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Oxidative Coupling of 1,7,8-Unsubstituted BODIPYs: Synthesis and Electrochemical and Spectroscopic Properties

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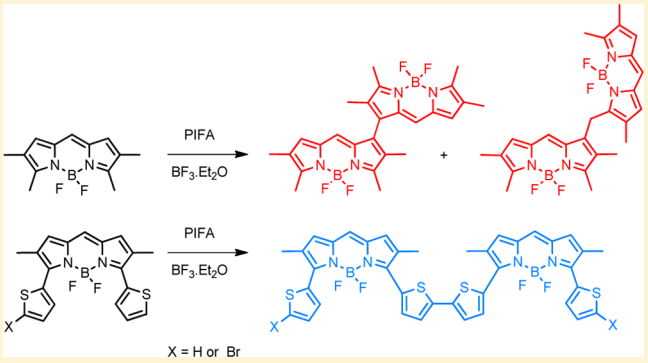
Supporting Information

ABSTRACT: We report the synthesis of BODIPYs with unsubstituted 1,7,8-positions and their dimerization by oxidative coupling with phenyliodine(III)-bis(trifluoroacetate) (PIFA). This dimerization was achieved for BODIPYs substituted in the 3,5-positions with either methyl or thienyl groups. The position and the type of the linkage in the resulting dimers depended on the nature of the substituent. The 3,5-dimethyl-BODIPY dyes were linked either via direct 1,1′-pyrrole−pyrrole coupling or via a 1,3′-methylene bridge. The 3,5-dithienyl-BODIPY dyes provided, in excellent yields, unique compounds linked exclusively via the α-thienyl positions. All dyes were unreactive in the 8-position. Electrochemical and spectroscopic measurements on the monomers and dimers provided evidence of interactions between the two halves of the dimers. Thus, oxidation and reduction potentials were split by up to 210 mV, and modest excitonic coupling and an internal charge transfer were observed in some cases.



INTRODUCTION

There is increasing interest in the design, preparation and study of task-specific fluorescent dyes that can be produced as very pure materials using straightforward protocols.[1,2] Many research groups have sought pathways to a fluorescent probe tailor-made in respect of its chemical and spectroscopic properties. In this regard, 4,4′-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) dyes have especially been of interest due to their exceptional 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.[3,4] They have found widespread applications as chemosensors,[5] laser dyes,[6] fluorescent labels,[7] active layers in photovoltaic cells,[8] two-photon absorbing dyes dedicated to cell imaging,[9] and recently in solar concentrators.[10] In some cases, substituents have been introduced to render the dye sensitive to the environment.[11] Many synthetic protocols are available today to introduce a reactive substituent at an appropriate position of the indacene core to extend the conjugation and to optimize the spectroscopic properties. Of the available protocols, Knoevenagel condensation with tetramethyl-susbstituted BODIPYs,[12] Liebeskind-Srögl reactions,[13] nucleophilic substitutions,[14] palladium promoted cross-coupling reactions[15] and electrophilic attack[16] on methyl-substituted BODIPYs are particularly readily applied. Most rely on the direct introduction of a specific group at the chosen substitution position. The use of a hypervalent iodine reagent,[17] such as PIFA, is one that enables direct production of BODIPY dimers without prior functionalization of the BODIPY core. Few such dyes have been prepared but some do display interesting properties linked to charge delocalization and exciton coupling, providing unusual fluorescence and redox properties. Recently studied examples include α,α-linked BODIPY dimers,[18] β,β-linked BODIPY dimers,[19] boron-butadiene-boron linked dimers[20] and cofacially arranged dibenzothiophene, dibenzofuran and 9,9-dimethylxanthene bis-BODIPY[21] dyes. The architecture of such oligomers is of special importance for the electro-generated chemiluminescence of thin films deposited on transparent electrodes.[19b]

BODIPY oligomers are also of interest as models for BODIPY-based conjugated polymers, in particular those linked at the β,β-positions using triple bonds, to understand their spectroscopic properties.[22] While exciton coupling of the subunits of β',β'-linked BODIPY oligomers is clearly possible, its occurrence has not yet been established.

Increasing interest in fluorophore dimers has further been due to their strong absorption and/or emission in the NIR spectral region ranging from 700 to 1000 nm. For diverse practical applications such as in solar cells, the materials should have good light-harvesting capability not only in the visible

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spectral range, but also in the NIR range, given that more than 50% of the energy in sunlight lies in the infrared region. In contrast, biological samples have low background fluorescence signals, and a concomitant high signal-to-noise ratio for emission in this spectral region. Moreover, NIR light can penetrate into sample matrices deeply due to low light scattering. Many advanced technologies including high-contrast bioimaging,[23] optical recording,[24] NIR laser filtering,[25] NIR photography,[26] and solar cells[27] could advantageously employ NIR absorbing dyes. However, many commercially available NIR dyes (e.g., cyanines and polyenes) suffer inherent drawbacks of insufficient photostability and solubility.[28] Thus, soluble and stable organic NIR dyes are highly desirable synthetic targets for organic chemists.

Here, we focus on the preparation of NIR-absorbing BODIPY dimers using a hypervalent iodine reagent. Phenyliodine(III)-bis(trifluoroacetate) (PIFA) has previously been used to prepare bis-aryl compounds in the presence of a Lewis acid or a fluoroalcohol as solvent,[29] *meso*−*meso*-linked linear arrays of porphyrins,[30] and fused diporphyrin scaffoldings.[31] Recently PIFA has been used to produce in a straightforward manner biphenyl-fused BODIPYs[32] through an oxidative fusion reaction in the 3,5-positions. Similarly, oxidation by $FeCl_3$ has been used to produce perylene-fused BODIPY[33] and porphyrins[34] with *meso*-substituents.

RESULTS AND DISCUSSION

Synthesis. Earlier work has shown that the oxidative coupling reactions of 1,3,5,7,8-pentamethyl-substituted BODIPYs using either PIFA or Fe(III) salts proceed very rapidly at the 2- and 6-substitution positions, leading to a variety of oligomers displaying unusual redox properties.[19a,b] Presently, to orientate the reaction in the 1-, 7- or 8-substitution positions of BODIPY, all the other positions were blocked. To minimize steric hindrance, methyl was chosen as the substituent for the 2,6-positions. Both methyl and thienyl derivatives were then chosen as substituents for the 3,5-positions (Figure 1). Thienyl substituents in those positions are known to give NIR BODIPY emitters.[15f]

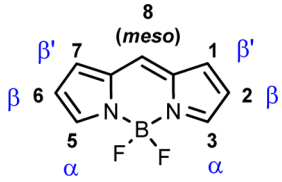


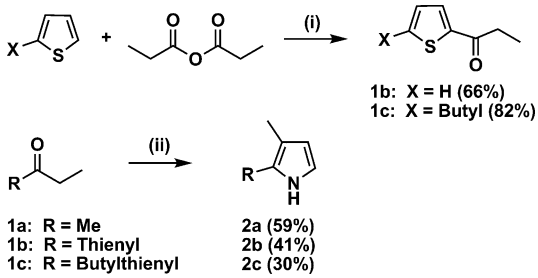
Figure 1. General formula of BODIPY with its numbering scheme.

The Trofimov reaction[35] allowed us to synthesize the pyrroles needed for the preparation of the BODIPY dyes. It can lead to various 2,3-disubstituted pyrroles depending upon the structure of the starting ketones. Pyrroles **2a**−**c**[36] were prepared according to this reaction using a one-pot literature procedure (Scheme 1).[37]

Either the ketones **1a**,[38] commercially available, or **1b**−**c**, obtained by acylation of thiophene with propanoic anhydride,[39] were condensed with hydroxylamine, and acetylene was fed into the reaction mixture under atmospheric pressure. The pyrroles were purified by column chromatography and isolated in quite acceptable yields (Scheme 1).

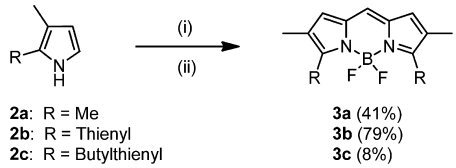
The synthesis of BODIPYs **3a**−**c** (Scheme 2) was conducted in two steps. Conversion of pyrroles **2a**−**c** into the intermediate

Scheme 1. Synthesis of Pyrroles 2a−c by the Trofimov Reaction[a]



[a]Reagents and conditions: (i) $BF_3{\cdot}Et_2O$ (0.1 equiv), 90−115 °C, 30 min; (ii) (a) NH_3OHCl, $NaHCO_3$, DMSO, rt, overnight; (b) acetylene, 100 °C, 30 min then KOH (1.5 equiv), 5 h.

Scheme 2. Synthesis of BODIPYs 3a−c with Triethyl Orthoformate[a]



[a]Reagents and conditions: (i) $HC(OEt)_3$ (15 equiv), TFA (6 equiv), CH_2Cl_2, rt; (ii) Evaporation, Et_3N (6 equiv), $BF_3{\cdot}Et_2O$ (8 equiv), CH_2Cl_2, rt, overnight.

dipyrromethenes by condensation with triethyl orthoformate followed a procedure established in porphyrin chemistry,[40] only one example being known for the preparation of BODIPY dyes.[41] This fast step was followed by *in situ* boron complexation to afford the desired compounds. Dye **3a** (Scheme 2) was obtained in a typical yield of 41% but **3b** in an excellent yield of 79%. Compound **3c** was very unstable on silica and alumina, so that chromatographic purification resulted in the very poor isolated yield of 8%.

To provide a comparison with oxidative coupling, at least with that involving 1,7-linking, the use of **3a** as a precursor of substrates for Pd-catalyzed cross-coupling was investigated (Scheme 3). Two pathways to dimerization were envisaged, one involving the direct linkage of two BODIPYs and another an acetylene bridge. While this work was in progress, others[42] reported dibromination of the 1,7-positions, Pd-catalyzed cross-coupling reactions and nucleophilic substitutions on chlorinated derivatives, while another study[43] concerned polyiodinated BODIPYs with some examples of 7-substitution. Recently, regioselective bromination on boron dipyrrins has also been explored.[44]

Our key compound was the monoiodinated derivative **4** (Scheme 3) obtained in good yield by using 1 equivalent of ICl (no trace of 1,7-diiodinated product was detected). The Sonogashira coupling reaction with TMS-acetylene was very efficient and led to **5** in 84% yield but failed completely when applied to the reaction between the deprotected compound **6** and the iodide **4**. The directly linked dimer could be prepared by Suzuki coupling between **4** and the pinacolboronate **7** in an acceptable yield. But it has been very difficult to obtain **7** as it is shown by the unsatisfactory yield of 16%. In comparison, the oxidative coupling reaction of **3a** using PIFA at room temperature in presence of $BF_3{\cdot}Et_2O$ (Scheme 4) gave better results. Dimer **8** was isolated by column chromatography in

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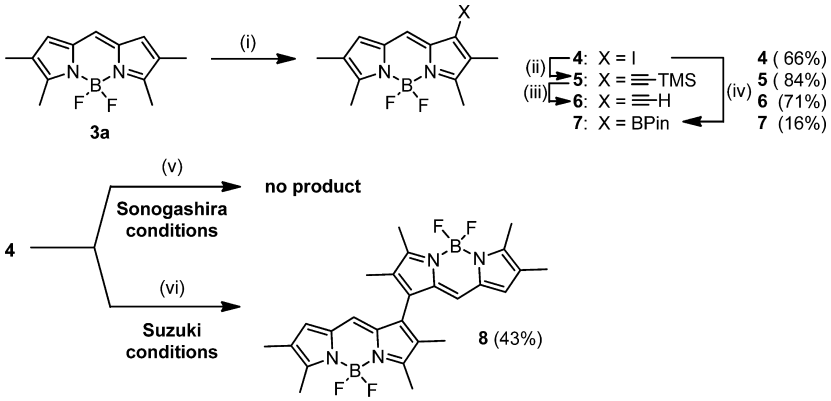
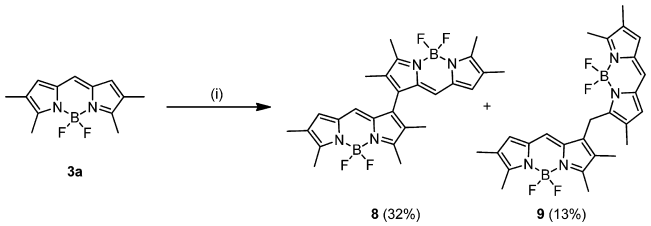
Scheme 3. Synthesis of the Dimer 8 by a Pd-catalyzed Cross-coupling Reaction[a]



[a]Reagents and conditions: (i) ICl (1 equiv), MeOH/DMF (1:1), rt, 45 min; (ii) TMS-acetylene, $[PdCl_2(PPh_3)_2]$ (6 mol %), CuI (6 mol %), $^iPrNH_2$, THF, rt, 1 h; (iii) K_2CO_3 (5 equiv), THF/H_2O/MeOH (10:5:2), rt, 20 min; (iv) Bis(pinacolato)diboron (2 equiv), CH_3CO_2K (1.5 equiv), $[PdCl_2(dppf)]$ (10%), dioxane, 90 °C, 24 h; (v) **6**, $[Pd(PPh_3)_4]$ (5%), Et_3N, THF, 60 °C, overnight; (vi) 7, CH_3CO_2K (1.5 equiv), $[PdCl_2(dppf)]$ (10%), dioxane, 90 °C, 24 h.

Scheme 4. Synthesis of the Dimers 8 and 9 by Oxidative Coupling[a]



[a]Reagents and conditions: (i) PIFA, BF_3·EtO, CH_2Cl_2, −78 °C to rt, overnight.

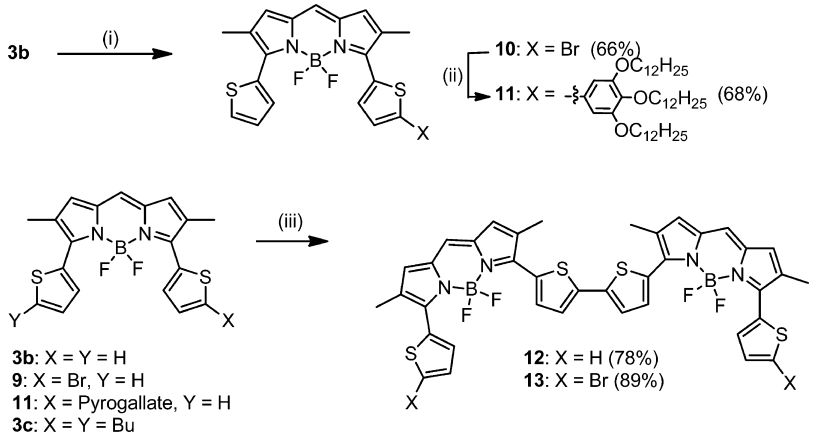
32% yield but was accompanied by the less polar compound **9** in 13% yield. This was characterized as a different dimer of **3a** in which the 1-position of one BODIPY was linked through a methylene bridge to the 3-position of another. In the absence of BF_3·Et_2O, only **9** was obtained, then in 27% isolated yield, a result of interest in regard to the reaction mechanism.[45]

Thus, it is known that Lewis acids such as BF_3·Et_2O can be used to increase the efficiency of PIFA-mediated oxidative coupling reaction, possibly by detaching by cleavage of one trifluoroacetoxy ligand of PIFA to generate a reactive cationic iodine(III) intermediate.[46] Oxidation of **3a** could lead to two electrophilic intermediates: a cation radical on the BODIPY core and a more stable benzylic-like cation.[47] Nucleophilic attack of a second molecule of **3a** could then produce both **8** and **9**, **8** only appearing when the more reactive reagent was used to create the higher energy intermediate. Where a methyl group was not present in the 3-position, as in compound **3b**, no methylene-bridged product could be detected.

When **3b** was reacted with PIFA/BF_3·Et_2O, a precipitate appeared and consumption of the starting BODIPY was complete in 30 min. The poorly soluble solid product could not be purified by column chromatography but only by successive washings and recrystallization to give a shiny dark blue powder in 78% yield.

This compound exhibited spectral data [IR, NMR (^1H, ^{11}B, ^{13}C, COSY, HSQC, HMBC, MS] and elemental analysis data consistent with the structure **12** (Scheme 5). The ^1H and ^{11}B NMR spectra were consistent with a symmetrical dimer although the aromatic proton signals were poorly resolved (Figure S41, Supporting Information). The COSY (Figure 2)

Scheme 5. Synthesis of the Dimers 12 and 13 by Oxidative Coupling[a]



[a]Reagents and conditions: (i) NBS (1 equiv), CH_2Cl_2/DMF (1:1), rt, 40 min; (ii) 3,4,5-tridodecyloxyphenylboronic acid pinacol ester, $[Pd(PPh_3)_4]$ (10%), Cs_2CO_3 (3 equiv), toluene, 60 °C, 18 h; (iii) PIFA, BF_3·Et_2O, CH_2Cl_2, rt, 30 min.

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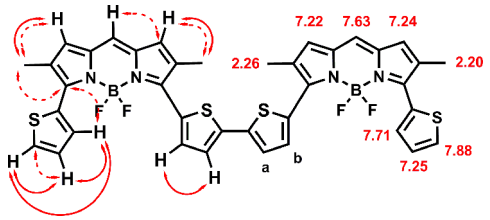

Figure 2. COSY (solid red line) and HMBC (dotted red line) correlations in compound **12**, and ^{1}H NMR chemical shifts in ppm.

correlations brought to light two major facts: no substituents in the 1,7 and 8-positions and two different thienyl groups in the molecule, one monosubstituted and the second one disubstituted. The COSY spectrum showed couplings between the protons at 7.88, 7.71, and 7.25 ppm, at 7.70 and 7.57 ppm, at 7.22 and 2.26 ppm and at 7.24 and 2.20 ppm. The HMBC correlations (Figure 2) between protons removed various ambiguities, namely the couplings between the proton at 2.20 ppm and the carbon at 149.4 ppm, the proton at 7.22 ppm and the carbon at 13.3 ppm, the proton at 7.24 ppm and the carbon at 13.2 ppm, the proton at 7.25 ppm and the carbon at 130.6 ppm, the proton at 7.63 ppm and the carbon at 130.4 ppm and the proton at 7.71 ppm and the carbon at 149.4 ppm. These are consistent with a dimer structure involving linkage through the thienyl units and, except for protons a and b (7.70/7.57 ppm), all of the signals have been assigned (Figure 2).

To increase the solubility of this dimer, BODIPYs substituted by butyl groups (**3c**, Scheme 2) and pyrogallate (**11**, Scheme 5) groups were synthesized. Bromination (Scheme 5) of **3b** was used to introduce the pyrogallate moiety by a Pd-catalyzed cross-coupling reaction. A single monobrominated compound was obtained with 1 equivalent of NBS. This electrophilic aromatic substitution took place in the α-position of the thiophene, not the 1-position of the BODIPY, in a good yield of 66%, to afford **10**. The Suzuki-Miyaura reaction of **10** with 1 equiv of 3,4,5-tridodecyloxyphenylboronic acid pinacol ester[48] led to the highly soluble dye **11** in good yield. Attempts to oxidatively couple **3c** and of **11** were carried out under our standard conditions (PIFA, $BF_3{\cdot}Et_2O$, rt) but no pure compound could be isolated from the product mixture, despite the fact that the dimer of **3b** was obtained (Scheme 5) in a yield of 89% under the same conditions. As for **12**, the poorly soluble product was purified by successive washings and recrystallization. This compound exhibited spectral data [IR, NMR (^{1}H, ^{11}B, ^{13}C, COSY, HSQC, HMBC, MS] and elemental analysis data consistent with the molecular structure **13**, which was unequivocally established by a single-crystal X-ray structure determination (*vide infra*).

X-Ray Molecular Structures. The X-ray crystal structures of the three compounds **3a**, **3b** and **13** were determined. Dye **3a**, which consists of a *F-BODIPY* core tetra-substituted by methyl groups, crystallizes in the orthorhombic space group, *Pccn* (no 56), and lies on a crystallographic 2-fold rotational axis that bisects the six-membered central ring along the direction given by the C7, B1 atoms (Figure 3). The BODIPY core (12 atoms) is almost perfectly planar with a root-mean-square (rms) deviation less than 0.01 Å. The B−N and B−F bond lengths are respectively 1.554(3) and 1.388(2) Å and the average N−B−N, F−B−F, and N−B−F angles are 107.4(2), 108.5(2), and 110.2(8)°, respectively. The pronounced double bond character for the C4−N1 bond [1.358(3) Å] in contrast with the longer C1−N1 bond lengths [1.390(3) Å] is once

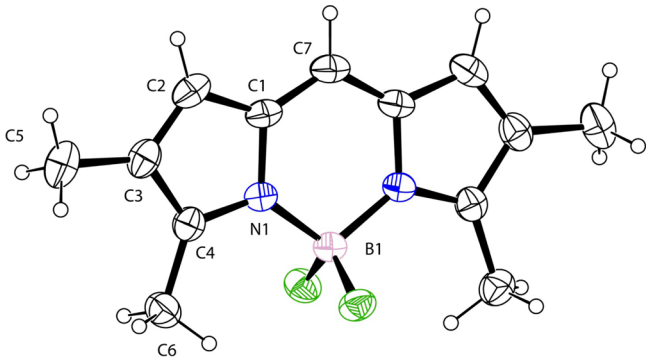

Figure 3. ORTEP view of dye **3a**. Displacements are drawn at the 30% probability level.

again observed, as for the two other crystal structures. Molecules **3a** are organized in layers stacking along the [0 0 1] direction (Figure 4). Within each layer, all the molecules are

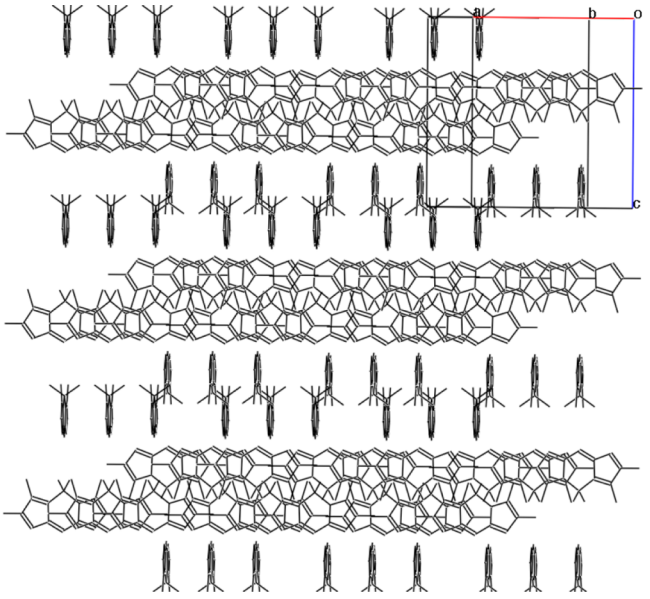

Figure 4. View perpendicular to the [1 3 0] plane of the **3a** crystal packing.

aligned parallel either to [1 −3 0] or [1 3 0], with a pyrrole group facing the second one in adjacent position along [0 1 0] with a centroid-centroid distance of 3.79 Å.

Substitution of methyl groups attached to C4 and C5 atoms by thienyl groups gave compound **3b**, which crystallized in the noncentrosymmetric orthorhombic space group, $Pna2_1$ (no 33). The molecules present a thienyl-ring flip disorder, with a major-minor orientation ratio refined to values of 0.604(7): 0.396(7) and 0.630(7): 0.370(7), respectively. The dihedral angles between the thienyl rings and the BODIPY core are respectively 48 and 38° (Figure 5). The thienyl group disorder likely contributes to the slight distortion of the BODIPY core despite the overall low rms deviation of 0.06 Å. The average B−N and B−F bond lengths are respectively 1.553(4) and 1.382(4) Å and the average N−B−N, F−B−F angles are 108.8(2), 109.9(3)°, whereas N−B−F angle values range from 107.8(3) to 111.3 (3)°.

The thienyl substitution in **3b** is associated with the absence of π−π stacking interactions between molecules, which are

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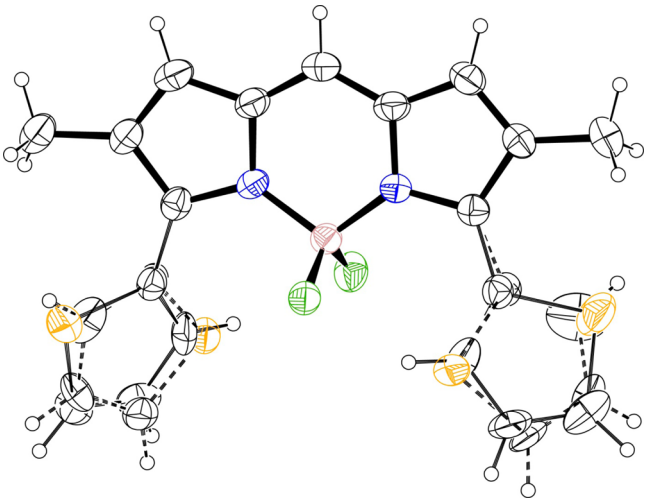

Figure 5. ORTEP view of dye **3b**. Displacements are drawn at the 30% probability level.

seemingly linked by weak C−H···C_g (π−ring) hydrogen bonds and also C−H···F bonds (2.356 Å for the shortest one) (Figure 6).

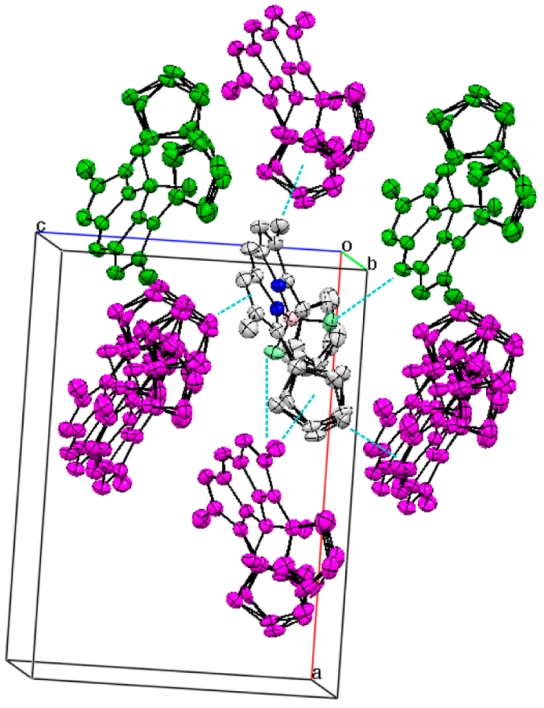

Figure 6. View down the ***b*** axis of the **3b** crystal packing. Dotted lines denote nonconventional H-bonds. Color code: molecules in general position (gray), related by a 2_1 axis (green), by a glide mirror ***c*** (magenta).

Finally, dye **13** is a dimer of the previous molecule **3b** by introducing a 1.45 Å C−C bond between two thienyl groups. These two groups lie basically in the same plane made by the two BODIPY cores and the S atoms face one another, 3.09 Å apart. The dimer crystallized in the monoclinic space group, *C*2/*c* (no 15) with 2-fold rotational crystallographic axis that bisects the C−C bond. The second pair of (bromo)-thienyl rings is tilted outward from the molecular platform by an approximately 60° angle, leaving the sulfur atoms on opposite sides with respect to the molecular plane (Figure 7).

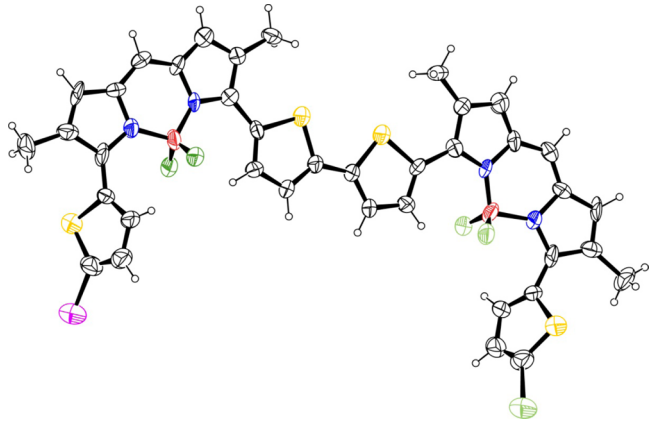

Figure 7. ORTEP view of dye **13**. Displacements are drawn at the 30% probability level.

The molecules **13** lie within infinite sheets parallel to the (2 0 1) plane, with an interplanar distance of ca. 4 Å indicating π−π interactions (Figure 8). Within the sheets, the molecules are regularly aligned with the crystallographic 2-fold rotational axis, the concavity of the molecule delineated by the thienyl substituents leaving room for cylindrical solvent channels running along the ***c*** axis (Figure 9).

Optical Properties. Spectroscopic data relevant to the present discussion are collected in Table 1 and typical spectra are given in Figures S53 to S59 (Supporting Information) for dyes **3a**−**c**, **4**−**7**. All these monomeric dyes exhibit absorption and emission patterns typical for BODIPY fluorophores,[49] with profiles and excited state lifetimes characteristic of singlet emitters. In particular the absorption spectrum shows a strong $S_0 \rightarrow S_1$ transition (of π−π^* nature), located at 537 nm for dye **3a** (Figure 10) which is shifted to lower energy for dye **3b** (λ_{abs} = 597 nm, Figure S54), highlighting the increase of conjugation by increasing the electronic density in the 3,5-substition positions. Such beneficial effects have previously been seen in thiophene-grafted BODIPY scaffoldings.[15f] The quantum yield remained very high for dye **3b** (78%) despite the notable decrease in energy of the main transition. Furthermore, for all dyes the absorption spectrum shows a broader absorption at higher energy with a lower extinction coefficient (around 10000 M^{-1} cm^{-1}), safely assigned in light of previous work to the $S_0 \rightarrow S_2$ transition (also of π−π^* nature).[49] In the case of the thienyl substituted derivatives, additional transitions at 319 and 301 nm are assigned to the π−π^* transition of the thienyl subunits. Both the fluorescence quantum yields and the excited-state lifetimes (nanosecond regime) recorded for all monomeric dyes are independent of excitation wavelength. In addition, the time-resolved fluorescence decay profile remains monoexponential under all conditions. The Stokes shifts (Δ_{SS} = 240 cm^{-1}) are very slight for the compound **3a** but greater for the thienyl based BODIPYs **3b**, **3c**, **10** and **11** (Δ_{SS} = 1229−1498 cm^{-1}, Table 1).

On substitution of the proton in **3a** by ethynyl groups in **5** and **6** or boronate in **7**, the absorption and emission profiles, quantum yields and excited state lifetimes remained essentially the same (Table 1). In the case of dye **4**, the presence of an iodo unit directly linked to the BODIPY core markedly decreases the quantum yield and the excited state lifetime due

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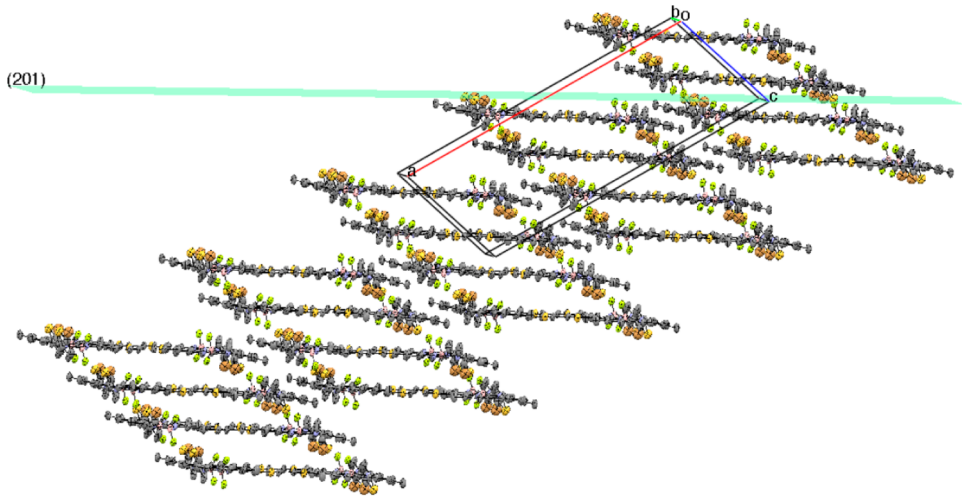

Figure 8. View down the ***b*** axis of the dye **13** crystal packing.

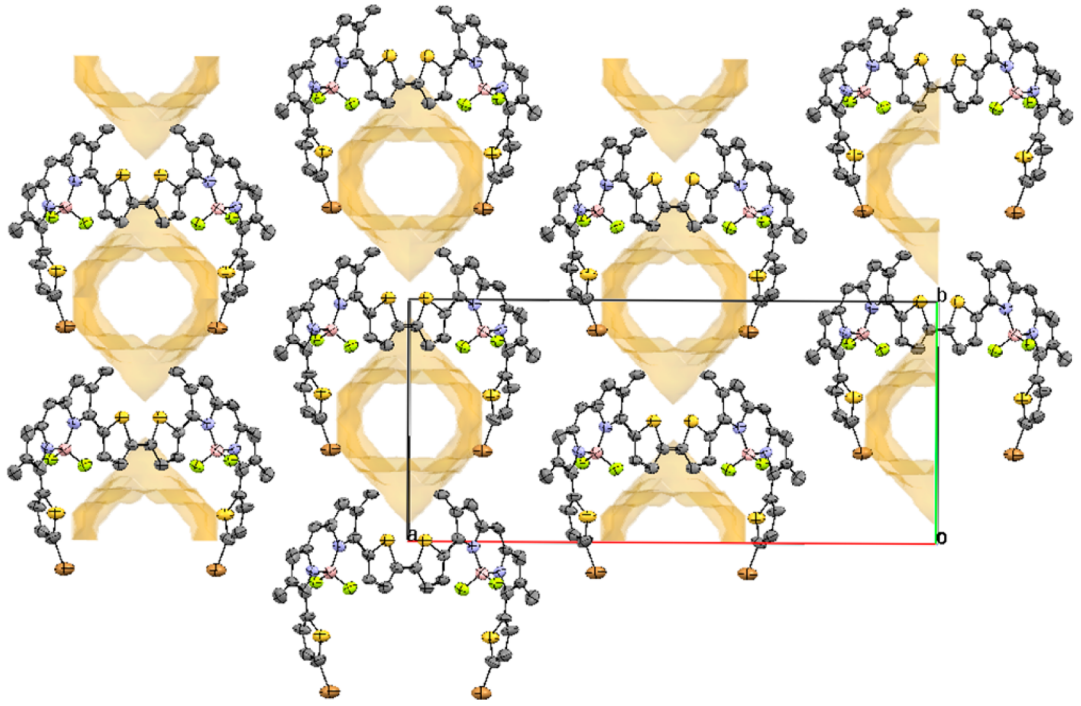

Figure 9. View of a 2-D sheet of dye **13** crystal packing. Columnar voids filled by diffuse solvent are running along the ***c*** axis.

to the heavy atom effect which favors intersystem crossing to the triplet state.[50] This provides an additional deactivation channel which causes a decrease of photoluminescence efficiency. This effect was much weaker in case of dye **10** with the bromo group attached to the thienyl residue. The quantum yield for dye **10** was 70% with respect to dye **3b** (78%) and the excited state lifetimes remained similar within experimental error. The substitution of the bromo groups by an electron rich pyrogallate platform in dye **11** shifted the emission wavelength to 692 nm (compared to 654 nm for dye **10**) whereas the quantum yield and excited state lifetime decreased by a factor of about 2 (see Table 1). Another point of interest is that for all monomeric dyes the absorption and emission profiles were not sensitive to the solvent polarity and that excitation spectra perfectly matched the absorption spectra, in keeping with the absence of aggregates (Figure 10). Finally, for the tetramethyl-BODIPY dyes and derivatives the fluorescence spectra showed good mirror symmetry with the lowest energy absorption transition, confirming that these transitions are due to the same weakly polarized excited state. This is not true for spectra of the thienyl-substituted dyes, which did not show mirror symmetry and had large Stokes shifts. We cannot at the present stage exclude some charge transfer from the electron rich thienyl subunits to the BODIPY core in its excited state.

For the dimers, the situation is not as would be expected for two close but independent chromophores. In the first series constructed from the tetramethyl-BODIPY core, two different situations were found (Figure 10). For dimer **8**, the absorption and emission profiles resembled that of the monomer **3a** with a set of vibronic bands extending to higher energies (spacing 1154 cm^{-1}), indicating minimal ground-state interaction or excitonic coupling between the two individual chromophores.[51] The emission spectrum was also similar to that of the

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Table 1. Selected Spectroscopic Data for the Monomers and the Dimers

dye	λ_{abs} (nm)	ε ($M^{-1}cm^{-1}$)	λ_{em} (nm)	Φ_F	τ_F (ns)	$k_r{}^a$ (10^8 s^{-1})	$k_{nr}{}^a$ (10^8 s^{-1})	solvent
3a	538	66000	545	0.93	11.0	0.8	0.06	Toluene
	537	76000	544	0.87	11.8	0.7	0.1	CH_2Cl_2
3b	606	58000	649	0.81	9.7	0.8	0.2	Toluene
	597	58000	647	0.78	9.2	0.8	0.2	CH_2Cl_2
3c	619	61000	670	0.66	9.5	0.7	0.3	CH_2Cl_2
4	539	93000	546	0.10	0.9	0.1	1.0	CH_2Cl_2
5	553	97000	559	0.80	10.1	0.8	0.2	CH_2Cl_2
6	550	96000	557	0.83	11.1	0.8	0.2	CH_2Cl_2
7	552	89000	560	0.85	12.1	0.7	0.1	CH_2Cl_2
8	560	69000	593	0.67	5.3	0.1	0.6	Toluene
	557	80000	598	0.05	1.9	0.3	4.9	CH_2Cl_2
	559	70000						DMSO
9	555	144000	563	0.36	4.9	0.7	1.3	Toluene
	553	139000	562	0.01	0.3	0.3	33.0	CH_2Cl_2
	550	136000	561	<0.01	0.1	1.3	124.0	DMSO
10	611	57000	657	0.73	9.2	0.8	0.3	Toluene
	603	59000	654	0.70	8.6	0.8	0.3	CH_2Cl_2
11	627	58000	692	0.41	4.2	1.0	1.4	CH_2Cl_2
12	687	41000	796	0.01	1.1	0.1	8.9	Toluene
	678	54000	790	<0.01				CH_2Cl_2
	672	36000						DMSO
13	701	58000	805	0.06	1.1	0.6	8.9	Toluene
	683	60000	801	0.03	0.7	0.4	14.6	CH_2Cl_2
	682	52000						DMSO

[a]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.

monomer. However, both the quantum yield and excited state lifetime were significantly reduced compared to those of the monomer **3a** (Table 1). Furthermore, the photoluminescence quantum efficiencies varied dramatically with the polarity of the solvent being 67% in toluene, 5% in dichloromethane and 0% in DMSO, although the shape of the absorption and emission spectra did not significantly vary with the solvent polarity (Figure S60−61, Supporting Information). Such behavior has been previously observed in *meso*-linked BODIPY dimers and it was hypothesized that a nonemissive charge-transfer state entailing some degree of symmetry breaking is responsible for the emission loss in polar solvents.[52] The possibility that dimer **8** could undergo symmetry-breaking internal charge transfer (ICT) was further assessed by cyclic voltammetry (*vide infra*).

The dimer **9** showed significantly different behavior compared to **8** (Figure 10c). The absorption spectrum indicated some excitonic coupling between the two BODIPY subunits and the absorption was split into two well-defined bands at 555 and 509 nm. The model compound **3a** showed a single absorption at 538 nm (in toluene). Dimer **9** exhibited a fluorescence maximum at 563 nm, independent of the excitation wavelength, with a quantum yield of 36% and a single decay lifetime of 4.94 ns (Table 1). The shape of the absorption spectrum but not that of the fluorescence band depended on the solvent polarity (Figure S62−63, Supporting Information). However, the photoluminescence efficiency dramatically decreased with increasing solvent polarity, indicating that a symmetry-breaking ICT was also effective in this case. The presence of a flexible methylene bridge in dimer **9** probably favors a modest excitonic coupling, as indicated by the splitting of the main absorption band into two overlapping bands rather than one which would be expected for an uncoupled dimer in which the low lying ICT is the main channel for deactivation of the excited state. This analysis is supported by the observations on the series of dimers based on bis-thiophene linkers. Dimers **12** and **13** also exhibited a splitting of the absorption band due to a modest excitonic coupling between both BODIPY moieties, whereas a single emission was found at 796 and 805 nm, respectively, in toluene (Figure 11). In both cases the photoluminescence efficiency remained low at 1 and 6%, respectively, for dimers **12** and **13**, while the excited state lifetimes were much shorter than those of the related monomer analogues: 1 ns versus about 9 ns for dyes **3b** and **10**. BODIPY dimers directly linked at the α- or β-positions do not exhibit such a nonradiative symmetry-breaking ICT.[18a,19a,b] However, dimers with an α,α-coupling exhibit very efficient excitonic coupling.[18]

Electrochemical Properties. Cyclic voltammograms were recorded in dichloromethane using tetrabutylammonium hexafluorophosphate as supporting electrolyte (electrochemical window from +1.9 to −2.2 V) and the ferricinium/ferrocene couple as internal reference and the results are given in Table 2. Those of monomer **3a** and dimer **8** are shown in Figure 12a. A reversible cathodic wave was observed at +1.02 V (ΔE_p = 70 mV), corresponding to a monoelectronic exchange and is attributed to the oxidation of the BODIPY core to its radical cation ($BOD/BOD^{\bullet+}$).[53] A second monoelectronic, irreversible reduction wave at −1.21 V is attributed to the formation of the BODIPY radical anion ($BODIPY/BODIPY^{\bullet-}$). For the dimer **8**, the oxidation waves appeared as two overlapping signals separated by 80 mV. Furthermore, two successive reduction waves separated by 210 mV were also clearly observed (Figure 12a). The first reduction is facilitated by 170 mV compared to the monomer **3a**. These results clearly reflect the breaking of the symmetry during the oxidation and the reduction of the dimer **8**. The fact that the splitting of the wave is more effective in reduction might reflect of better delocalization of the charge over the BODIPY cores. Within the same family of dyes the

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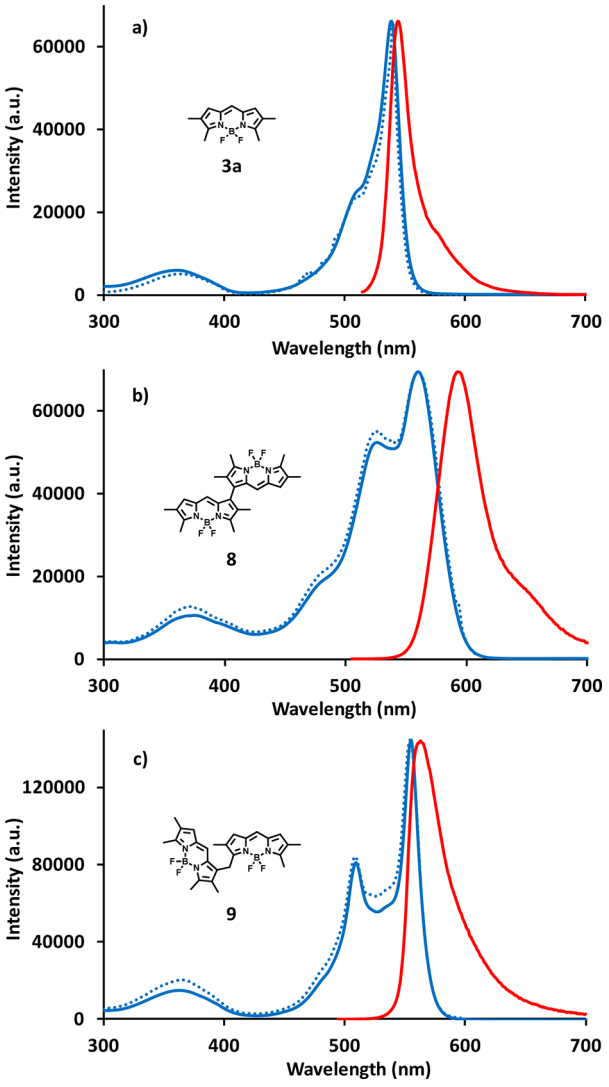

Figure 10. Absorption (blue trace), emission (red trace) and excitation (blue dashed trace) spectra for dyes at rt in toluene at c = 8 to 18 × 10^{-6} M for the absorption, c = 0.8 to 1.8 × 10^{-6} M for the emission and c = 4.4 × 10^{-8} to 5.3 × 10^{-6} M for the excitation.

methylene bridged dimer **9** also displayed a pronounced splitting of both cathodic and anodic waves (Figure 12b). In this case, the cathodic waves were separated by 200 mV and the anodic waves by 180 mV. This is a remarkable result which highlights the electronic interaction between the two parts of the molecules and the breaking of symmetry as hypothesized above. Worth noting is the fact that in the second family of dimers based on thienyl modules exhibited the same splitting of the cathodic and anodic waves (Figure 12c). However, the splitting was less pronounced than in the previous cases, with differences of 90 mV in oxidation and 80 mV in reduction. The nature and size of a dithienyl bridge versus that of a direct linkage or a methylene bridge makes the electronic interaction weaker.

CONCLUSION

In conclusion, we have designed and synthesized a series of novel monomeric and dimeric BODIPY dyes constructed from 2,3,5,6-substituted cores. The nature of the substituent drives the dimerization process when PIFA is the oxidant. With methyl groups in 3,5-positions, two types of dimers are

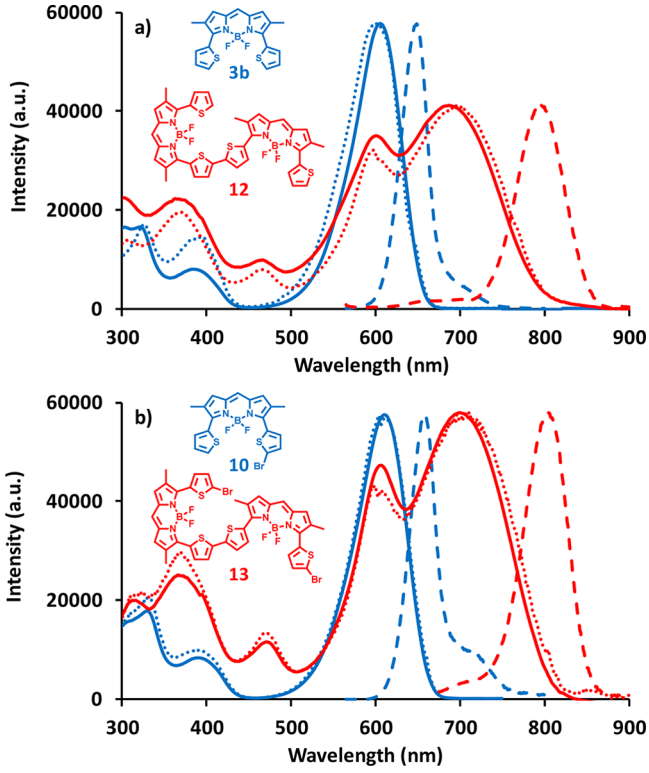

Figure 11. (a) Absorption (plain trace), emission (dashed trace) and excitation (dotted trace) spectra for the monomer **3b** (blue trace) and dimer **12** (red trace). (b) Absorption (plain trace), emission (dashed trace) and excitation (dotted trace) spectra for the monomer **10** (blue trace) and dimer **13** (red trace). All spectra in toluene at rt with c = 2.1 to 12 × 10^{-6} M for the absorption, c = 9.6 × 10^{-7} to 2.1 × 10^{-5} M for the emission and c = 4.8 × 10^{-7} to 2.1 × 10^{-6} M for the excitation.

Table 2. Solution Electrochemical Properties of the Monomeric and Dimeric Dyes[a]

compounds	E_{ox}, V (ΔE, mV)	E_{red}, V (ΔE, mV)
3a	+1.02 (70)	−1.21 (irr.)
3b	+0.93 (70)	−0.90 (irr.)
8	+1.06 (60); +1.14 (60)	−1.04 (60); −1.25 (60)
9	+1.02 (70); +1.22 (60)	−1.17 (irr.); −1.35 (70)
10	+0.95 (75)	−0.88 (irr.)
11	+0.82 (70); +1.07 (70)	−0.93 (irr.)
12	+0.62 (irr.); +0.80 (40); +0.95 (70)	−0.58 (irr.); −0.83 (irr.)
13	+0.82 (50); +0.91 (60)	−0.78 (irr.); −0.86 (irr.)

[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 mM and at rt. Potentials are given versus the saturated calomel electrode (SCE) and standardized vs ferrocene (Fc) as internal reference assuming that $E_{1/2}$ (Fc/Fc^+) = +0.38 V (ΔE_p = 70 mV) vs SCE. The error in half-wave potentials is ±15 mV. Where the redox processes are irreversible, the peak potentials (E_{ap} or E_{cp}) are quoted. All reversible redox steps result from one-electron processes unless otherwise specified.

obtained, one directly linked through the BODIPY 1-positions and the second one with a methylene bridge. In the latter case, one methyl of one partner and the pyrrole of the second partner are used to form the linkage. In the thiophene cases, thienyl−thienyl coupling is preferred and allows the preparation of dimers in excellent yields. The dimers exhibit a marked splitting of the oxidation and reduction waves as great as 210

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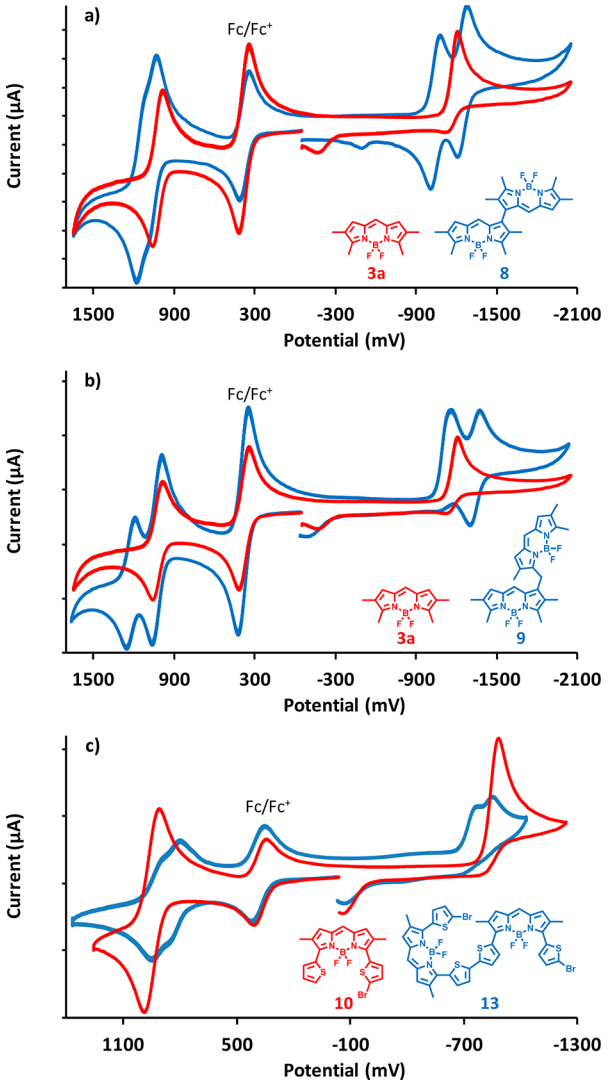

Figure 12. Cyclic voltammograms of (a) monomer **3a** (red trace) and dimer **8** (blue trace), (b) **3a** (red trace) and dimer **9** (blue trace), (c) monomer **10** (red trace) and dimer **13** (blue trace). Concentration of dyes 1.5×10^{-3} M in CH_2Cl_2 (0.1 M, $^nBu_4NPF_6$), Fc^+/Fc refers to the ferricinium/ferrocene couple used as internal reference $E_{1/2}$ (Fc^+/Fc) = +0.38 V (ΔE_p = 60 mV).

and 180 mV in the best cases, highlighting a pronounced electronic interaction and symmetry breaking during electron exchange processes. For the dimers, modest excitonic coupling is observed in apolar solvents and the photoluminescence efficiency is dramatically sensitive to the solvent polarity. The absence of emission in DMSO is likely due to an internal charge transfer state likely formed by symmetry breaking in the excited state. These results should be extremely useful for the further design of relevant fluorescent compounds absorbing in the red and NIR with tunable emission properties. Current work is focused on enhancing the fluorescence properties by restricting the rotation of the thienyl rings.

EXPERIMENTAL SECTION

General Methods. ^1H and ^{13}C spectra were recorded at rt on 200, 300, and 400 MHz spectrometers using perdeuterated solvents as internal standards. Chemical shifts of ^1H and ^{13}C spectra are given in ppm relative to residual protiated solvent and relative to the solvent respectively. 11B spectra were recorded at rt on a 400 MHz spectrometer using $BF_3{\cdot}Et_2O$ as reference. FT-IR spectra were recorded using a spectrometer equipped with an ATR "diamond" apparatus. Chromatographic purification was conducted using 40−63 μm silica gel or aluminum oxide 90 standardized. Thin layer chromatography (TLC) was performed on silica gel or aluminum oxide plates coated with fluorescent indicator. All mixtures of solvents are given in v/v ratio. All anhydrous reactions were carried out under dry argon by using Schlenk tube techniques.

Spectroscopic Measurements. UV−visible spectra were recorded using a dual-beam grating spectrophotometer with a 1 cm quartz cell. All fluorescence spectra were corrected. The fluorescence quantum yield ($_{\Phi cmp}$) was calculated from eq 1:

$$\Phi_{cmp} = \Phi_{ref}\frac{I}{I_{ref}}\frac{OD_{ref}}{OD}\frac{n^2}{n_{ref}^2} \quad (1)$$

Here, I denotes the integral of the corrected emission spectrum, OD is the optical density at the excitation wavelength and n is the refractive index of the medium. The reference systems used were Rhodamine 6G (Φ_{em} = 0.78 in H_2O) and Cresyl violet (Φ_{em} = 0.53 in CH_3OH).[54]

Luminescence lifetimes were measured on a spectrofluorimeter using software with Time-Correlated Single Photon Mode coupled to a stroboscopic system. The excitation source was a laser diode (λ = 310 nm). No filter was used for the excitation. The instrument response function was determined by using a light-scattering solution (LUDOX).

Electrochemistry. Electrochemical studies employed cyclic voltammetry with a conventional 3-electrode system using a voltammetric analyzer equipped with a platinum micro disk (2 mm2) working electrode and a silver wire counter electrode. Ferrocene was used as an internal standard and was calibrated against a saturated calomel reference electrode solution (SSCE) separated from the electrolysis cell by a glass frit presoaked with electrolyte solution. Solutions contained the electroactive substrate in deoxygenated and anhydrous CH_2Cl_2 containing doubly crystallized tetra-n-butylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The electrochemical cell was flushed with anhydrous nitrogen gas.

Materials. All chemicals were used as received from commercial sources without further purification. CH_2Cl_2 was distilled over P_2O_5 and THF was distilled over sodium and benzophenone under an argon atmosphere. $[Pd(PPh_3)_4]$,[55] $[PdCl_2(PPh_3)_2]$,[56] $[PdCl_2(dppf)]$,[57] 1-(thien-2-yl)propan-1-on,[58] 2,3-dimethyl-1*H*-pyrrole,[59] 3-methyl-2-(thien-2-yl)-1*H*-pyrrole[60] and 4,4,5,5-tetramethyl-2-[3,4,5-tris(dodecyloxy)phenyl]-1,3,2-dioxaborolane[61] were synthesized according to the literature procedures. *N*-Bromosuccinimide was recrystallized from hot water.

Representative Procedure for the Synthesis of Ketones 1b−c. *1-(Thien-2-yl)propan-1-on (**1b**).* In a two-necked flask equipped with a reflux condenser to a mixture of propionic anhydride (37.2 mL, 290 mmol, 1.16 equiv) and thiophene (20.0 mL, 250 mmol, 1 equiv) was added $BF_3{\cdot}Et_2O$ (3.1 mL, 25 mmol, 0.1 equiv) at rt. The temperature rose rapidly to 90−115 °C upon the addition of the catalyst. After 30 min the mixture had cooled to rt and water was added. The reaction mixture was extracted with Et_2O. The combined extracts were washed with a saturated solution of $NaHCO_3$ and dried over $MgSO_4$. The residue was distilled under vacuum (110 °C at 22 mmHg). The product **1b** was obtained as a colorless oil in 66% yield (23.10 g): ^1H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.70 (dd, ^3J = 3.8 Hz, ^4J = 1.1 Hz, 1H), 7.61 (dd, ^3J = 5.0 Hz, ^4J = 1.1 Hz, 1H), 7.12 (dd, ^3J = 5.0 Hz, ^3J = 3.8 Hz, 1H), 2.94 (q, ^3J = 7.4 Hz, 2H), 1.23 (t, ^3J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 193.8, 144.2, 133.1, 131.5, 128.0, 32.6, 8.5.

*1-(5-Butylthien-2-yl)propan-1-one (**1c**).* Colorless oil. Yield 82%. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.53 (d, ^3J = 3.8 Hz, 1H), 6.79 (d, ^3J = 3.8 Hz, 1H), 2.86 (q, ^3J = 7.3 Hz, 2H), 2.84 (q, ^3J = 7.6 Hz, 2H), 1.67 (m, 2H), 1.38 (m, 2H), 1.21 (t, ^3J = 7.4 Hz, 3H), 0.93 (t, ^3J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 193.6, 155.3, 141.5, 131.9, 125.4, 33.4, 32.1, 30.3, 22.1, 13.7, 8.7; IR (ν, cm^{-1}): 2958, 2934, 2873, 1659, 1533, 1455, 1417; EI-MS *m*/*z* (nature of the peak,

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relative intensity): 196.1 ([M]$^+$, 100); Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22. Found: C, 67.54; H, 8.42.

Representative Procedure for the Synthesis of Pyrroles 2a–c. *2,3-Dimethyl-1H-pyrrole (**2a**).* To a solution of hydroxylamine hydrochloride (1.92 g, 27.7 mmol, 1 equiv) in DMSO (55 mL) were added $NaHCO_3$ (2.33 g, 27.7 mmol, 1 equiv) and the ketone **1a** (2.48 mL, 27.7 mmol, 1 equiv). The mixture was allowed to stand for a night. Then the mixture was heated to 100–110 °C and acetylene was fed upon stirring for 30 min. After addition of potassium hydroxide (2.33 g, 41.6 mmol, 1.5 equiv), acetylene feeding was continued at the same temperature for 5 h at a rate of ∼15 cm^3min^{-1}. Then the mixture was cooled down, diluted with water and extracted with Et_2O. The extracts were washed with water and dried over $MgSO_4$. The residue was purified by column chromatography (Al_2O_3, petroleum ether/Et_2O 75:25). The product **2a** was obtained as a brown oil in 59% yield (1.57 g): ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ = 7.72 (brs, 1H), 6.59 (t, J_{H1H4H5} = 2.7 Hz, 1H), 6.00 (t, J_{H1H4H5} = 2.7 Hz, 1H), 2.19 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 123.6, 114.8, 114.1, 110.0, 10.9, 10.8.

*3-Methyl-2-(thien-2-yl)-1H-pyrrole (**2b**).* Purification by column chromatography (Al_2O_3, petroleum ether/Et_2O 80:20). Brown oil. Yield 52% (3.63 g). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ = 8.14 (brs, 1H), 7.21 (dd, ^3J = 5.1 Hz, ^4J = 1.3 Hz, 1H), 7.06 (dd, ^3J = 5.1 Hz, ^3J = 3.5 Hz, 1H), 7.00 (dd, ^3J = 3.5 Hz, ^4J = 1.3 Hz, 1H), 6.73 (t, J_{H1H4H5} = 2.7 Hz, 1H), 6.13 (t, J_{H1H4H5} = 2.7 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ = 141.6, 135.9, 127.4, 122.8, 121.8, 117.4, 116.9, 112.0, 12.4.

*2-(5-Butylthien-2-yl)-3-methyl-1H-pyrrole (**2c**).* Purification by column chromatography (Al_2O_3, petroleum ether). Yellow oil. Yield 30% (2.21 g). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 8.04 (brs, 1H), 6.79 (d, ^3J = 3.5 Hz, 1H), 6.71 (d, ^3J = 3.5 Hz, 1H), 6.69 (t, J_{H1H4H5} = 2.8 Hz, 1H), 6.10 (t, J_{H1H4H5} = 2.8 Hz, 1H), 2.81 (t, ^3J = 7.9 Hz, 2H), 2.26 (s, 3H), 1.68 (m, 2H), 1.42 (m, 2H), 0.95 (t, ^3J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 143.6, 133.3, 124.3, 123.3, 121.6, 116.9, 116.3, 111.9, 33.8, 29.7, 22.2, 13.8, 12.4. This compound was quite unstable even in the freezer and has been used right after.

Representative Procedure for the Synthesis of BODIPY 3a–c. *4,4′-Difluoro-2,3,5,6-tetramethyl-4-bora-3a,4a-diaza-s-indacene (**3a**).* To a solution of pyrrole **2a** (800 mg, 8.4 mmol, 2 equiv) in dry CH_2Cl_2 (100 mL) were successively added triethyl orthoformate (10.5 mL, 63.1 mmol, 15 equiv) and trifluoroacetic acid (1.9 mL, 25.2 mmol, 6 equiv). The mixture was stirred at rt for 45 min, concentrated and the excess of triethyl orthoformate was removed under vacuum. The residue was resolubilized in dry CH_2Cl_2 (40 mL) and triethylamine (3.5 mL, 25.2 mmol, 6 equiv) was added. After 10 min of stirring, $BF_3{\cdot}Et_2O$ (4.2 mL, 33.6 mmol, 8 equiv) was added. The solution was stirred at rt for a night, then poured into a saturated solution of $NaHCO_3$ and stirred further for 1 h (2 × 50 mL). The reaction mixture was washed with water, with brine, dried over $MgSO_4$, filtered and evaporated. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 60:40) and the product **3a** was recrystallized from CH_2Cl_2/EtOH to afford green metallic crystals in 41% yield (429 mg): mp 230–232 °C; ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ = 6.83 (s, 1H), 6.65 (s, 2H), 2.51 (s, 6H), 2.02 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ = 156.3, 133.0, 127.9, 124.4, 30.9, 12.7 (t, J_{C-F} = 2.3 Hz), 11.0; ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ = 0.85 (t, ^1J = 33.3 Hz); UV–vis (CH_2Cl_2) λ nm (ε, $M^{-1}cm^{-1}$): 537 (77000), 510 (32000), 359 (8000), 232 (15000); IR (ν, cm^{-1}): 3076, 2926, 2864, 1612, 1596, 1462, 1409, 1367; EI-MS *m*/*z* (nature of the peak, relative intensity): 248.0 ([M]$^+$, 100), 229.0 ([M − F]$^+$, 30); Anal. Calcd for $C_{13}H_{15}BF_2N_2$: C, 62.94; H, 6.09; N, 11.29. Found: C, 62.64; H, 5.85; N, 10.96.

*4,4′-Difluoro-2,6-dimethyl-3,5-(dithien-2-yl)-4-bora-3a,4a-diaza-s-indacene (**3b**).* Purification by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 60:40) and recrystallization. Blue metallic crystals. Yield 79%. mp 203–206 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.76 (dd, ^3J = 3.8 Hz, ^4J = 1.0 Hz, 2H), 7.51 (dd, ^3J = 5.2 Hz, ^4J = 1.0 Hz, 2H), 7.15 (dd, ^3J = 3.8 Hz, ^3J = 5.2 Hz, 2H), 7.00 (s, 1H), 6.85 (s, 2H), 2.22 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 150.0, 134.9, 132.3, 131.8 (t, J_{C-F} = 5.8 Hz), 130.4, 129.4, 128.8, 127.6, 124.8, 13.5; ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ = 1.24 (t, ^3J = 32.9 Hz); UV–vis (CH_2Cl_2) λ nm (ε, $M^{-1}cm^{-1}$): 597 (60000), 383 (9000), 319 (17000), 301 (17000), 232 (19000); IR (ν, cm^{-1}): 3099, 3068, 2916, 2856, 1601, 1515, 1451, 1435, 1397, 1345, 1278; EI-MS *m*/*z* (nature of the peak, relative intensity): 384.0 ([M]$^+$, 100); Anal. Calcd for $C_{19}H_{15}BF_2N_2S_2$: C, 59.39; H, 3.93; N, 7.29. Found: C, 59.21; H, 3.77; N, 7.02.

*3,5-[Di-(5-butylthien-2-yl)]-4,4′-difluoro-2,6-dimethyl-4-bora-3a,4a-diaza-s-indacene (**3c**).* Purification by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 70:30) and recrystallization. Pink metallic needles. Yield 8%. mp 260–263 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.66 (d, ^3J = 3.8 Hz, 2H), 6.90 (s, 1H), 6.83 (d, ^3J = 3.8 Hz, 2H), 6.79 (s, 2H), 2.86 (t, ^3J = 7.6 Hz, 4H), 2.24 (s, 6H), 1.71 (m, 4H), 1.45 (m, 4H), 0.95 (t, ^3J = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 150.1, 149.8, 134.8, 132.0 (t, J_{C-F} = 6.3 Hz), 130.00, 129.95, 129.1, 125.1, 123.4, 33.5, 29.9, 22.4, 13.84, 13.81; ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ = 1.35 (t, ^1J = 32.9 Hz); UV–vis (CH_2Cl_2) λ nm (ε, $M^{-1}cm^{-1}$): 619 (61000), 396 (10000), 336 (19000), 307 (17000), 232 (20000); IR (ν, cm^{-1}): 3082, 2954, 2926, 2871, 2855, 1594, 1552, 1493, 1465, 1453, 1427, 1399, 1337, 1317; EI-MS *m*/*z* (nature of the peak, relative intensity): 496.2 ([M]$^+$, 100); Anal. Calcd for $C_{27}H_{31}BF_2N_2S_2$: C, 65.32; H, 6.29; N, 5.64. Found: C, 65.07; H, 5.89; N, 5.38.

*4,4′-Difluoro-1-iodo-2,3,5,6-tetramethyl-4-bora-3a,4a-diaza-s-indacene (**4**).* To a solution of **3a** (100 mg, 0.40 mmol, 1 equiv) in MeOH/DMF (20 mL, 1:1) was added dropwise a solution of ICl (71 mg, 0.44 mmol, 1 equiv) in MeOH (5 mL) at rt. The reaction was monitored by TLC inspection. After 45 min the reaction mixture was diluted with CH_2Cl_2, washed with a saturated solution of $Na_2S_2O_3$, abundantly with water and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$. The solvent was removed under vacuum. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 60:40) and recrystallized from CH_2Cl_2/EtOH. The product **4** was obtained as green metallic crystals in 66% yield (99 mg): mp 196–198 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 6.90 (s, 1H), 6.75 (s, 1H), 2.55 (s, 3H), 2.50 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 158.9, 153.4, 134.2, 134.0, 131.1, 129.5, 129.1, 124.4, 92.4, 13.2, 12.9, 12.7, 11.2; ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ = 0.79 (t, ^1J = 32.9 Hz); UV–vis (CH_2Cl_2) λ nm (ε, $M^{-1}cm^{-1}$): 539 (93000), 512 (36000), 376 (8000), 231 (19000); IR (ν, cm^{-1}): 2918, 2851, 1591, 1464, 1406, 1371, 1340; EI-MS *m*/*z* (nature of the peak, relative intensity): 374.0 ([M]$^+$, 100), 247.0 ([M − I]$^+$, 30); Anal. Calcd for $C_{13}H_{14}BF_2IN_2$: C, 41.75; H, 3.77; N, 7.49. Found: C, 41.62; H, 3.37; N, 7.31.

*4,4′-Difluoro-2,3,5,6-tetramethyl-1-(trimethylsilylethynyl)-4-bora-3a,4a-diaza-s-indacene (**5**).* To a solution of **4** (100 mg, 0.27 mmol, 1 equiv) in a mixture of THF (15 mL) and diisopropylamine (2.4 mL) were added $PdCl_2(PPh_3)_2$ (11 mg, 0.016 mmol, 0.06 equiv) and CuI (3 mg, 0.016 mmol, 0.06 equiv). The solution was degassed for 30 min. Ethynyltrimethylsilane (53 mg, 0.53 mmol, 2 equiv) was then added. The solution was stirred at rt and monitored by TLC. After 1 h the solvent was removed under vacuum. The residue was treated with water, extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was removed under vacuum. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 60:40) and recrystallized from CH_2Cl_2/EtOH. The product **5** was obtained as green metallic crystals in 94% yield (87 mg): mp 202–205 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.01 (s, 1H), 6.75 (s, 1H), 2.53 (s, 3H), 2.47 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 0.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 158.8, 153.3, 134.6, 133.9, 129.6, 129.5, 129.4, 129.0, 122.0, 104.9, 97.1, 12.9, 12.5, 11.2, 10.0, 0.1; ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ = 0.74 (t, ^1J = 33.9 Hz); UV–vis (CH_2Cl_2) λ nm (ε, $M^{-1}cm^{-1}$): 553 (97000), 523 (35000), 404 (8000), 223 (19000); IR (ν, cm^{-1}): 2953, 2919, 2856, 2148, 1597, 1465, 1414, 1392; EI-MS *m*/*z* (nature of the peak, relative intensity): 344.1 ([M]$^+$, 100), 325.1 ([M − F]$^+$, 20); Anal. Calcd for $C_{18}H_{23}BF_2N_2Si$: C, 62.80; H, 6.73; N, 8.14. Found: C, 62.72; H, 6.59; N, 8.09.

*1-Ethynyl-4,4′-difluoro-2,3,5,6-tetramethyl-4-bora-3a,4a-diaza-s-indacene (**6**).* To a solution of **5** (50 mg, 0.15 mmol, 1 equiv) in

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THF (10 mL) was added a solution of K_2CO_3 (104 mg, 0.75 mmol, 5 equiv) in water (5 mL) and MeOH (2 mL). The mixture was stirred for 20 min at rt. The solvent was removed under vacuum. The residue was treated with water and extracted with CH_2Cl_2. The organic layer was washed with water, with brine and dried over $MgSO_4$. The solvent was removed under vacuum. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 60:40) and recrystallized from CH_2Cl_2/EtOH. The product **6** was obtained as green metallic crystals in 71% yield (29 mg): mp 192−193 °C; ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ = 7.04 (s, 1H), 6.74 (s, 1H), 3.51 (s, 1H), 2.53 (s, 3H), 2.48 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 159.5, 152.8, 134.6, 134.0, 129.8, 129.7, 129.3, 122.1, 120.4, 86.2, 76.2, 13.0, 12.5, 11.2, 9.9; ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ = 0.74 (t, ^1J = 31.8 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}cm^{-1}$): 550 (96000), 522 (37000), 395 (8000), 223 (21000); IR (ν, cm^{-1}): 3266, 3058, 2925, 2857, 1608, 1560, 1502, 1465, 1416, 1387; EI-MS *m*/*z* (nature of the peak, relative intensity): 272.1 ([M]$^+$, 100); Anal. Calcd for $C_{15}H_{15}BF_2N_2$: C, 66.21; H, 5.56; N, 10.30. Found: C, 66.04; H, 5.29; N, 10.19.

*4,4′-Difluoro-2,3,5,6-tetramethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-bora-3a,4a-diaza-s-indacene (**7**).* **4** (50 mg, 0.13 mmol, 1 equiv), bis(pinacolato)diboron (66 mg, 0.26 mmol, 2 equiv), potassium acetate (20 mg, 0.20 mmol, 1.5 equiv) and $PdCl_2$(dppf) (10 mg, 0.013 mmol, 0.1 equiv) were dissolved in dioxane (5 mL) and heated at 90 °C for 24 h. The reaction mixture was diluted with CH_2Cl_2, washed with water, and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$. The solvent was removed under vacuum. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 60:40) and recrystallized from CH_2Cl_2/EtOH. The product **7** was obtained as green metallic crystals in 16% yield (8 mg): mp 231−234 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.46 (s, 1H), 6.75 (s, 1H), 2.52 (s, 3H), 2.50 (s, 3H), 2.19 (s, 3H), 2.03 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 157.3, 154.8, 138.3, 136.0, 134.0, 128.8, 128.43, 128.41, 126.0, 83.2, 24.9, 12.8, 12.3, 11.2, 11.1; ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ = 0.87 (t, ^1J = 31.8 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}cm^{-1}$): 552 (89000), 365 (9000), 233 (12000); IR (ν, cm^{-1}): 2980, 2922, 2856, 1600, 1521, 1461, 1406; EI-MS *m*/*z* (nature of the peak, relative intensity): 374.1 ([M]$^+$, 100); Anal. Calcd for $C_{19}H_{26}B_2F_2N_2O_2$: C, 61.01; H, 7.01; N, 7.49. Found: C, 60.77; H, 6.89; N, 7.22.

*1,1′-Bi-(4,4′-difluoro-2,3,5,6-tetramethyl-4-bora-3a,4a-diaza-s-indacene) (**8**).* **Suzuki coupling procedure: 4** (25 mg, 0.07 mmol, 1 equiv), potassium acetate (10 mg, 0.10 mmol, 1.5 equiv), **7** (25 mg, 0.07 mmol, 1 equiv) and $PdCl_2$(dppf) (5 mg, 0.007 mmol, 0.1 equiv) were dissolved in dioxane (5 mL) in a Schlenk flask and heated at 90 °C for 24 h. The reaction mixture was diluted with CH_2Cl_2, washed with water, and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$. The solvent was removed under vacuum. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 60:40), then recrystallized from CH_2Cl_2/cyclohexane. The product **8** was obtained as a red powder in 43% yield (15 mg). **Oxidative coupling procedure: 3a** (200 mg, 0.80 mmol, 1 equiv) was dissolved in dry CH_2Cl_2 (20 mL) in a Schlenk flask. The solution was cooled to −78 °C and PIFA (172 mg, 0.40 mmol, 0.5 equiv), then BF_3·Et_2O (0.1 mL, 0.80 mmol, 1 equiv) were added. The solution was allowed to rise at rt during the night. After 18 h the mixture was poured into water and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$. The solvent was removed under vacuum. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 60:40 to 40:60) and recrystallized from CH_2Cl_2/EtOH. The product **8** was obtained as a red powder in 32% yield (63 mg): mp >260 °C dec.; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 6.66 (s, 2H), 6.62 (s, 2H), 2.58 (s, 6H), 2.55 (s, 6H), 2.03 (s, 6H), 1.92 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 157.6, 155.0, 133.7, 132.9, 132.5, 128.8, 128.6, 126.5, 124.0, 12.83, 12.82, 11.1, 10.1; ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ = 0.97 (t, ^1J = 33.9 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}cm^{-1}$): 557 (80000), 523 (57000), 371 (12000); IR (ν, cm^{-1}): 2926, 2863, 1590, 1555, 1463, 1406; EI-MS *m*/*z* (nature of the peak, relative intensity): 494.1 ([M]$^+$, 100), 456.1 ([M − 2F]$^+$, 10); Anal. Calcd for $C_{26}H_{28}B_2F_4N_4$: C, 63.20; H, 5.71; N, 11.34. Found: C, 62.84; H, 5.54; N, 11.09.

*4,4′-Difluoro-5-(4,4′-difluoro-2,3,5,6-tetramethyl-4-bora-3a,4a-diaza-s-indacen-1-yl)methyl-2,3,6-trimethyl-4-bora-3a,4a-diaza-s-indacene (**9**).* **3a** (200 mg, 0.80 mmol, 1 equiv) was dissolved in dry CH_2Cl_2 (20 mL) in a Schlenk flask. PIFA (172 mg, 0.40 mmol, 0.5 equiv) was added and the mixture was stirred at rt. The reaction was monitored by TLC. When the consumption of **3a** was stabilized (1 h), $NaBH_4$ (14 mg, 0.40 mmol, 0.5 equiv) was added. After 15 min the reaction mixture was poured into water and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$. The solvent was removed under vacuum. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 60:40 to 40:60) and recrystallized from CH_2Cl_2/EtOH. The product **9** was obtained as a red powder in 27% yield (52 mg): mp >260 °C dec.; ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ = 6.91 (s, 1H), 6.85 (s, 1H), 6.75 (s, 1H), 6.63 (s, 1H), 6.58 (s, 1H), 4.28 (s, 2H), 2.54 (s, 3H), 2.51 (s, 3H), 2.48 (s, 3H), 2.06 (s, 3H), 1.98 (s, 3H), 1.91 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 158.3, 155.9, 155.2, 154.5, 136.6, 133.6, 132.8, 132.7, 132.3, 129.2, 128.8, 128.7, 128.2, 128.0, 127.4, 126.2, 125.1, 122.6, 24.1, 12.88, 12.86, 12.6, 11.4, 11.1, 11.0, 9.0; ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ = 0.97 (t, ^1J = 33.9 Hz), 0.85 (t, ^1J = 33.9 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}cm^{-1}$): 553 (143000), 507 (82000), 362 (16000); IR (ν, cm^{-1}): 2924, 2856, 1602, 1464, 1410, 1377; EI-MS *m*/*z* (nature of the peak, relative intensity): 494.1 ([M]$^+$, 100), 456.1 ([M − 2F]$^+$, 10); Anal. Calcd for $C_{26}H_{28}B_2F_4N_4$: C, 63.20; H, 5.71; N, 11.34. Found: C, 62.82; H, 5.54; N, 11.24.

*3-(5-Bromothien-2-yl)-4,4′-difluoro-2,6-dimethyl-5-(thien-2-yl)-4-bora-3a,4a-diaza-s-indacene (**10**).* To a solution of **3b** (500 mg, 1.30 mmol, 1 equiv) in CH_2Cl_2/DMF (100 mL, 1:1) was added *N*-bromosuccinimide (231 mg, 1.30 mmol, 1 equiv) at rt. The reaction was monitored by TLC. After 40 min the reaction mixture was washed with water (5 × 150 mL), extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was removed under vacuum. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 70:30 to 60:40) and recrystallized from CH_2Cl_2/EtOH. The product **10** was obtained as blue metallic crystals in 66% yield (399 mg): mp 186−187 °C; ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ = 7.80 (dd, ^3J = 3.8 Hz, ^4J = 1.1 Hz, 1H), 7.54 (dd, ^3J = 5.1 Hz, ^4J = 1.1 Hz, 1H), 7.45 (d, ^3J = 4.0 Hz, 1H), 7.18 (dd, ^3J = 5.1 Hz, ^3J = 3.8 Hz, 1H), 7.10 (d, ^3J = 4.0 Hz, 1H), 7.00 (s, 1H), 6.86 (s, 1H), 6.81 (s, 1H), 2.23 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 150.9, 147.6, 135.2, 134.7, 134.0, 132.0 (t, J_{C-F} = 6.3 Hz), 131.7 (t, J_{C-F} = 5.5 Hz), 130.9, 130.8, 130.5, 130.0, 129.9, 129.2, 129.0, 127.7, 125.0, 116.1, 13.6, 13.3; ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ = 1.18 (t, ^1J = 32.9 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}cm^{-1}$): 603 (59000), 395 (10000), 327 (20000), 304 (17000), 233 (21000); IR (ν, cm^{-1}): 3094, 2957, 2920, 2851, 1599, 1515, 1452, 1432, 1410, 1394, 1339; EI-MS *m*/*z* (nature of the peak, relative intensity): 463.9 ([M, ^{81}Br]$^+$, 95), 461.9 ([M, ^{79}Br]$^+$, 100), 383.1 ([M − Br]$^+$, 35); Anal. Calcd for $C_{19}H_{14}BBrF_2N_2S_2$: C, 49.27; H, 3.05; N, 6.05. Found: C, 48.88; H, 2.72; N, 5.82.

*4,4′-Difluoro-2,6-dimethyl-5-(thien-2-yl)-3-{[5-(3,4,5-tridodecyloxy)phen-1-yl]thien-2-yl}-4-bora-3a,4a-diaza-s-indacene (**11**).* **10** (31 mg, 0.07 mmol, 1 equiv), Cs_2CO_3 (65 mg, 0.20 mmol, 3 equiv) and 4,4,5,5-tetramethyl-2-[3,4,5-tris(dodecyloxy)phenyl]-1,3,2-dioxaborolane (50 mg, 0.07 mmol, 1 equiv) were dissolved in toluene (4 mL) in a Schlenk flask and degassed for 30 min. Then $Pd(PPh_3)_4$ (8 mg, 0.0066 mmol, 0.1 equiv) was added and the solution was heated to 60 °C. The reaction was monitored by TLC inspection. After 18 h the reaction was stopped by addition of water (30 mL), extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was removed under vacuum. The residue was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2 70:30 to 60:40). The product **11** was obtained as blue-green amorphous solid in 68% yield (48 mg): ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.85 (d, ^3J = 3.6 Hz, 1H), 7.77 (d, ^3J = 3.6 Hz, 1H), 7.51 (d, ^3J = 5.0 Hz, 1H), 7.26 (d, ^3J = 3.8 Hz, 1H), 7.16 (dd, ^3J = 5.0 Hz, ^3J = 3.8 Hz, 1H), 6.95 (s, 1H), 6.83 (s, 2H), 6.81 (s, 2H), 4.01 (m, 6H), 2.30 (s, 3H), 2.22 (s, 3H), 1.77 (m, 6H), 1.50 (m, 6H), 1.28 (m, 48H), 0.89 (t, ^3J = 6.8 Hz,

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9H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 153.4, 149.7, 149.3, 148.4, 138.7, 135.2, 134.8, 133.2, 132.4, 131.6, 131.2, 130.4, 130.1, 129.7, 129.1, 129.0, 128.7, 127.5, 124.1, 123.8, 105.5, 73.5, 69.3, 31.92, 31.91, 30.3, 29.74, 29.73, 29.69, 29.64, 29.61, 29.42, 29.38, 29.36, 26.1, 22.7, 14.1, 13.9, 13.4; ^{11}B NMR (128 MHz, $CDCl_3$, ppm): δ = 1.33 (t, ^1J = 31.8 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}cm^{-1}$): 627 (59000), 349 (20000), 308 (22000), 232 (30000); IR (ν, cm^{-1}): 2918, 2851, 1603, 1548, 1524, 1455, 1395; EI-MS m/z (nature of the peak, relative intensity): 1012.4 ([M]$^+$, 100); Anal. Calcd for $C_{61}H_{91}BF_2N_2O_3S_2$: C, 72.30; H, 9.05; N, 2.76. Found: C, 72.12; H, 8.84; N, 2.42.

Representative Procedure for the Synthesis of Dimers 12 and 13 of BODIPY. *5,5′-Di-[4,4′-difluoro-2,6-dimethyl-3-(thien-2-yl)-4-bora-3a,4a-diaza-s-indacen-5-yl]-2,2′-bithiophene (**12**).* To a solution of BODIPY **3b** (50 mg, 0.14 mmol, 1 equiv) in dry CH_2Cl_2 (10 mL) in a Schlenk flask, PIFA (36 mg, 0.08 mmol, 0.6 equiv) and $BF_3{\cdot}Et_2O$ (24 mg, 0.17 mmol, 1.2 equiv) were added. The reaction mixture was stirred at rt for 30 min, then diluted with petroleum ether (10 mL) and centrifugated. The solid was washed with petroleum ether (10 mL), water (10 mL), EtOH (10 mL), Et_2O (5 mL), pentane (5 mL), then recrystallized from THF/EtOH. The product **12** was obtained as a blue metallic powder in 78% yield (42 mg): mp >260 °C dec.; ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ = 7.88 (dd, ^3J = 5.0 Hz, ^4J = 1.0 Hz, 2H), 7.71 (dd, ^3J = 3.6 Hz, ^4J = 1.0 Hz, 2H), 7.70 (d, ^3J = 4.1 Hz, 2H), 7.63 (s, 2H), 7.56 (d, ^3J = 4.1 Hz, 2H), 7.25 (dd, ^3J = 5.0 Hz, ^3J = 3.6 Hz, 2H), 7.23 (s, 2H), 7.21 (s, 2H), 2.25 (s, 6H), 2.20 (s, 6H); ^{13}C NMR (500 MHz, DMSO-d_6, ppm): δ = 149.5, 147.0, 139.1, 134.9, 134.7, 133.0 (t, J_{C-F} = 4.9 Hz), 131.8 (t, J_{C-F} = 4.9 Hz), 131.6, 131.5, 130.7, 130.6, 130.4, 130.3, 130.0, 127.7, 126.2, 125.6, 13.3, 13.2; ^{11}B NMR (128 MHz,, ppm): δ = 1.12 (t, ^1J = 33.9 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}cm^{-1}$): 679 (55000), 597 (53000), 458 (10000), 368 (24000), 305 (20000); IR (ν, cm^{-1}): 3112, 3053, 2962, 2922, 2865, 1591, 1521, 1501, 1435, 1394; EI-MS m/z (nature of the peak, relative intensity): 766.1 ([M]$^+$, 100); Anal. Calcd for $C_{38}H_{28}B_2F_4N_4S_4$: C, 59.54; H, 3.68; N, 7.31. Found: C, 59.37; H, 3.44; N, 7.08.

*5,5′-Di-[4,4′-difluoro-2,6-dimethyl-3-(5-bromothien-2-yl)-4-bora-3a,4a-diaza-s-indacen-5-yl]-2,2′-bithiophene (**13**).* Blue metallic crystals. Yield 89%. Mp 283−285 °C; ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ = 7.76 (d, ^3J = 4.1 Hz, 2H), 7.67 (s, 2H), 7.63 (d, ^3J = 4.1 Hz, 2H), 7.46 (d, ^3J = 4.0 Hz, 2H), 7.38 (d, ^3J = 4.0 Hz, 2H), 7.27 (s, 2H), 7.22 (s, 2H), 2.28 (s, 6H), 2.17 (s, 6H); ^{13}C NMR (500 MHz, DMSO-d_6, ppm): δ = 148.2, 146.8, 139.5, 135.2, 134.7, 133.4 (t, J_{C-F} = 5.1 Hz), 133.3, 132.3 (t, J_{C-F} = 3.5 Hz), 131.5, 131.2, 131.0, 130.6, 130.2, 130.1, 126.5, 126.0, 115.8, 13.4, 12.9; ^{11}B NMR (128 MHz, DMSO-d_6, ppm): δ = 1.05 (t, ^1J = 33.9 Hz); UV−vis (CH_2Cl_2) λ nm (ε, $M^{-1}cm^{-1}$): 683 (59000), 600 (53000), 459 (14000), 369 (33000); IR (ν, cm^{-1}): 3075, 2966, 2922, 2856, 1594, 1529, 1502, 1453, 1435, 1393; EI-MS m/z (nature of the peak, relative intensity): 923.1 ([M], 100), 921.1 ([M], 50), 845.0 ([M − Br], 40), 843.0 ([M − Br], 40); Anal. Calcd for $C_{38}H_{26}B_2Br_2F_4N_4S_4$: C, 49.38; H, 2.84; N, 6.06. Found: C, 49.28; H, 2.54; N, 5.73.

■ ASSOCIATED CONTENT

Supporting Information

Optimized experimental conditions for use of PIFA; proton, carbon and boron NMR traces for all compounds; COSY, HSQC and HMBC spectra; spectroscopic data and crystallographic data of compounds **3a**, **3b** and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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