic conditions in the presence of nanostructured TiO$_2$. It was found that as a result of the reaction at room temperature, monosubstituted dipyrromethane 5a is formed in a yield of 23%, while under refluxing resinification of the reaction mass occurs, which is probably due to the thermal instability of these compounds in an acidic medium. Replacing acetic acid with trifluoroacetic acid or using boron trifluoride etherate as a Lewis acid did not lead to the desired result. In the course of further optimization, the reaction was carried out in dichloromethane with the addition of 20 equiv. of acetic acid in the presence of the oxidizing system air O$_2$/TiO$_2$ catalyst/light irradiation. It was found that, as a result, compound 5a is formed at room temperature, and when the reaction mass is heated to 50 °C, disubstituted dipyrromethane 5b is formed in 48% and 63% yields, respectively. Varying the reaction temperature from 30 °C to 45 °C resulted in a mixture of compounds 5a and 5b. Thus, the optimal conditions for carrying out oxidative C-H/C-H couplings of azines with dipyrromethanes is performing the reactions in dichloromethane in the presence of 20 equiv. of acetic acid.

We found that compounds 3a–e react with azines 4a–c under aerobic conditions in the presence of the TiO$_2$ photocatalyst. In order to increase the activity of TiO$_2$ and avoid coagulation of nanosized particles, the mixture of the starting compounds was sonicated for 5 min. The reactions of dipyrromethanes 3a–e (1 equiv.) with acridine 4a and 6-phenyl-[1,2,5]oxadiazolo[3,4-b]pyrazine 4b (2 equiv.) were carried out in dichloromethane in the presence of 20 equiv. of acetic acid for 5 h (Table 2).
Table 1. Optimization of reaction conditions 1.

| Entry | Acid       | Solution | Temperature, °C | 5a [%] 2 | 5b [%] 2 |
|-------|------------|----------|-----------------|----------|----------|
| 1     | CH₃COOH    | -        | rt              | 23       | 0        |
| 2     | CH₃COOH    | -        | 120             | 0        | 0        |
| 3     | CF₃COOH    | CH₂Cl₂   | rt              | 0        | 0        |
| 4     | BF₃OEt₂    | CH₂Cl₂   | rt              | 0        | 0        |
| 5     | CH₃COOH    | CH₂Cl₂   | rt              | 48       | 0        |
| 6     | CH₃COOH    | CH₂Cl₂   | 30              | 40       | 10       |
| 7     | CH₃COOH    | CH₂Cl₂   | 45              | 10       | 40       |
| 8     | CH₃COOH    | CH₂Cl₂   | 50              | 0        | 63       |
| 9     | CH₃COOH    | CH₂Cl₂   | >50             | 0        | 0        |

1 General conditions: 3a (0.5 mmol), 4a (1 mmol), TiO₂ catalyst (10 mass%), an appropriate acid and solvent were irradiated with a 425 nm blue LED (18 W; 33 mW/cm²) with air oxygen bubbling through the reaction mixture. 2 Isolated yields.

It was shown that 5-(4-bromophenyl)dipyrromethane 3a, 5-(4-methylphenyl)dipyrromethane 3b and 5-(4-N,N′-dimethylaminophenyl)dipyrromethane 3c react with 4a at room temperature to form monosubstituted dipyrromethanes 5a,d,f (Table 2). The coupling reactions of 5-(4-nitrophenyl)dipyrromethane 3d and 5-(4-cyanophenyl)dipyrromethane 3e with 4a under similar conditions lead to the formation of dissubstitution products 5i,j. When the temperature rises to 50 °C, dipyrromethanes 3a–e react with acridine 4a to form dissubstitution products 5b,e,g. Yields of compounds 5 range from 38% to 79%.

In turn, 6-phenyl-[1,2,5]oxadiazolo[3,4-b]pyrazine 4b undergoes the coupling reactions with dipyrromethanes 3a,c at room temperature with the formation of exclusively dissubstituted products 5c,h in 57% and 36% yields, respectively (Table 2). However, in the case of 5-(4-methylphenyl)dipyrromethane 3b, 5-(4-nitrophenyl)dipyrromethane 3d and 5-(4-cyanophenyl)dipyrromethane 3e, the target products could not be obtained. It was found that dipyrromethanes 3a–e easily react with acridine hydrochloride 4e in n-BuOH at room temperature and with air bubbling for 5 h using the TiO₂ photocatalyst to form compounds 5k–o in 80–85% yields (Table 2).

Treatment of hydrochlorides 5k–o with an aqueous solution of NaOH leads to the formation of products 5b,e,g,i,j. The NMR spectra of compounds 5a–j are available in Supplementary Materials. When using other azines (pyridine, pyrimidine, quinoxaline, quinazoline, 3,6-diphenyltriazine, quinoxalone) in the reaction under similar conditions, the target products could not be isolated.
Table 2. Synthetic procedure and yields of dipyrromethane 5a–o.

| Compound | R₁  | R₂        | R₃         | Additive       | Solution     | Temperature, °C | Yield, % |
|----------|-----|-----------|------------|----------------|--------------|-----------------|----------|
| 5a       | Br  | acridine  | H          | CH₃COOH       | CH₂Cl₂       | rt              | 48 †     |
| 5b       | Br  | acridine  | acridine   | CH₃COOH       | CH₂Cl₂       | 50              | 63 †     |
| 5c       | Br  | acridine  | 6-phenyl-[1,2,5]oxadiazolo[3,4-β]pyrazine | CH₃COOH       | CH₂Cl₂       | rt              | 57 †     |
| 5d       | CH₃ | acridine  | H          | CH₃COOH       | CH₂Cl₂       | rt              | 60 †     |
| 5e       | CH₃ | acridine  | acridine   | CH₃COOH       | CH₂Cl₂       | 50              | 76 †     |
| 5f       | NMe₂| acridine  | H          | CH₃COOH       | CH₂Cl₂       | rt              | 59 †     |
| 5g       | NMe₂| acridine  | acridine   | CH₃COOH       | CH₂Cl₂       | 50              | 38 †     |
| 5h       | NMe₂| acridine  | 6-phenyl-[1,2,5]oxadiazolo[3,4-β]pyrazine | CH₃COOH       | CH₂Cl₂       | rt              | 36 †     |
| 5i       | NO₂ | acridine  | acridine   | CH₃COOH       | CH₂Cl₂       | rt              | 49 †     |
| 5j       | CN  | acridine  | acridine   | CH₃COOH       | CH₂Cl₂       | rt              | 79 †     |
| 5k       | Br  | acridine hydrochloride | acridine hydrochloride | -             | n-BuOH       | rt              | 85 †     |
| 5l       | CH₃ | acridine hydrochloride | acridine hydrochloride | -             | n-BuOH       | rt              | 80 †     |
| 5m       | NMe₂| acridine hydrochloride | acridine hydrochloride | -             | n-BuOH       | rt              | 82 †     |
| 5n       | NO₂ | acridine hydrochloride | acridine hydrochloride | -             | n-BuOH       | rt              | 85 †     |
| 5o       | CN  | acridine hydrochloride | acridine hydrochloride | -             | n-BuOH       | rt              | 85 †     |

1 Isolated yields. 2 The yield was determined by NMR spectroscopy.

BODIPY derivatives 6a–j were prepared according to a standard synthesis procedure by oxidation of dipyrromethanes 5a–j using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and subsequent cyclization with BF₃·OEt₂. For compounds 6a,d–i, triethylamine was used as a base, and in the case of 6b,c,j, disopropylethylamine (DIPEA) was used. All reactions were carried out under inert conditions, yields of products 6 were 32–70% (Table 3). The NMR spectra for the synthesized BODIPY dyes 6a–j are shown in Supplementary Materials.

Similar BODIPY derivatives without α-substituents were also synthesized: 4,4-difluoro-8-(4-R-phenyl)-4-boron-3z,4a-diaza-s-indacenes, where R = NMe₂ (7a), Me (7b), Br (7c), CN (7d), NO₂ (7e).
Table 3. Synthesis of BODIPY 6a-j.

| Compound | R₁ | R₂          | R₃            | Base     | Yield, % ¹ |
|----------|----|-------------|---------------|----------|------------|
| 6a       | Br | acridine    | H             | NEt₃     | 32         |
| 6b       | Br | acridine    | acridine      | DIPEA    | 38         |
| 6c       | Br | [1,2,5]-oxadiazolo[3,4-b]pyrazine | [1,2,5]-oxadiazolo[3,4-b]pyrazine | DIPEA    | 42         |
| 6d       | CH₃| acridine    | H             | NEt₃     | 46         |
| 6e       | CH₃| acridine    | acridine      | NEt₃     | 70         |
| 6f       | NMe₂| acridine     | acridine      | NEt₃     | 59         |
| 6g       | NMe₂| acridine    | acridine      | NEt₃     | 56         |
| 6h       | NMe₂| [1,2,5]-oxadiazolo[3,4-b]pyrazine | [1,2,5]-oxadiazolo[3,4-b]pyrazine | NEt₃     | 52         |
| 6i       | NO₂| acridine    | acridine      | NEt₃     | 48         |
| 6j       | CN | acridine    | acridine      | DIPEA    | 46         |

¹ Isolated yields.

2.2. Photophysical Properties

For all synthesized dyes, absorption and luminescence spectra were recorded, and also electrochemical measurements were carried out. The absorption spectra of the synthesized dyes are shown in Figure 2 and spectral-luminescent properties are given in Table 4.

As can be seen from Table 4, introduction of azinyl substituents at the positions 3 and 5 of the meso-aryl substituted BODIPYs leads in most cases to a red shift of the absorption and emission spectra and to an increase in the photoluminescence quantum yield. The effect is most pronounced when furazanopyrazine substituents are introduced into 7c, leading to 6c: the photoluminescence quantum yield in benzene increases from 0.036 to 0.81, while the peak of the emission spectrum shifts by 94 nm. This correlation holds for all BODIPY in this study except those having dimethylamino group because their properties are affected by photoinduced electron transfer from the phenyl meso-substituent to the indacene framework of the molecule. For all dyes having a dimethylamino group there is a strong dependence of the luminescent properties on the solvent. A small Stokes shift and a relatively high quantum yield are observed in nonpolar tetrachlorethylene, which indicates locally excited luminescence. However, when going to only slightly more polar benzene, the quantum yield drops sharply and the Stokes shift increases. For the dyes synthesized here without the dimethylamino group, the luminescence observed in tetrachlorethylene and benzene is locally excited and does not show features of the photoinduced charge transfer.
Figure 2. The absorption spectra of compounds 6a-j, 7a-e.
Table 4. The photophysical properties of the synthesized dyes in tetrachlorethylene and benzene: the position of the long-wavelength peak of the absorption spectrum $\lambda_{\text{abs}}$, the position of the peak of the luminescence spectrum $\lambda_{\text{em}}$, the quantum yield of luminescence $\varphi$.  

| Compound | Solvent  | $\lambda_{\text{abs}}$/nm | $\lambda_{\text{em}}$/nm | $\varphi$ |
|----------|----------|---------------------------|---------------------------|----------|
| 7a       | C$_2$Cl$_4$ | 500                       | 536                       | 0.284    |
| 7a       | benzene   | 499                       | 635                       | 0.049    |
| 6f       | C$_2$Cl$_4$ | 510                       | 570                       | 0.319    |
| 6f       | benzene   | 508                       | 637                       | 0.054    |
| 6g       | C$_2$Cl$_4$ | 520                       | 600                       | 0.289    |
| 6g       | benzene   | 519                       | 634                       | 0.068    |
| 6h       | benzene   | 557                       | 782                       | 0.0025   |
| 7b       | C$_2$Cl$_4$ | 503                       | 519                       | 0.063    |
| 7b       | benzene   | 503                       | 519                       | 0.063    |
| 6d       | C$_2$Cl$_4$ | 513                       | 576                       | 0.155    |
| 6d       | benzene   | 512                       | 581                       | 0.140    |
| 6e       | C$_2$Cl$_4$ | 524                       | 611                       | 0.249    |
| 6e       | benzene   | 523                       | 614                       | 0.228    |
| 7c       | C$_2$Cl$_4$ | 507                       | 525                       | 0.027    |
| 7c       | benzene   | 506                       | 525                       | 0.036    |
| 6a       | C$_2$Cl$_4$ | 517                       | 589                       | 0.077    |
| 6a       | benzene   | 516                       | 594                       | 0.082    |
| 6b       | C$_2$Cl$_4$ | 529                       | 626                       | 0.160    |
| 6b       | benzene   | 527                       | 628                       | 0.160    |
| 6c       | C$_2$Cl$_4$ | 556                       | 613                       | 0.70     |
| 6c       | benzene   | 555                       | 619                       | 0.81     |
| 7d       | C$_2$Cl$_4$ | 511                       | 535                       | 0.0072   |
| 7d       | benzene   | 510                       | 537                       | 0.0078   |
| 6j       | C$_2$Cl$_4$ | 533                       | 640                       | 0.055    |
| 6j       | benzene   | 512                       | 544                       | 0.061    |
| 7e       | C$_2$Cl$_4$ | 513                       | 541                       | 0.0058   |
| 7e       | benzene   | 512                       | 544                       | 0.0064   |
| 6i       | C$_2$Cl$_4$ | 535                       | 646                       | 0.036    |
| 6i       | benzene   | 533                       | 649                       | 0.041    |

2.3. Electrochemical Properties

The electrochemical properties of functionalized BODIPYs 6a–j were recorded by cyclic voltammetry (CV) technique in dichloromethane using tetrabutylammoniumhexafluorophosphate (TBAPF$_6$) as a supporting electrolyte. The representative CV plot is shown in Figure 3 and the data are summarized in Table 5.

Table 5. Electrochemical data for compounds 6a–j in CH$_2$Cl$_2$.

| Compound | $E_{\text{onset, red vs. Fe/Fe}^\cdot}$, V | $E_{\text{LUMO}}$, eV | $E_{\text{onset, ox vs. Fe/Fe}^\cdot}$, V | $E_{\text{HOMO}}$, eV | $E_{\text{gap}}$, eV |
|----------|----------------------------------------|-----------------------|----------------------------------------|---------------------|---------------------|
| 6a       | −1.09                                  | −4.01                 | -                                      | -                   | -                   |
| 6b       | −1.08                                  | −4.02                 | -                                      | -                   | -                   |
| 6c       | −0.61                                  | −4.49                 | -                                      | -                   | -                   |
| 6d       | −1.16                                  | −3.94                 | 0.99                                   | −6.09               | 2.15                |
| 6e       | −1.13                                  | −3.97                 | 1.02                                   | 6.12                | 2.15                |
| 6f       | −1.24                                  | −3.86                 | 0.50                                   | −5.60               | 1.74                |
| 6g       | −1.14                                  | −3.96                 | 0.42                                   | −5.52               | 1.56                |
| 6h       | −0.72                                  | −4.38                 | 0.48                                   | −5.58               | 1.2                 |
| 6i       | −0.97                                  | −4.13                 | -                                      | -                   | -                   |
| 6j       | −0.96                                  | −4.14                 | 1.07                                   | 6.17                | 2.03                |

$^1 E_{\text{LUMO}} = -(E_{\text{onset, red vs. Fe/Fe}^\cdot} + 5.1)$ (eV). $^2 E_{\text{HOMO}} = -(E_{\text{onset, ox vs. Fe/Fe}^\cdot} + 5.1)$ (eV).
Figure 3. Cyclic voltammograms of BODIPYs 6a–j.

All compounds are characterized by a reversible first reduction peak. For compounds 6c, h, i, j, there are additional reduction peaks apparently related to the substituents: NO$_2$ group (6i), CN group (6j), and for 6c, h these are furazanopyrazine fragments. A number of compounds also has an irreversible oxidation peak. For NMe$_2$ derivatives potential $E_{\text{onset, ox}}$ is in the range of 0.42–0.50 V, for compound 6e with CH$_3$ substituent $E_{\text{onset, ox}}$ is much higher and amounts to 1.02 V. The introduction of the electron-withdrawing CN group, compound 6j, leads to an even greater increase in the oxidation potential. For 6i containing NO$_2$ group the potential could not be fixed in the accessible region.

Compounds containing furazanopyrazine substituents 6c, h undergo reduction most easily; $E_{\text{onset, red}}$ is $-0.61$ and $-0.72$, respectively. In general, derivatives with one acridine moiety 6a, d, f are more difficult to reduce, the values of reduction potentials are in the range from $-1.24$ to $-1.09$. Compounds 6b, g are reduced at $-1.08$ and $-1.14$ V. The presence of electron-withdrawing NO$_2$ group and CN group in 6i, j leads to a decrease in the potential to $-0.97$ and $-0.96$, respectively.

3. Materials and Methods

3.1. General

The starting materials and reagents were purchased from commercial sources and used without further purification. $^1$H-NMR (400 MHz), $^{13}$C-NMR (101 MHz), $^{11}$B-NMR (128 MHz) and $^{19}$F-NMR (376 MHz) spectra were recorded on an Avance II instrument (Bruker, Germany) in DMSO-d$_6$ and CDCl$_3$ using SiMe$_4$ as internal reference. Chemical shifts (d) are reported in parts per millions (ppm) and spin multiplicities are given as singlet (s), doublet (d), triplet (t), or multiplet (m). Coupling constants (J) are reported in Hz. Electrospray mass spectra were recorded in positive mode with maXis impact high resolution Q-TOF mass spectrometer (Bruker Daltonics, Bremen, Germany) in 50–2500 Da
mass range by direct infusion of sample solutions in methanol using kdScientific syringe pump at 120 uL/hr flow rate. The mass spectra were recorded on a GCMS-QP2010 Ultra mass spectrometer (Shimadzu, Japan) with sample ionization by electron impact (EI). The elemental analysis was carried out on an automated PE 2400 series II CHNS analyzer (Perkin Elmer, Norwalk, CT, USA).

The course of the reactions was monitored by TCL on 0.25 mm silica gel plates (60F254). silica gel 60 (0.04–0.063 mm, Macherey-Nagel GmbH & Co, Düren, Germany) was used for column chromatography. Melting points were determined on a SMP10 melting point apparatus (Stuart, Stone, Staffordshire, United Kingdom) and are uncorrected.

Photochemical reactions were performed in a PhotoRedOx box (EvoluChem™, Beverly, MA, USA) equipped with an EvoluChem™ LED, 18 W, 425 nm (HCK1012-01-012).

Dipyrromethanes 3a–e were prepared according to the procedures described in the literature [44–47]. BODIPYS 7a–e were prepared according to the procedures described in the literature and identified by comparing their 1H-NMR spectra with those given in the literature [49–52]. DDQ (0.3 mmol) in dry CH2Cl2 (2.5 mL) was added to dipyrromethane 3a–e (0.3 mmol) in 20 mL of dry CH2Cl2, cooled in an ice bath under Ar atmosphere. The reaction mixture was stirred for 15 min. To the reaction mixture triethylamine (2 mL) was added immediately followed by BF3·Et2O (2 mL). The reaction mixture was further stirred for another 3 h at room temperature and washed with 0.2 M NaOH solution (50 mL) and water (100 mL). The organic layer was collected and dried over anhydrous Na2SO4, and the solvent was removed. The reaction mixture was concentrated in vacuum. The residue was purified by column chromatography on silica gel.

3.2. Optical Measurements

All optical measurements were carried out at room temperature in luminescent quartz cells 10 mm × 10 mm. Benzene (99%, Sigma-Aldrich, Saint Louis, MO, USA), tetrachlorethylene (99%, Acros, Belgium) and ethanol (95%) were used as solvents.

The absorption spectra of the dyes were measured on a Shimadzu UV 3101PC spectrophotometer. Stationary luminescence measurements were carried out on a Shimadzu RF-6000 spectrofluorimeter, in which the manufacturer implemented the correction of obtained spectra for the spectral sensitivity of the detecting system and the spectrum of the excitation source. Light filters, which do not transmit light of higher diffraction orders on the monochromators of the instrument, were placed on the paths of the exciting and recorded beams. Nominal bandwidths of the excitation and observation monochromators were 5 nm each. Identically recorded luminescence spectra of pure solvents were subtracted from the measured luminescence spectra of the dyes. Optical densities of solutions in the luminescence measurements did not exceed 0.1 at the excitation wavelength and 0.05 in the observation band.

The luminescence quantum yields of the dyes were determined relative to an ethanol solution of rhodamine 6G, the luminescence quantum yield of which was set equal to 0.95. Excitation of the dyes was carried out near the maxima of their absorption spectra. When calculating the quantum yield of luminescence, the refractive indices of the corresponding solvents were taken into account.

3.3. Electrochemical Measurements

Cyclic voltammetry was carried out on an Autolab PGSTAT128N potentiostat (Metrohm, Utrecht, Netherlands) using a standard three-electrode configuration. Typically, a three electrodes cell equipped with a glass carbon working electrode, a Ag/AgNO3 (0.01M) reference electrode, and a glass carbon rod counter electrode was employed. The measurements were done in dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte under an argon atmosphere at a scan rate of 100 mV/s. The potential of the Ag/AgNO3 reference electrode was calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc+).
3.4. General Synthesis of Dipyromethanes 5a–g

A 20-mL vial containing a solution of dipyromethane 3a–e (0.5 mmol), heterocycle 4a, b (1.0 mmol), TiO₂ (10 mass%) and acetic acid (20 mmol) in CH₂Cl₂ (10 mL) was treated in an ultrasonic bath for 5 min to obtain a suspension. The resulting mixture was irradiated in an Evoluchem™ PhotoRedOx box (equipped with an EvoluChem™ LED, 18 W, 425 nm) on a stirrer plate with air oxygen bubbling through the reaction mixture at room temperature (for 5a, c, d, f, h) or 50 °C (for 5b, e, g). The reaction was stopped after 5 h. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel.

1-(Acridine-9-yl)-meso-(4-bromphenyl)dipyrrometane (5a). The residue was purified by column chromatography on silica gel, eluting with a mixture of hexane/ethyl acetate (8/2) to give the compound as a yellow solid (0.115 g, 48% yield), mp 216–218 °C. ¹H-NMR (DMSO-d₆): δ 124.36 (s, 2H), 121.05 (t, J = 15.7, 8.4 Hz, 2H), 118.14 (d, J = 8.4 Hz, 2H), 112.60 (d, J = 8.4 Hz, 2H), 112.90 (s, 2H), 108.42, 108.39, 108.15, 108.07, 108.42, 108.15, 43.64. MS (EI): m/z 479 [M+H]+. Anal. calcd. for C₂₈H₂₀BrN₃: C, 70.40; H, 4.20; N, 8.75. Found: C, 70.40; H, 4.20; N, 8.75.

1,9-Di(acridine-9-yl)-meso-(4-bromphenyl)dipyrrometane (5b). The residue was purified by column chromatography on silica gel, eluting with a mixture of hexane/ethyl acetate (8/2) to give the compound as a red-brown solid (0.198 g, 57% yield), mp 178–180 °C. ¹H-NMR (CDCl₃): δ 147.90, 141.97, 139.09, 134.94, 131.75, 131.49, 130.48, 129.98, 128.01, 126.67, 125.17, 124.61, 124.36, 121.05, 118.14, 112.60, 109.07, 108.42, 108.15, 43.64. MS (EI): m/z 479 [M+H]+. Anal. calcd. for C₂₈H₂₀BrN₃: C, 70.40; H, 4.20; N, 8.75.

1-(Acridine-9-yl)-meso-(4-methylphenyl)dipyrrometane (5c). The residue was purified by column chromatography on silica gel, eluting with a mixture of hexane/ethyl acetate (8/2) to give the compound as a yellow solid (0.115 g, 48% yield), mp 216–218 °C. ¹H-NMR (CDCl₃): δ 9.37 (s, 2H), 7.97–7.95 (d, J = 8.7 Hz, 4H), 7.86–7.84 (d, J = 8.7 Hz, 4H), 7.49–7.45 (m, 6H), 7.33–7.31 (d, J = 7.8 Hz, 2H), 7.22–7.18 (m, 4H), 6.56 (s, 2H), 6.47 (s, 2H), 5.92 (s, 2H), 43.47. MS (EI): m/z 479 [M+H]+. Anal. calcd. for C₂₈H₂₀BrN₃: C, 70.40; H, 4.20; N, 8.75.

1,9-Di(acridine-9-yl)-meso-(4-methylphenyl)dipyrrometane (5d). The residue was purified by column chromatography on silica gel, eluting with a mixture of hexane/ethyl acetate (8/2) to give the compound as a yellow solid (0.224 g, 76% yield), mp 235–237 °C. ¹H-NMR (CDCl₃): δ 7.97–7.95 (d, J = 8.7 Hz, 4H), 7.86–7.84 (d, J = 8.7 Hz, 4H), 7.49–7.45 (m, 6H), 7.33–7.31 (d, J = 7.8 Hz, 2H), 7.22–7.18 (m, 4H), 6.56 (s, 2H), 6.47 (s, 2H), 5.92 (s, 2H), 2.46 (s, 3H). ¹C-NMR (DMSO-d₆): δ 148.41, 139.15, 136.42, 135.41, 130.00, 129.19, 128.78, 128.15, 127.13, 125.68, 124.93, 123.31, 112.36, 107.99, 43.18, 20.65. MS (EI): m/z 591 [M+H]+. Anal. calcd. for C₄₂H₃₀N₄: C, 85.40; H, 5.12; N, 9.48. Found: C, 85.47; H, 5.13; N, 9.51.
1-(Acridine-9-yl)-meso-(4-N,N-dimethylaminophenyl)dipyrrometane (5f). The residue was purified by column chromatography on silica gel, eluting with a mixture of hexane/ethyl acetate (8/2) to give the compound as a brown solid (0.118 g, 36% yield), mp 178–180 ºC. 1H-NMR (CDCl$_3$): δ 9.78 (s, 2H), 7.65–7.61 (m, 6H), 7.57–7.53 (m, 4H), 7.08 (d, $J = 8.7$ Hz, 2H), 6.71 (d, $J = 8.7$ Hz, 2H), 5.88–5.86 (m, 2H), 5.70–5.68 (m, 2H), 5.40 (s, 1H), 2.99 (s, 6H). 13C-NMR (CDCl$_3$): δ 163.13, 151.17, 150.70, 150.43, 150.25, 141.83, 137.74, 130.90, 128.99, 128.92, 128.71, 128.58, 128.54, 128.45, 127.53, 127.50, 126.79, 126.54, 124.29, 123.74, 112.89, 108.31, 43.25, 40.86. MS (EI): m/z 619 [M]+. Anal. calcd. for C$_{37}$H$_{25}$N$_{3}$O$_{2}$: C, 83.84; H, 4.52; N, 11.64. Found: C, 83.95; H, 4.47; N, 11.59.

1,9-Di(acridine-9-yl)-meso-(4-N,N-dimethylaminophenyl)dipyrrometane (5g). The residue was purified by column chromatography on silica gel, eluting with a mixture of hexane/ethyl acetate (1/1) to give the compound as a brown solid (0.238 g, 79% yield), mp 254–256 ºC. Anal. calcd. for C$_{30}$H$_{26}$N$_{4}$: C, 81.42; H, 5.92; N, 12.66. Found: C, 81.40; H, 5.92; N, 12.68.

1,9-Di(6-phenyl-[1,2,5]oxadiazolo[3,4-b]pyrazine-5-yl)-meso-(4-N,N-dimethylaminophenyl)-dipyrrometane (5h). The residue was purified by column chromatography on silica gel, eluting with a mixture of hexane/ethyl acetate (1/1/1) to give the compound as a red-brown solid (0.152 g, 49% yield), mp 272–274 ºC. Anal. calcd. for C$_{37}$H$_{25}$N$_{3}$O$_{2}$: C, 83.37; H, 5.34; N, 11.26. Found: C, 83.37; H, 5.34; N, 11.26.

3.5. General Procedure for BODIPYs 6a–g

DDQ (0.3 mmol) in dry CH$_2$Cl$_2$ (2.5 mL) was added to dipyrromethane 5a–i (0.3 mmol) in 20 mL of dry CH$_2$Cl$_2$ cooled in an ice bath under Ar atmosphere. The reaction mixture was stirred for 15 min. To the reaction mixture triethylamine (for 6a,d–i) or diisopropylethylamine (for 6b,c,j) (2 mL) was added immediately followed by BF$_3$·Et$_2$O (2 mL). The reaction mixture was further stirred for another 3 h at room temperature and washed with 0.2 M NaOH solution (50 mL) and water (100 mL). The organic layer was collected and dried over anhydrous Na$_2$SO$_4$, and the solvent was removed. The reaction mixture was concentrated in vacuum. The crude product was purified by column chromatography on silica gel.
4,4-Difluoro-3-(acridine-9-yl)-8-(4-bromophenyl)-4-bora-3a,4a-diaza-s-indacene (6a). The residue was purified by column chromatography on silica gel, eluting with a mixture of hexane/ethyl acetate (7/3) to give compound as a red solid (0.051 g, 32% yield), mp 218–220 °C. 1H-NMR (CDCl3): δ 8.22 (d, J = 8.8 Hz, 2H), 7.75–7.65 (m, 6H), 7.62 (s, 1H), 7.51 (d, J = 8.3 Hz, 2H), 7.46–7.37 (m, 2H), 7.09 (d, J = 3.9 Hz, 1H), 6.88 (d, J = 3.9 Hz, 1H), 6.60 (d, J = 3.9 Hz, 1H), 6.44 (d, J = 3.5 Hz, 1H). 13C-NMR (CDCl3): δ 152.15, 147.49, 144.69, 144.48, 136.10, 134.49, 133.91, 131.56, 130.96, 130.75, 129.79, 129.09, 128.64, 125.68, 125.00, 124.70, 124.48, 121.15, 118.54. 19F-NMR (CDCl3): δ -143.20. 11B-NMR (CDCl3): δ 0.34. MS (EI): m/z 525 [M+H]+. Anal. calcd. for C28H17BFrF3N2: C, 64.16; H, 3.27; N, 8.02. Found: C, 64.21; H, 3.20; N, 8.00.

4,4-Difluoro-3,5-di(acridine-9-yl)-8-(4-bromophenyl)-4-bora-3a,4a-diaza-s-indacene (6b). The residue was purified by column chromatography on silica gel, eluting with a mixture of hexane/ethyl acetate (8/2) to give a compound as a red solid (0.08 g, 38% yield), mp > 300 °C. 1H-NMR (CDCl3): δ 8.11 (d, J = 9.0 Hz, 4H), 7.87 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 8.1 Hz, 2H), 7.70–7.60 (m, 8H), 7.45–7.34 (m, 4H), 7.23 (d, J = 4.0 Hz, 2H), 6.62 (d, J = 4.0 Hz, 2H). 13C-NMR (CDCl3): δ 123.31, 125.15, 125.81, 125.88, 126.56, 129.54, 129.89, 131.10, 132.10, 132.16, 135.86, 136.68, 148.27, 154.46. 19F-NMR (CDCl3): δ -141.19. 11B-NMR (CDCl3): δ 0.65. HRMS m/z calcd. for C41H25BFrF3N4 [M+H]+ 701.1324, found: m/z 701.1244.

4,4-Difluoro-3,5-di(6-phenyl-[1,2,5]oxadiazo1[3,4-b]pyrazine-5-yl)-8-(4-bromophenyl)-4-bora-3a,4a-diaza-s-indacene (6c). The residue was purified by column chromatography on silica gel, eluting with a mixture of hexane/benzene/ethyl acetate (1/3/0.1) to give the compound as a dark brown solid (0.093 g, 42% yield), mp 185–187 °C. 1H-NMR (CDCl3): δ 7.76–7.73 (m, 5H), 7.54–7.49 (m, 4H), 7.44–7.39 (m, 5H), 6.89 (d, J = 4.4 Hz, 2H), 6.25 (d, J = 4.4 Hz, 2H). HRMS m/z calcd. for C35H22BFrF3N11O2 [M+NH4]+ 756.1202, found: m/z 758.1182.

4,4-Difluoro-3-(acridine-9-yl)-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene (6d). The residue was purified by column chromatography on silica gel, eluting with a mixture of hexane/ethyl acetate (8/2) to give the compound as a red solid (0.063 g, 46% yield), mp 246–248 °C. 1H-NMR (CDCl3): δ 8.25 (d, J = 8.7 Hz, 2H), 7.71 (t, J = 7.8 Hz, 4H), 7.60 (s, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.42 (dd, J = 8.3, 6.4 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 3.9 Hz, 1H), 6.93 (d, J = 4.1 Hz, 1H), 6.58 (d, J = 4.0 Hz, 1H), 6.42 (d, J = 3.7 Hz, 1H), 2.44 (s, 3H). 13C-NMR (CDCl3): δ 21.55, 119.21, 121.68, 125.67, 126.08, 126.92, 129.04, 129.37, 130.49, 130.77, 130.99, 132.17, 135.21, 135.81, 141.69, 144.89, 147.80, 151.78. 19F-NMR (CDCl3): δ -143.11. 11B-NMR (CDCl3): δ 0.37. MS (EI): m/z 459 [M]+. Anal. calcd. for C29H25BFrF3N2O: C, 75.84; H, 4.39; N, 9.15. Found: C, 75.88; H, 4.40; N, 9.13.

4,4-Difluoro-3,5-di(acridine-9-yl)-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene (6e). The residue was purified by column chromatography on silica gel, eluting with a mixture of hexane/ethyl acetate (8/2) to give the compound as a brown solid (0.063 g, 70% yield), mp > 300 °C. 1H-NMR (CDCl3): δ 8.00 (d, J = 8.7 Hz, 4H), 7.70 (d, J = 7.9 Hz, 2H), 7.61–7.50 (m, J = 16.6, 8.3 Hz, 8H), 7.41 (d, J = 7.8 Hz, 2H), 7.33–7.24 (m, 4H), 7.20–7.18 (m, 2H), 6.50 (d, J = 4.1 Hz, 2H), 2.49 (s, 3H). 13C-NMR (CDCl3): δ 21.58, 29.70, 122.87, 125.26, 125.79, 126.72, 129.46, 129.86, 130.92, 131.12, 136.36, 136.13, 137.07, 141.70, 147.50, 148.27, 153.54. 19F-NMR (CDCl3): δ -141.22. 11B-NMR (CDCl3): δ 0.69. HRMS m/z calcd. for C35H22BFrF3N11O2 [M+H]+ 637.2375, found: m/z 637.2369.

4,4-Difluoro-3-(acridine-9-yl)-8-(4,N,N-dimethylaminophenyl)-4-bora-3a,4a-diaza-s-indacene (6f). The residue was purified by column chromatography on silica gel, eluting with a mixture of hexane/ethyl acetate (8/2) to give the compound as a brown dark solid (0.086 g, 59% yield), mp 292–294 °C. 1H-NMR (CDCl3): δ 8.31 (d, J = 8.7 Hz, 2H), 7.85–7.76 (m, 4H), 7.72 (d, J = 8.8 Hz, 2H), 7.63 (s, 1H), 7.54–7.45 (m, 2H), 7.34 (d, J = 4.0 Hz, 1H), 7.12 (d, J = 4.0 Hz, 1H), 6.89 (d, J = 8.9 Hz, 2H), 6.68 (d, J = 4.0 Hz, 1H), 6.55–6.49 (m, 1H), 3.17 (s, 6H). 13C-NMR (CDCl3): δ 40.17, 118.55, 118.26, 121.08, 121.73, 125.77, 125.86, 127.11, 129.54, 130.02, 130.32, 131.24, 133.33, 134.60, 135.45, 138.15, 142.47, 148.46, 148.57, 149.97, 152.76.
4. Conclusions

An approach for the oxidative C-H/C-H coupling of dipyrromethanes with azines in the presence of the heterogeneous O$_2$/TiO$_2$/visible light irradiation photocatalytic system was proposed for the first time. Mono- and disubstituted dipyrromethanes were used in the synthesis of new derivatives of BODIPY family fluorophores. Fifteen derivatives of 4,4-difluoro-8-phenyl-4-boron-3a,4a-diaza-s-indacene were synthesized, 10 of which are new compounds. The introduction of azinyl substituents at the positions 3 and 5 of the meso-aryl substituted BODIPYs leads in most cases to a red shift of the absorption and emission spectra and to an increase in the photoluminescence quantum yield. Dye containing furazanopyrazine groups at the positions 3 and 5 of the meso-bromophenyl substituted BODIPYs exhibits an increased fluorescence quantum yield (0.81 in benzene) compared with BODIPY without an azine substituent (0.036 in benzene).

Supplementary Materials: The following are available online: NMR spectra of compounds 5a–j and 6a–j.
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