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Phenyliodine(III) Bis(trifluoroacetate) (PIFA)-Promoted Synthesis of Bodipy Dimers Displaying Unusual Redox Properties

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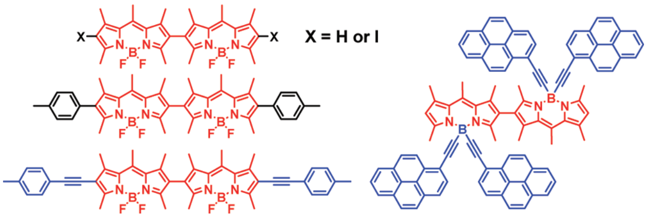
ABSTRACT



Phenyliodine(III) bis(trifluoroacetate) (PIFA) in conjunction with a Lewis acid promotes C−C coupling of Bodipy monomers leading to mixtures of various oligomers. When a single position is blocked with an iodo or phenyl group, formation of the dimer is favored. These dimers display two successive oxidation and two reduction waves separated on average by 260 and 130 mV, respectively, corresponding to each Bodipy subunit.

4,4′-Difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene (Bodipy) dyes have received renewed interest in recent years due to their outstanding optical properties such as high absorption coefficients and relatively sharp emission lines, high fluorescence quantum yields, excellent chemical and photochemical stability, high solubility, and ease of functionalization at will.[1] They have found widespread applications as chemiosensors,[2] laser dyes,[3] fluorescent labels,[4] active layers in photovoltaic cells,[5] and two-photon absorbing dyes dedicated to cell imaging,[6] as well as recently in solar concentrators.[7]

In contrast, Bodipy dimers have received little attention despite their interesting properties linked to charge delocalization and exciton coupling, providing unusual fluorescence and redox properties. Of this family, α,α′-linked Bodipy dimers,[8] boron-butadiene-boron linked dimers,[9] and cofacially arranged dibenzothiophene, dibenzofuran, and 9,9-dimethylxanthene bis-Bodipy[10] dyes have been recently prepared.

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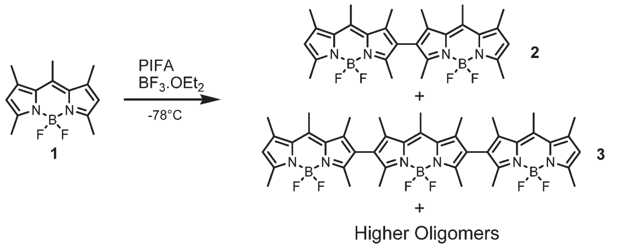
Bodipy-based conjugated oligomers and polymers have also been prepared using palladium-mediated cross-coupling chemistry, in particular at the β,β'-positions using triple bonds as linkers.[11] While exciton coupling of the subunits of $\beta-\beta$ linked Bodipy oligomers is clearly possible, its occurrence has not yet been established.

Herein, we focus on the preparation of such Bodipy dimers using a hypervalent iodine reagent.[12] Phenyliodine(III) bis(trifluoroacetate) (PIFA) has previously been used to prepare *bis*aryls in the presence of a Lewis acid or a fluoroalcohol as a solvent,[13] such as *meso*−*meso*-linked linear arrays of porphyrins,[14] and fused diporphyrin scaffoldings.[15]

Scheme 1. Synthesis of Bodipy Oligomers



Initially, we concentrated on the use of 4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3*a*,4*a*-diaza-*s*-indacene **1** as the starting material plus PIFA (0.3 equiv) at low temperature. In the absence of a strong Lewis acid, no reaction occurs but fast oligomerization even at −78 °C is found in the presence of $BF_3 \cdot OEt_2$ (0.6 equiv) (Scheme 1). A series of oligomers were isolated by column chromatography (dimer **2**, 10%; trimer **3**, 4%),[16] and higher oligomers were characterized in particular by ^{1}H NMR (Figure S1). In each case, the degree of oligomerization was readily deduced by integration of the signals in the ^{1}H NMR spectra for the methyl groups and the two β-pyrrolic protons. The major drawbacks of this coupling reaction are the difficulty in stopping the reaction and in controlling the oligomer distribution and the separation of the oligomers (tetramer, pentamer,...). The use of various treatments designed to quench PIFA or the reaction intermediate after a given time (e.g., with aqueous $NaHCO_3$ or $Na_2S_2O_3$, aqueous ascorbic acid, H_2 or $NaBH_4$) was unsuccessful.

The single-crystal molecular structure of dimer **2** reveals a 64.1(1)° dihedral angle between the mean planes of the two indacene units (Figure 1). As expected, in each Bodipy unit the central six-membered ring lies coplanar with the two adjacent five-membered rings. The rms deviation from planarity including the methyl substituents is 0.041 and 0.064 Å, and the maximum deviation is observed for the boron atom which is 0.111 (13) and −0.271 (11) Å away from the mean plane, respectively. The elongated dimers propagate along the *b* direction forming chevron-like columns. Nonclassic H-bonds involving either the methyl hydrogen and the fluorine atoms (with a bond distance of ca. 2.4 Å) or methyl hydrogen atoms contribute to connect columns to their inverted neighbors generated by a half-unit translation along the *c* axis (Figure 1).

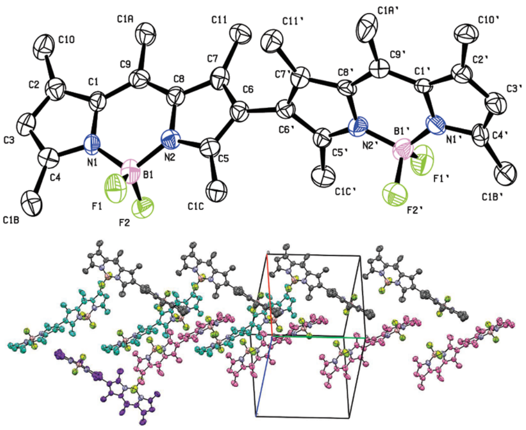


Figure 1. ORTEP view for **2** with thermal ellipsoids plotted at the 30% level. H atoms are omitted for clarity. Molecular packing along the *b* axis.

Our next subsequent synthesis concerned that of dimers with one of the β-pyrrolic positions occupied by an iodo or phenyl moiety in order to control the rate of the coupling reaction. For this purpose, we first prepared the monoiodo derivative **4**,[17] the monotolyl dye **5**, and monoethynyltolyl dye **6**,[17] as shown in Scheme 2.

Dimerization of monomers **4** and **5** was efficient in the presence of PIFA (0.9 and 0.6 equiv, respectively) and $BF_3 \cdot OEt_2$ (0.6 equiv) at −78 °C (Scheme 2). Dimers **7** and **8** were isolated by column chromatography. After some experimentation, we found that adding PIFA in portions of 0.3 equiv up to a total of 0.9 equiv over a 10 min period limited the degradation of the dyes at −78 °C. Under these PIFA-mediated coupling conditions, compound **6** does not give the desired dimer **9**, due to fast degradation of the dye.

Fortunately, the three dimers **2**, **7**, and **8** showed essentially the same stability and reaction pathways as those of monomeric Bodipy dyes. Extension of the π conjugation of dimer **7** by substitution of both iodo residues with ethynyltolyl

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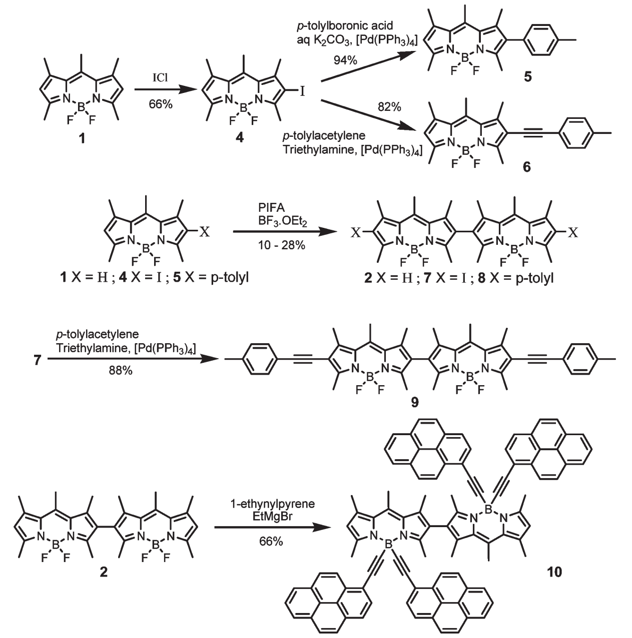
Scheme 2. Synthesis of Bodipy Monomers and Dimers



modules through palladium-catalyzed cross-coupling with *p*-tolylacetylene proved facile, affording dimer **9** in 88% yield. Dimer **2** was also appealing as a substrate for the introduction of arylethynyl units on the boron atom as possible absorbing units for excitonic energy transfer (*vide infra*). The use of excess ethynyl-Grignard reagent led to rapid substitution of the fluorine atom and allowed the preparation of compound **10** in good yield (Scheme 2).

Photophysical parameters are gathered in Table 1. Linked Bodipy dimers and trimers all show high absorption coefficients (> 150 000 M^{-1} cm^{-1}) and relatively high fluorescence quantum yields, except those having a iodo atom on the β-position which show reduced fluorescence lifetimes and quantum yields (Table 1). This is largely due to an efficient intersystem crossing leading to a low-lying triplet state.[19] Interestingly, the electronic absorption profiles are shifted by 30 nm in dimer **2** and by 58 nm in trimer **3** with respect to the monomer **1** and by 43 nm in dimer **9** with respect to the monomer **6** (Figure 2). This observation indicates that some electronic communication between the subunits is effective. In the emission spectra a progressive shift of 51 nm for dimer **2** and 79 nm for trimer **3** was also observed.

The Stokes shifts progressively increase from 515 cm^{-1} for **1** to 1200 cm^{-1} for the dimer **2**. In all cases, the emission band shows good mirror symmetry with the lowest-energy band and the radiative deactivation rate is higher by 1 order of magnitude than the nonradiative deactivation rate (Table 1). Furthermore, the nanosecond deactivation regime of the excited state is in keeping with a singlet emitter and confirms that little rearrangement occurs in the excited state.

Interestingly, the substitution of the boron center by 1-ethynylpyrene fragments has no effect on the emission properties, as would be expected by the absence of empty orbitals on the boron center.[1d] The structured absorption bands localized around 285 and 369 nm are attributed to the $\pi-\pi^*$ transitions of the pyrene moieties. Irradiation in these bands resulted in the absence of pyrene emission at 370−380 nm[20] but intense emission of the Bodipy dimer at 562 nm. This indicates that almost quantitative (> 99%)

Table 1. Optical Data Measured in Dichloromethane Solution

dyes	λ_{abs} (nm)	ε ($M^{-1}\cdot cm^{-1}$)	λ_F (nm)	τ_F (ns)	$\Phi_F{}^a$	$k_r{}^b$ 10^8 s^{-1}	$k_{nr}{}^b$ 10^8 s^{-1}
1	496	94 000	509	7.6	90	1.2	1.3
4	509	90 000	529	<1	14	-	-
5	509	68 800	544	5.9	86	1.5	2.4
6	526	72 000	575	3.2	47	1.5	1.7
2	526	155 000	562	4.3	67	1.6	7.7
3	554	176 000	588	4.2	69	1.6	7.4
7	544	185 000	579	2.0	15	7.5	4.2
8	546	187 000	581	4.1	66	1.6	8.3
9	569	207 000	601	4.3	60	1.4	0.3
10	520	147 000	562	5	70	1.4	6.0
	360	175 000	-	-	70	-	-

[a] Using Rhodamine 6G as reference, $\Phi = 0.78$ in water,[18] $\lambda_{ex} = 488$ nm. [b] Calculated using the following equations: $k_r = \Phi_F/\tau_F$, $k_{nr} = (1 - \Phi_F)/\tau_F$, assuming that the emitting state is produced with unit quantum efficiency.

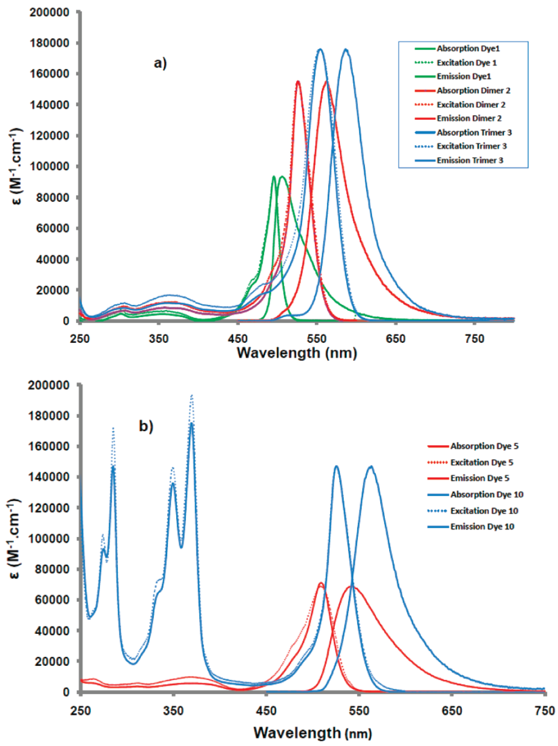


Figure 2. Absorption, emission, and excitation spectra measured in dichloromethane: (a) green lines **1**, red lines **2**, blue lines **3**; (b) red lines **5** and blue lines **10**. For the excitation spectra the emission is scaled at 600 nm for **1**, 620 nm for **2**, 640 nm for **3**, 580 nm for **5**, and 610 nm for **10**.

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excitonic energy transfer is occurring from the pyrene to the dimeric Bodipy framework. The efficiency of this process is likely due to a good spectral overlap between the emission of the pyrene and the second excited state of the Bodipy subunits. As shown in Figure 2, the excitation spectra match the absorption spectra fairly well over the entire absorption window (250 to 560 nm).

Table 2. Electrochemical Data for the Bodipy Monomers and Dimers[a]

dyes	E'°_{oxy}, V (ΔE, mV)	E'°_{red}, V (ΔE, mV)
1	+ 1.11 (70)	−1.33 (60)
2	+ 1.07 (60); + 1.33 (70)	−1.27 (70) ; −1.40 (70)
3	+ 1.06 (80)[b]; + 1.18 (70)	−1.29 (100)[b]; −1.49 (70)
4	+ 1.18 (70)	−1.23 (70)
7	+ 1.16 (60); + 1.36 (70)	−1.16 (60); −1.23 (70)
6	+ 1.16 (60)	−1.30 (60)
9	+ 1.06 (70); + 1.19 (60)	−1.17 (70); −1.30 (70)
5	+ 1.07 (70)	−1.32 (70)
10	+ 1.23 (irrev.)[c]	−1.37 (60); −1.52 (70)

[a] Potentials determined by cyclic voltammetry in deoxygenated CH_2Cl_2 solutions, containing 0.1 M $TBAPF_6$, at a solute concentration range of 1.5 $\times 10^{-3}$ M, at rt. Potentials were standardized using added ferrocene (Fc) as an internal reference and converted to SCE assuming that $E_{1/2}$ (Fc/Fc^+) = +0.38 V (ΔE_p = 60 mV) vs SCE. Error in half-wave potentials is ±15 mV. [b] Two-electron process. [c] The peak potential is quoted.

The electrochemical activity of the new dyes was determined in dichloromethane using tetrabutylammonium hexafluorophosphate as a supporting electrolyte (electrochemical window from +1.7 to −2.1 V), and the results are gathered in Table 2. All four monomers exhibit a reversible one-electron oxidation around +1.1 V and a reversible one-electron reduction around −1.2 V, demonstrating that the β-substitution position has little electronic effect on the redox activity of the central Bodipy core. These redox processes are reversible ($i_{pa}/i_{pc} \approx 1$), with a shape that is characteristic of Nernstian one-electron processes (ΔE_p = 60 mV). A typical example is given in Figure 3, the characteristics being closely similar to those obtained with simpler Bodipy dyes.[21]

Interestingly, all dimers display two reversible one-electron waves on both reduction and oxidation (Figure 3 and Table 2), and addition to the dimer solution of the corresponding monomer clearly increases the first reduction and oxidation potentials, demonstrating only a slight influence of the second unit on the redox properties of the first. The degree of separation between the first and second oxidation and reduction potentials and the gap between the first and second oxidation do not depend on the substituents of the dimers (Table 2). Remarkably, in the case of dimer **10** the substitution of the fluoro groups by ethynylpyrene shifted the reduction potentials anodically by 100 mV while maintaining the degree of separation.

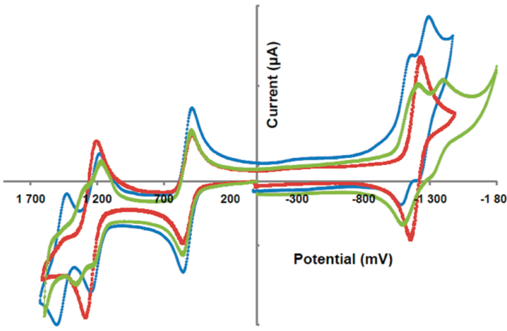

Figure 3. Cyclic voltammograms in dichloromethane at rt for the monomer **1** (mauve trace), the dimer **2** (blue trace), and trimer **3** (green trace). The redox couple at +0.55 V vs Pt is due to added ferrocene (Fc) in all cases.

The cyclic voltammogram of trimer **3** shows that both first reduction and oxidation potentials are bielectronic and resulted from an overlapping between two successive but very close single redox processes which can just be deconvoluted. These first redox processes are close to that observed for dimer **2** (Table 2). However, both of these processes are followed by monoelectronic ones less cathodic by 150 mV in oxidation and more anodic by 90 mV in reduction with respect to dimer **2**. These results are in line with the simultaneous oxidation and reduction of the two Bodipy subunits at the periphery of the trimer resulting in a dielectronic process very close to that observed for the dimer. The second redox process is assigned to the oxidation and reduction of the central Bodipy residue.

In summary, we have developed an unprecedented oxidative coupling reaction of Bodipy dyes using PIFA with a Lewis acid providing Bodipy oligomers linked by C−C tethers at the β pyrrolic positions. This combination of reagents provides an electrophilic intermediate (likely a radical cation)[13c] which rapidly reacts with electron-rich Bodipy's to provide fluorescent oligomers or preferentially dimers when one of the pyrrolic sites is blocked. The absorption and emission properties of the dimers are shifted to lower energies, with a maximum shift of 2640 cm^{-1} and Stokes shift of ~1200 cm^{-1} with respect to the monomers. All dimers display two reversible monoelectronic reduction and oxidation waves separated by 130 and 260 mV, respectively. In the trimers, both Bodipy units at the periphery are oxidized and reduced at similar but distinguishable potentials from those of the central unit. Future work will include the preparation of mixed valence dyes to determine the rate of charge transfer between the Bodipy subunits and the influence on the optical properties.

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Supporting Information Available. Synthetic procedures and analytical data reported herein (PDF). Centre under the number 796243. This material is available free of charge via the Internet at http://pubs.acs.org.

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