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Engineering Tuneable Light-Harvesting Systems with Oligothiophene Donors and Mono- or Bis-Bodipy Acceptors

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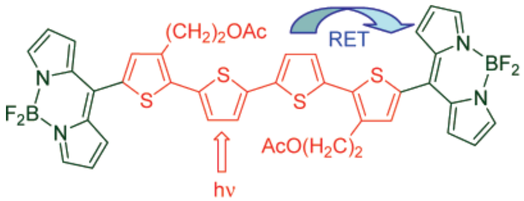

Oligothiophene−Bodipy-based donor−acceptor systems for light harvesting have been synthesized and characterized. Absorption, excitation, and emission spectra indicate a tuneable and efficient resonance energy transfer from quaterthiophene as donor to mono- and bis-Bodipy as acceptors. This shows that engineering tuneable light harvesting systems is possible based on the combination of oligothiophenes with one or two Bodipy(s).

In recent years, α-linked regioregular oligothiophenes have received much attention as electronic structural models for higher molecular weight polythiophenes. Undoubtedly, this infatuation relies on an acceptable synthetic accessibility and a perfectly controlled architecture that allows a fine-tuning of the intrinsic electronic properties.[1] The latter are tightly correlated to the low aromatic stabilization energy (ASE) of thiophenes[2] and have found utility in a wide range of nonlinear optical (NLO) materials[3] or semiconducting devices. In addition, the highly polarizable character of oligothiophenes found interesting applications for electron- and energy transfer reactions.[4]

It is well-established that the substitution and the chain length critically influence the electronic properties of oligothiophenes.[5] Based on these considerations, we decided to investigate whether we could adopt the latter strategy for extending the conjugation between an oligothiophene moiety and the 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene−Bodipy−dye. Bodipy was first discovered by Treibs et al.[6] but has more recently gained renewed interest[7−10] because it exhibits sharp fluorescence emissions and high quantum yields in addition to elevated chemical and photostabilities.[11] Bodipy has very recently been used as both the donor in conjunction with perylenediimide as the acceptor[12] as well as the acceptor in conjunction with pyrene as the donor.[13] Interestingly, the combination of oligothiophenes with Bodipy as an acceptor has not been reported so far. Indeed, to the best of our knowledge, the most similar system reported to date in the literature incorporated a thiophenesulfonamide and a Bodipy-modified fluorescent inhibitor that was used for cell labeling and enzyme localization.[14]

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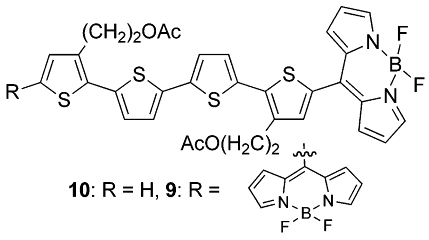
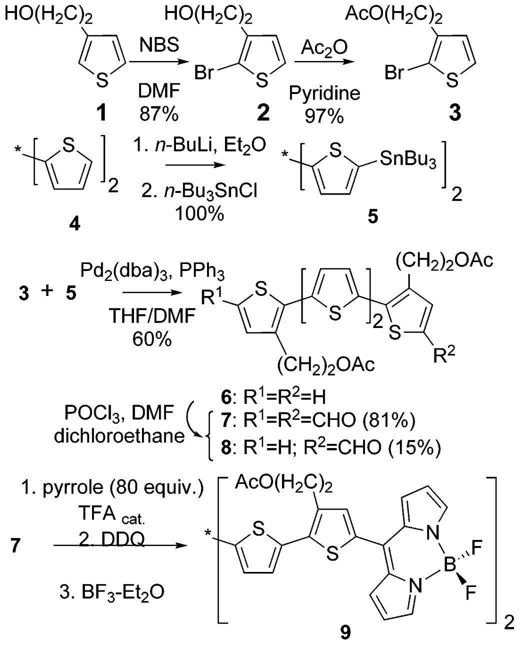


FIGURE 1. Structure of the target chromophores.

SCHEME 1. Synthesis of the bis-Bodipy Chromophore



When two emissive chromophores show a spectral overlap between the emission spectrum of the higher-energy absorbing chromophore and the absorption spectrum of the lower energy absorbing one, a so-called nonradiative resonance energy transfer (RET) may occur from the former—the donor—to the latter—the acceptor.[15] The efficiency of the RET is primarily determined by the above-mentioned spectral overlap. Depending on the distance, two different mechanisms can be responsible for this transfer. For short distances between donor and acceptor, energy transfer by electron exchange can occur, according to the so-called Dexter mechanism. For longer distances, energy transfer can occur through Coulombic dipole−dipole interaction in the so-called Förster transfer. Making the distinction between the two mechanisms requires elaborate, time-resolved emission data.

In this paper, we report on the combination of a "donor" quaterthiophene with one or two Bodipy "acceptor(s)" (Figure 1) and demonstrate how these combinations constitute efficient energy-transfer couples. As both the number of thiophene and Bodipy units may be altered, one can further engineer the chromophore and favor an optimal overlap with the specific spectral properties of the light source or the energetic properties of the process to be light-driven.

The structure of the oligothiophene target relies on several considerations. First, we decided to adopt a convergent strategy based on the exploitation of the readily available 2,2′-bithiophene subunit.[16] As 2-(3-thienyl)ethanol **1** was proven very versatile for the elaboration of soluble polythiophenes,[17] we envisioned the synthesis of **6** according to Scheme 1.

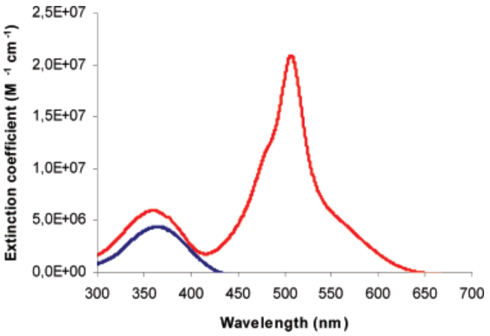


FIGURE 2. Absorption spectra of **6** (blue) and **9** (red) in $CHCl_3$.

In the first step, the regioselective bromination of **1** with *N*-bromosuccinimide in DMF afforded **2** in 87% yield.[18] Next, the monobrominated adduct **2** was converted to the corresponding acetate derivative in 97% yield with acetic anhydride. In parallel, **4** was reacted with *n*-BuLi and quenched with *n*-Bu_3SnCl.[19] After evaporation of the solvents, the expected bis-stannylated species was directly used without further purification, and the Stille coupling[20] between **5** and 2 equiv of **3** afforded the expected quaterthiophene **6** in 60% yield. Next, **6** was formylated with $POCl_3$/DMF according to the Vilsmeier−Haack conditions.[21] The bis-formylated species **7** was isolated in 81% yield as well as the monoformylated derivative **8** in 15% yield. Noteworthy, the yield of the formylation was proven strongly dependent on the nature of the alcohol protecting group. Indeed, in the course of our study, we also tested the benzyl and TBDMS protecting groups. In both cases, the presence of the benzyloxy- or -OTBDMS functionalities induced either a lack of regioselectivity or side reactions such as the substitution of the benzyloxy group by a chloride ion. Finally, the reaction of the formyl thiophenes **7** or **8** with a large excess of pyrrole in the presence of TFA afforded the expected dipyrromethanes that were directly oxidized with DDQ.[22] The corresponding mono- or bis-Bodipy derivatives **9** and **10** were isolated after reaction of the dipyrromethene with BF_3−Et_2O in the presence of triethylamine.[23] The overall yield for the last three steps reached 43−45% in both cases.

The absorption spectra for quaterthiophene **6** and the Bodipy-disubstituted quaterthiophene **9** are disclosed in Figure 2. The absorption properties of Bodipy have been thoroughly described in the literature and are characterized by a strong $S_0 \rightarrow S_1$ ($\pi - \pi^*$) transition at 500 nm and a weaker broad band around 350 nm attributed to the $S_0 \rightarrow S_2$ ($\pi - \pi^*$) transition.[24] We clearly observe for oligothiophene **6** the high energy ($\pi - \pi^*$) transition

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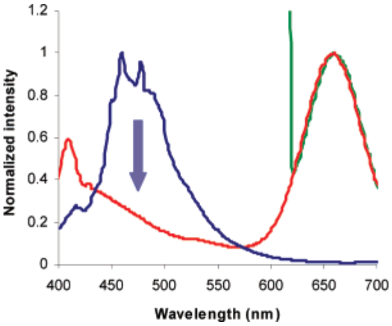

FIGURE 3. Normalized emission of **6** (blue, λ_{exc}= 365 nm), **9** (green, λ_{exc}= 605 nm) and **9** (red, λ_{exc}= 365 nm) in $CHCl_3$.

at 370 nm related to the specific conjugation length for a quaterthiophene.[25] For the engineered compound **9**, we observe the simple linear sum of the latter (**6**) and the former (Bodipy) spectra (except for the appearance of a long-wavelength tail), indicating that in the ground state, no electronic interaction between the Bodipy and the quaterthiophene moieties occurs (except for some conjugation for those conformers where bodipy is coplanar with the thiophenes).

The excitation and emission spectra of **6** are in agreement with the absorption spectrum for quaterthiophene **6**. The excitation spectrum mimics the absorption spectrum, while the emission spectrum (Figure 3, blue) shows a typical mirror relationship with a reasonable Stokes shift.

In addition, the excitation spectrum for Bodipy-disubstituted quaterthiophene **9** is as expected on the basis of its composite absorptive properties and shows the two peaks, attributed to the quaterthiophene and the Bodipy moieties. The emission spectrum of **9** (Figure 3, red and green), however, only shows one single emission band, centered at 660 nm. The lack of the emission from the quaterthiophene moiety has been confirmed by excitation at 365 nm. The quenching of this emission is clearly observed. There are two issues to explain. The first is the large Stokes shift observed for the emission of the engineered compound **9**. In the latter case, the emission maximum is located at 660 nm, while for Bodipy, the emission maximum is typically around 510 nm. This is not caused by a delocalization of the emissive state. Please note that compound **9** exhibits two Bodipy moieties covalently connected. We conjectured that the proximity of the two moieties results in an electronic interaction, facilitated by π-stacking, resulting in excimer formation. The Stokes shift of 4800 cm^{-1} is typical for this phenomenon.[25] To test this hypothesis, we have studied the emissive properties of a mono-Bodipy-substituted quaterthiophene **10**[26] (Figure 1) as a function of concentration to mimic the intramolecular interaction between the two Bodipy units in **9** (independent of concentration). In this case, we have clearly observed a concentration dependence of the emission properties. There is a noticeable shift of the wavelength for the maximal emission from 570 nm for 10^{-10} M to 650 nm for 10^{-4} M (see also the Supporting Information). Undoubtedly, this indicates the formation of excimers (dimer formation in the excited state). For the mono-Bodipy-substituted quaterthiophene **10**, this only occurs intermolecularly, hence, only at high concentration. On the other hand, the large Stokes shift observed for the bis-Bodipy-substituted quaterthiophene **9** is independent from the concentration because the two Bodipy units are covalently linked in close proximity. This already shows that the emission range of the donor used in the RET system can be easily changed depending on the energetic demands of the light-driven application, by using either one or two accepting Bodipy moieties.

The second issue concerns the quenching of the quaterthiophene emission that can readily be explained by RET, based on the significant overlap between emission spectrum of the oligothiophene moiety (extending from 450 to 550 nm) and absorption spectrum of the Bodipy part (centered around 500 nm). The detailed analysis of Figure 3 indicates that the relative emission for compound **9** is a sensitive function of the absorption profile of Bodipy, where the absorption of Bodipy displays a local minimum (around 410 nm) a relative increase is observed for the quaterthiophene emission feature. In addition, the slight discrepancy overlap or the spectral shift between the emission of quaterthiophene (largely between 450 and 500 nm, with a tail toward 550 nm) and the absorption of Bodipy (maximum at 500 nm) results in a skewed quenching between 450 and 550 nm. This spectral information clearly indicates that a very efficient excitation energy transfer from the quaterthiophene moiety to Bodipy exists. Therefore, the oligothiophene part acts as the energy donor, while the Bodipy chromophore constitutes the energy acceptor. As stated earlier,[5] it is quite easy to fine-tune these spectral properties by varying the number of thiophene units for an optimal spectral overlap of the emission spectrum with the absorption spectrum of an acceptor fluorophore. A variation of the absorption maximum from 270 to 430 nm can be realized by extending the thiophene moiety from mono- to sexithiophene.[27] Concomitantly, the donor emission is accordingly varied. This strategy allows for optimizing the overlap integral by adjusting the emission maximum of the thiophene donor.

It has also proven possible to fine-tune the optical properties of Bodipy by functionalization. Absorption and emission maxima can be significantly red-shifted by the number and nature of the substituents.[23b,28] As we have demonstrated here, the incorporation of two Bodipy acceptors also results in an increased Stokes shift. Optimization of the absorption spectrum of the Bodipy-derived acceptor allows for optimizing the overlap integral in a second way. It should be clear that the best oligothiophene donor length has to be chosen for a specific Bodipy derivative acceptor.

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We have shown that efficient RET can be achieved in an engineered multichromophoric assembly consisting of oligothiophene as the donor and Bodipy as the acceptor moiety. By using a bis-Bodipy-substituted quaterthiophene, we have red-shifted the emission range of the donor, showing the possibility to engineer the energetic properties of the acceptor in a RET donor−acceptor coupling. From the length dependence of the absorption and emission wavelength in oligothiophenes, the energetic properties of the donor in such a couple can also be engineered. In conclusion, a RET donor−acceptor couple allowing engineering of the energetic properties of both donor and acceptor as a function of the boundary conditions of both the photon source and the final light-driven process has been demonstrated.

Experimental Section

3,3‴-Bis(2-acetoxyethyl)-2,2′:5′,2″:5″,2‴-quaterthiophene, 6. $Pd_2(dba)_3 \cdot CHCl_3$ (40 mg, 44 μmol) and PPh_3 (275 mg, 1.05 mmol) were dissolved in a mixture of THF/DMF (1/1, 8 mL). The resulting mixture was thoroughly degassed for 20 min under nitrogen and sonication. A solution of 2-(2-bromothienyl-3)ethyl acetate **3** (1.56 g, 6.3 mmol) in DMF (7 mL) and a solution of 5,5′-bis-(tributylstannyl)-2,2′-bisthiophene **5** (895 mg, 1.2 mmol) in THF (7 mL) were added sequentially. Once more, the mixture was degassed and sonicated for 20 min and then brought to reflux for 56 h. After cooling, the reaction mixture was poured into water (100 mL) and extracted with ethyl acetate (2 × 100 mL). The organic layers were combined, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (ether/cyclohexane, 3/7) to afford a yellow solid (909 mg, yield = 60%): ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.23 (d, 2H, $J = 5.20$ Hz, H_{5Th}), 7.15 (d, 2H, $J = 3.80$ Hz, $H_{3'-4'}Th$), 7.07 (d, 2H, $J = 3.80$ Hz, $H_{3'-4'}Th$), 6.99 (d, 2H, $J = 5.20$ Hz, H_{4Th}), 4.31 (t, 4H, $J = 6.94$ Hz, H_{1Alk}), 3.13 (t, 4H, $J = 6.94$ Hz, H_{2Alk}), 2.05 (s, 6H, H_{Me}); ^{13}C NMR ($CDCl_3$, 100 MHz) 171.4, 137.4, 134.9, 132.4, 130.3, 127.5, 124.9, 124.5, 64.4, 28.8, 21.3; MS *m/z* calcd for $C_{24}H_{22}O_4S_4$ 502.04, found 502. UV−vis (CH_2Cl_2) λ_{max} (ϵ) 373 (21185); mp = 64−66 °C. Anal. Calcd for $C_{24}H_{22}O_4S_4$: C, 57.34; H, 4.41. Found: C, 57.20; H, 4.57.

3,3‴-Bis(2-acetoxyethyl)-5,5‴-diformyl-2,2′:5′,2″:5″,2‴-quaterthiophene, 7. DMF (0.46 mL, 5.94 mmol) was added to $POCl_3$ (0.56 mL, 6 mmol) without stirring at 0 °C. A solution of quaterthiophene **6** (160 mg, 0.318 mmol) in 25 mL of dry dichloroethane was then added to the white solid formed. The reaction mixture was stirred and refluxed for 15 h. The solution turned red. After 1 M sodium acetate solution (30 mL, 30 mmol) was added, the reaction mixture was refluxed for 2 h. The yellow aqueous suspension was extracted with dichloromethane (3 × 100 mL). The combined organic layers were washed with water and dried over Na_2SO_4, filtered, and concentrated in vacuo to afford a dark solid that was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 99/1) to give the expected product **7** as a red powder (134 mg, yield = 81%). Compound **8** was also isolated (25 mg, yield = 15%). **7**: ^1H NMR ($CDCl_3$, 200 MHz) δ (ppm) 9.85 (s, 2H, H_{CHO}), 7.65 (s, 2H, H_{4Th}), 7.27 (d, 2H, $J = 3.71$ Hz, $H_{3'-4'}Th$), 7.23 (d, 2H, $J = 3.71$ Hz, $H_{3'-4'}Th$), 4.37 (t, 4H, $J = 6.71$ Hz, H_{1Alk}), 3.19 (t, 4H, $J = 6.71$ Hz, H_{2Alk}), 2.06 (s, 6H, H_{Me}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 182.7, 171.2, 142.2, 141.3, 139.1, 138.7, 135.8, 134.2, 129.1, 125.4, 63.6, 28.9, 21.2; MS *m/z* calcd for $C_{26}H_{22}O_6S_4$ 558.0299, found 558.0354; UV−vis (CH_2Cl_2) λ_{max} (ϵ) 419 (40528); mp 144−146 °C.

5,5‴-Bis-Bodipy-3,3‴-bis(2-acetoxyethyl)-2,2′:5′,2″:5″,2‴-quaterthiophene, 9. Compound **7** (100 mg, 0.179 mmol) was dissolved in freshly distilled pyrrole (1 mL, 14.4 mmol), and 3 drops of trifluoroacetic acid (TFA) were added. The reaction was allowed to proceed for 2.5 h at room temperature. The reaction mixture was then poured in 0.1 M NaOH solution (20 mL) and extracted with ethyl acetate (3 × 20 mL). The organic layers were dried over Na_2SO_4, filtered, and evaporated, and the excess of pyrrole was removed by distillation in vacuo. The mixture was taken in CH_2Cl_2 (10 mL) and directly oxidized with a solution of DDQ (87 mg, 0.35 mmol) in CH_2Cl_2 (10 mL) at room temperature. The reaction was allowed to proceed for 1 h at room temperature. Triethylamine (1.73 mL, 12.39 mmol) was added to the solution, which was stirred for 10 min. $BF_3 \cdot Et_2O$ (2.11 mL, 16.64 mmole) was added, and stirring was maintained for 1 h. The reaction mixture was washed with 0.1 M NaOH solution. The aqueous solution was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated. The crude product was purified by silica gel column chromatography (CH_2Cl_2) to afford a purple powder (66 mg, overall yield = 43%): ^1H NMR ($CDCl_3$, 200 MHz) δ (ppm) 7.94 (s, 4H, H_{pyr}), 7.50 (s, 2H, H_{Th}), 7.37 (d, 4H, $J = 3.76$ Hz, H_{Th}), 7.27 (s, 4H, H_{pyr}), 6.61 (d, 4H, $J = 4.28$ Hz, H_{pyr}), 4.43 (t, 4H, $J = 6.63$ Hz, CH_2), 3.25 (t, 4H, $J = 6.63$ Hz, CH_2), 2.09 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): 177.2, 144.1, 139.2, 138.9, 138.6, 136.1, 136.4, 134.3, 133.8, 133.3, 131.4, 128.8, 125.4, 118.9, 63.9, 31.3, 29.1, 21.3; MS *m/z* calcd for $C_{42}H_{32}B_2F_4N_4O_4S_4$ 882.1429, found: 863.1454 $[M - F]^+$; UV−vis (CH_2Cl_2) λ_{max} (ϵ) 368 (38900), 514 (117100); sublimes >150 °C.

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Supporting Information Available: Experimental procedures and complete characterization of **3**, **8**, and **10**; emission and excitation spectra of **6** and **9**; copies of the ^1H and ^{13}C spectra of compounds **3** and **6**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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