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Oligothienyl-BODIPYs: Red and Near-Infrared Emitters

Arnaud Poirel, Antoinette De Nicola,* and Raymond Ziessel*

*Laboratoire de Chimie Organique et Spectroscopies Avancées (LCOSA), UMR 7515 au
CNRS, École de Chimie, Polymères et Matériaux de Strasbourg (ECPM),
25, Rue Becquerel, 67087 Strasbourg, Cedex 02, France*

denicola@unistra.fr; ziessel@unistra.fr

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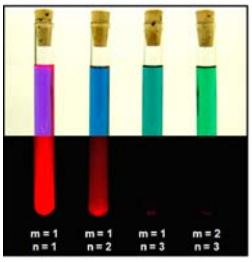
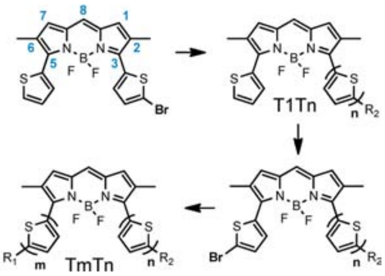
ABSTRACT





The synthesis of unsymmetrical 3,5-dioligothienyl-BODIPY derivatives and their optical and redox properties are reported. The key step is the monobromination of the 2,6-dimethyl-3,5-dithienyl-BODIPY at the α position of the thiophene moiety. The additional thiophene modules are attached by palladium-catalyzed cross-coupling reactions. Increasing the number of modules on each side of the BODIPY core progressively shifts the absorption to 677 nm and the emission to 769 nm.

There has been in the past few years a surge of interest in the preparation and study of new fluorescent red and near-infrared dyes. The research on NIR materials is due to their numerous applications in the fields of energy conversion, communications, biology, and medicine.[1]

In the family of organic fluorophores, boron dipyrromethene (BODIPY) dyes have increasingly attracted attention over the past decade.[2] The BODIPY core has been structurally modified by various strategies to yield numerous BODIPY dyes showing a wide range of absorption and emission wavelengths. In particular, bathochromic shifts[3] have been achieved by suitable modifications such as extension of the conjugation length (by aryl, ethynylphenyl, styryl, or polymethine substitutions,[4] aromatic ring fusion,[5] introduction of a nitrogen atom in the *meso* position (aza-BODIPY),[6] and combinations thereof).[7]

Heteroaryl residues,[8] especially in the 3,5-positions, are known to endow BODIPYs with spectral transitions that are significantly red-shifted. Nevertheless, there are few

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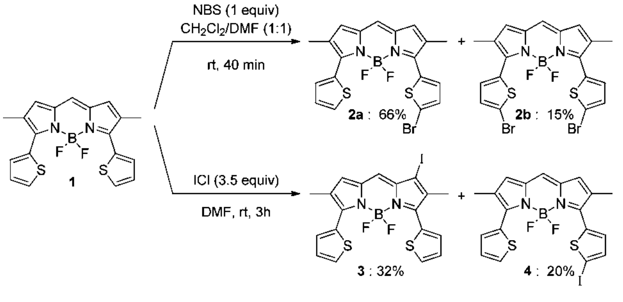
reports on such BODIPY dyes, even those containing the more common five-membered-ring moieties.[9] The 3,5-dithienyl-BODIPYs[10] are very interesting because they exhibit a red shift of ~60 nm in absorption and emission compared to the 3,5-diphenyl analogue.[10b,c] Of those 2,6-dithienyl-BODIPYs[11] that have been synthesized, however, substitution at the 1,7- and 3,5-positions by akyl chains increases the dihedral angle between the BODIPY core and the thienyl ring and results in rather small red-shifts.

There are even fewer examples of oligothiophenes attached to BODIPY derivatives,[12] some being those with oligothiophenes attached in the *meso* position to give donor–acceptor materials. Only a single report by Wu et al.[12a] describes the grafting of short conjugated oligothiophene chains to the 3,5-positions of dibenzopyrrometheneboron difluoride compounds.

Herein, a linear synthesis and convergent construction of unsymmetrical 3,5-di(oligothienyl)-BODIPYs (TmTn) by increasing the number of thiophene modules through Pd-catalyzed coupling reactions are reported. The strategy used has been to connect either thienyl or dithienyl building blocks on preorganized bromothienyl-BODIPY dyes.

The starting material BODIPY **1** (T1T1) was synthesized[13] from 3-methyl-2-(thien-2-yl)pyrrole, first obtained by a Trofimov protocol.[14] The first reaction was the key step of the synthesis (Scheme 1). Treatment of **1** with NBS gave exclusive bromination at the α position of the thiophene moiety with respect to the bromination of the pyrrole, providing the monobrominated compound **2a** in 66% yield and 15% of the dibrominated derivative **2b**. In contrast, iodination provided the regioisomers **3** and **4** substituted at the 1-position of the BODIPY and at the α position of the thiophene. This occurred independently of the nature of the iodinating agent. NIS and ICl gave the same results, with a yield of 32% for **3** and 20% for **4**. Thus, as well as lacking regioselectivity, this reaction involved predominantly substitution at position 1 of the BODIPY (Scheme 1).

Scheme 1. Regioselective Halogenation of **1**



In order to increase the number of thienyl subunits, compounds **5a**,**b**[15] and **7**[16] (Figure 1) were synthesized and purified according to literature procedures. Compound **6** is commercially available.

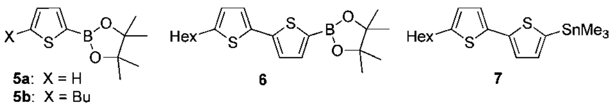


Figure 1. Boronates and organostannic building blocks.

Linkage to **2a** through Suzuki coupling provided longer oligothienyl chains on the 3-position (Scheme 2). The reaction with **5a** and **5b** gave dithienyl-BODIPYs (T1T2) **8a** and **8b**, respectively, in 80% and 53% yields. The terthienyl-BODIPY (T1T3) **9** was obtained from **6** in a relatively poor yield of 36%. Consequently, the organostannane **7** was used to insert a dithienyl block by a Stille cross-coupling reaction. The presence of alkyl chains (butyl for **8b** and hexyl for **9**) increased the solubility of these dyes but also blocked the position against electrophilic attack. Compound **8b** was thereby regioselectively brominated at the α position of the single thiophene moiety located at the other side of the molecule, providing compound **8c** in 44% yield. The latter was allowed to react with the stannyl compound **7** under standard conditions[17] to provide the terthienyldithienyl-BODIPY **10** (T2T3) in a satisfactory yield of 61%. By changing this protocol (absence of LiCl and temperatures up to 100 °C), **7** was efficiently coupled (76% yield) to the iodo derivative **3** to give the unsymmetrical dye **11**. This reaction highlighted the thermal stabilty of these oligothienyl-BODIPYs.

Spectroscopic data for the thienyl- and oligothienyl-BODIPY dyes are given in Table 1. The extension of the oligomer chains in the 3,5-positions of the BODIPYs led to predictable bathochromic effects. From T1T1 to T2T3, there was a shift of 180 nm in absorption and 122 nm in emission. In contrast, substitution of the 1-position with a bithienyl moiety had little effect, as expected, on the λ_{max}. The absorption and emission properties of compound **11**

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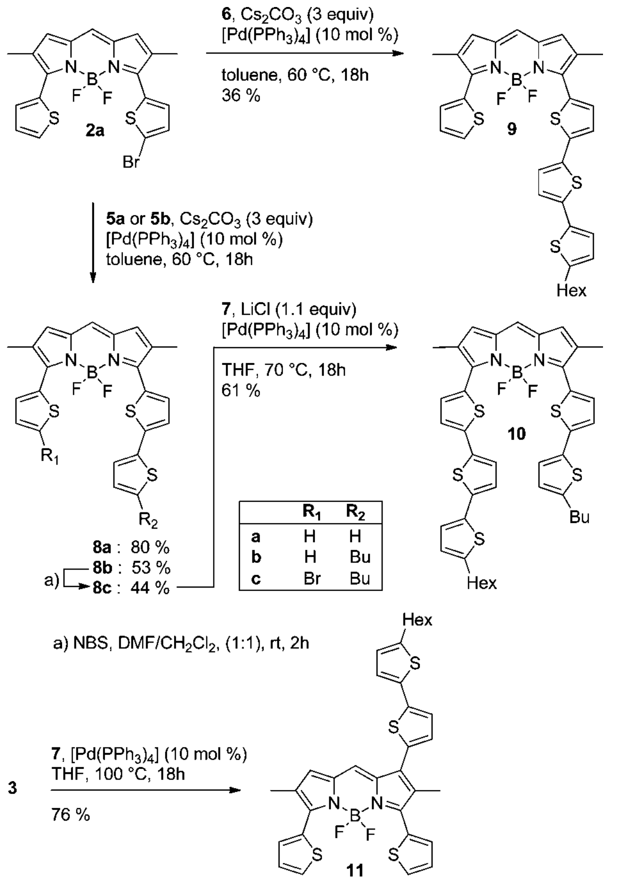
Scheme 2. Synthesis of Oligothienyl-BODIPY Derivatives



were more like those of the series T1T1 and very different from dye **9** including the same number of thiophene units (namely 4). In this case the bathochromic shift was 32 nm in absorption and 58 nm in emission. Each addition of thiophene unit in 3,5-positions resulted in a red-shift of 11 to 33 nm.

The shape of the main absorption band enlarge as the oligothienyl chain lenghtened (Figure 2). This is likely due to the existence of several oligomer conformations along the lateral appendage.

Table 1. Spectroscopic Data of Thienyl- and Oligothienyl-BODIPY Dyes in CH_2Cl_2

dyes	series	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_F (%)	τ_F (ns)	Stokes shift (cm^{-1})
1	T1T1	597	58000	647	78	9.2	1290
2a	T1T1	603	59000	654	70	8.6	1290
2b	T1T1	609	60000	663	73	7.7	1340
8a	T1T2	626	57000	690	44	6.2	1480
8b	T1T2	634	51000	703	34	5.5	1550
8c	T1T2	642	59000	712	31	5.0	1530
9	T1T3	645	50000	725	10	1.7	1710
10	T2T3	677	53000	769	14	2.6	1770
11	T1T1	613	69000	667	11	5.2	1320

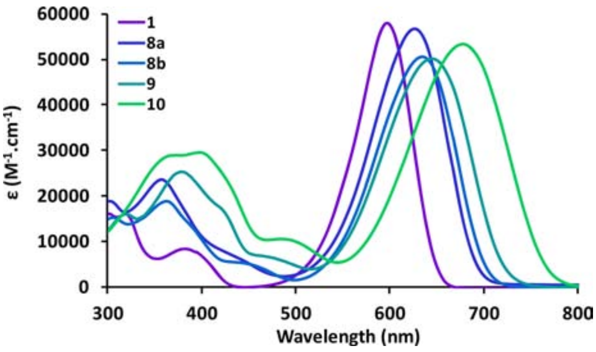


Figure 2. Absorption spectra of thienyl- and oligothienyl-BODIPY derivatives in CH_2Cl_2.

The emission spectra (Figure 3) show evidence for a single emitting state with excited state lifetimes in the 1.7 to 9.2 ns range (Table 1). The Stokes shifts lie in the range of 1290 to 1770 cm^{-1} and are larger than typical BODIPY dyes (average value 300 cm^{-1}). It is also worth noting that the quantum yields and extinction coefficients decreased but remained quite high for these red-emitting dyes. The compound **10** with a quantum yield of 14% at λ_{em} of 769 nm is an interesting candidate for particular applications. Notice that the photophysical properties of most of these novel dyes does not change significantly by using polar or nonpolar solvent such DMSO, toluene or dichloromethane [see Figure S48 (Supporting Information) for dye **10**].

The redox behavior of the oligothienyl-BODIPY dyes was investigated by cyclic voltammetry (CV) in dichloromethane (DCM) containing 0.1 M $TBAPF_6$ as supporting electrolyte (Figure 4). All oligothienyl derivatives and the starting material **1** present a single irreversible reduction around −0.90 V likely due to the reduction of the BODIPY core (Table 2).[18] This reduction is insensitive to the number of thienyl moieties and their substituents.

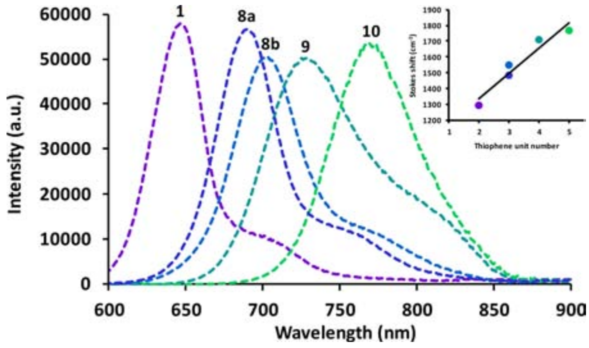


Figure 3. Emission spectra of thienyl- and oligothienyl-BODIPY derivatives in CH_2Cl_2.

Dye **1** displayed a single reversible oxidation wave at $E_{1/2}$ = +0.93 V, a potential very close to that of BODIPY oxidation to the radical cation.[18] Interestingly, for all other dyes two oxidation waves appeared in the CVs in the

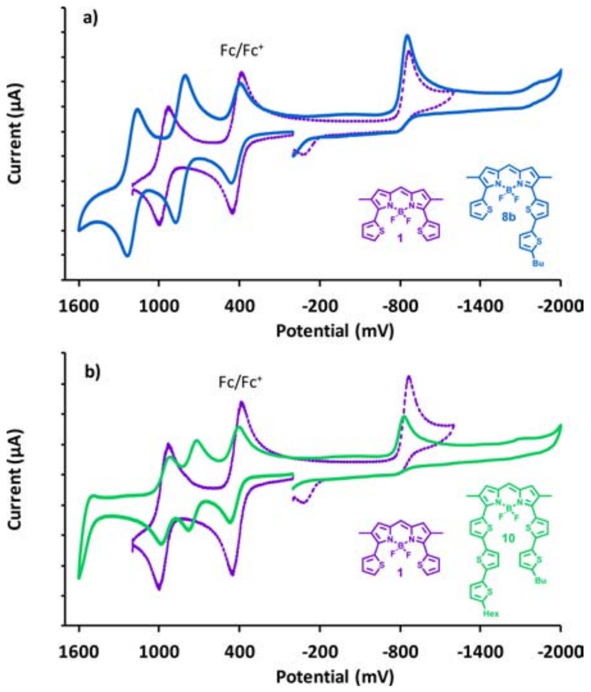


Figure 4. CVs of selected dyes. F_C accounts for ferrocene.

Table 2. Redox Data for Selected Thienyl- and Oligothienyl-BODIPY Dyes in CH_2Cl_2[a]

dyes	series	E_{ox}, V (ΔE, mV)		E_{red}, V (ΔE, mV)	HOMO (eV)	LUMO (eV)	E_{Gap} (eV)
1	T1T1	+0.93 (70)		−0.90 (irrv)	−5.33	−4.38	0.95
8a	T1T2	+0.83 (70)	+1.26 (70)	−0.89 (irrv)	−5.25	−4.41	0.84
8b	T1T2	+0.79 (70)	+1.15 (70)	−0.90 (irrv)	−5.20	−4.41	0.79
9	T1T3	+0.76 (60)	+0.97 (60)	−0.90 (irrv)	−5.19	−4.43	0.76
10	T2T3	+0.69 (60)	+0.89 (60)	−0.89 (irrv)	−5.15	−4.42	0.73

[a] All potentials are reported vs Fc/Fc^+, and HOMO and LUMO energies are derived from the electrochemical data based on the assumption that the Fc/Fc^+ redox couple is −4.78 eV relative to vacuum.[20]

potential range +0.69 to +1.15 V. These processes were highly reversible ($i_{pa}/i_{pc} \approx 1$), with a shape characteristic of Nernstian one-electron processes (ΔE_p = 60−70 mV). Increasing the number of thiophene subunits from 3 to 5 decreased the first oxidation potential by 100 mV and the second by 260 mV. The first wave is tentatively assigned to the oligothienyl oxidation with a formal potential value dependent on the number of thiophene units.[19] This is in accord with the greater electron-donating capacity of oligothiophene moieties relative to a single thiophene module. The second reversible wave is due to the BODIPY oxidation to its radical cation, as previously observed within the same family of compounds.[18] Note that on increasing the number of thiophene units, the separation of the first and second oxidation processes decreases from 360 mV for 3T to 200 mV for 5T. The LUMO and HOMO energies for selected dyes estimated by CV are collected in Table 2 and have interesting features for possible solar cell applications.

In conclusion, the novel oligothienyl-BODIPY dyes presently characterized have a variety of interesting optical and redox properties. Their syntheses are efficient and their purification is facilititated by the presence of pendent alkyl chains. All dyes are emissive in the 640 to 769 nm range with quantum yields ranging from 78 to 14%. Two reversible oxidation processes are observed for all dyes with more than two thiophene fragments. Works to fine-tune the optical and electronic properties through molecular design are currently in progress, with the intention to use these dyes in optical sensing and energy conversion devices.

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Supporting Information Available. Experimental procedures and analytical data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.