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α-Fused Dithienyl BODIPYs Synthesized by Oxidative Ring Closure

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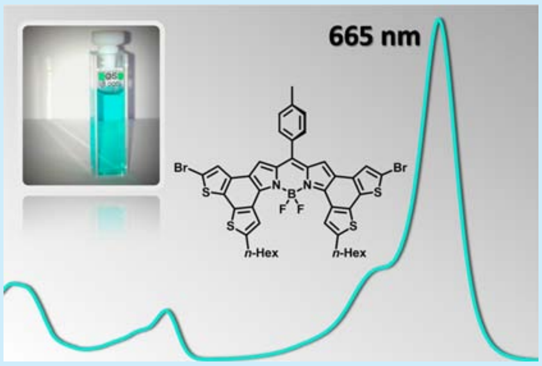
S *Supporting Information*

ABSTRACT: Both symmetrical and unsymmetrical α-fused dithienyl-BODIPY dyes have been prepared by oxidative ring closure induced by anhydrous $FeCl_3$. Extension of the π-system in the fused BODIPY leads to a progressive shift to 579 and 665 nm respectively for the absorption wavelength maxima of the mono- and difused dyes relative to the unfused species (λ_{abs} = 502 nm). Linking such dyes to an NIR emitting module provides a panchromatic chromophore with a large absorption cross section in the visible range associated with efficient intramolecular cascade energy transfer.



4,4′-Difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene dyes, more commonly known as BODIPY dyes, have gained tremendous attention over the past two decades due to the diversity of applications based on their spectacular optical properties.[1] Their absorption bands are sharp with high extinction coefficients, and their intense fluorescence is attributed to the chelation of B(III), which rigidifies the structure and consequently reduces the number of nonradiative decay channels. The facility of their chemical modification enables ready tuning of both their spectroscopic and physical properties including solubility in diverse solvents, ease of film formation, crystallinity, and mesogenicity. Ongoing research is directed toward shifting the spectroscopic properties toward the near-IR region by increasing the electronic density on the BODIPY core through the connection of electron-rich modules to the pyrrolic units.[2] There are, however, only a few instances known of the use to this end of α- or β-fused aromatic units derived from, e.g., benzene,[3] phenanthrene,[4] naphthalene,[5] porphyrin,[6a] BODIPY,[6b] furan,[7] or thiophene.[8] These fused BODIPY dyes have been obtained by synthesizing fused pyrrolic building blocks or by oxidative ring closure, but only one paper describes the use of oxidative ring closure to give intramolecular fusion of phenyl-BODIPY dyes.[4b]

Here, we discuss first the formation and oxidative ring closure reactions of singly substituted (unsymmetrical) BODIPYs to illustrate the procedures before considering the analogous reactions of disubstituted (symmetrical) derivatives. The unsymmetrical α-fused dithienyl-BODIPYs (**2T**) were obtained by a multistep protocol, using a convergent synthesis to link, via a Pd cross-coupling reaction, the BODIPY dye and the alkylated dithienyl unit and in a final step oxidative ring closure mediated by anhydrous $FeCl_3$. The dithienyl unit used in this work was synthesized in three steps according to reported procedures for similar species (Scheme S1).[9] The unsubstituted tolyl-BODIPY **4** was prepared using a standard two-step procedure.[10] Monoiodination on the 2-position of compound **4** was achieved at 55 °C with ICl,[11] limiting undesired polyhalogenation in the 1- and 6-positions (Scheme 1). At 35 °C, in the presence of the $P(^tBu)_3$ and Pd, the monoiodinated BODIPY **5** and the dithienyl unit **3a** were coupled in excellent yield (**2T-1**, 81%), via a Suzuki reaction.[12] From previous work on oxidative reactions of BODIPY dyes, it was known that the BODIPY 6-position[13] and the α-position of the dithienyl moiety have to be blocked[14] in order to obtain intra- rather than intermolecular Scholl-type reactions. Thus, these positions were substituted selectively via electrophilic aromatic reactions: first on the dithienyl moiety using NBS at 0 °C (**2T-2**, 83%) and then with ICl on the BODIPY 6-position (**2T-3**, 85%). The final oxidative coupling step was achieved using anhydrous $FeCl_3$ as a reagent giving inappreciable side reactions compared to other oxidants tested (DDQ, PIFA).

In principle, it is possible that the coupling to give **2T-4** could occur to give either the α- or γ-fused species (Scheme 1). The ^1H NMR spectrum of **2T-4** clearly showed the absence of one singlet of the BODIPY unit around 6.90 ppm corresponding to the proton in position 1 or γ of the parent and the simplification of the doublets from the dithienyl unit (6.71 and 6.89 ppm). Only one singlet, corresponding to the *meso* tolyl group and integrating for 3H, was observed at 2.52

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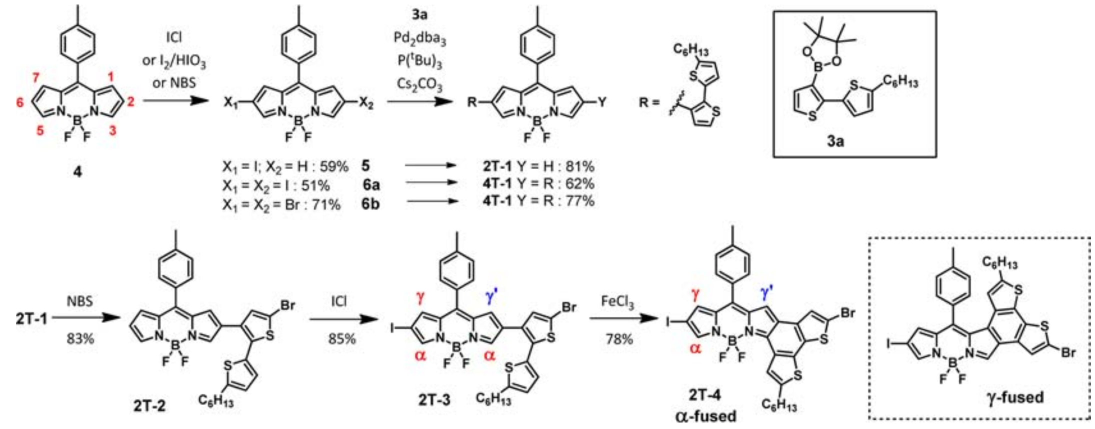
Scheme 1



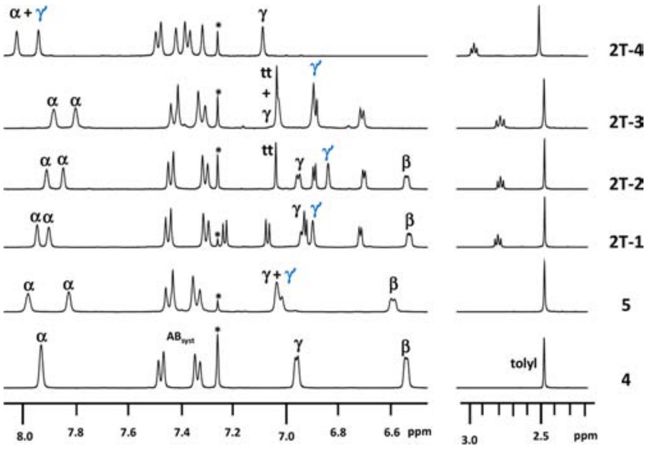


Figure 1. ^{1}H NMR superposition of **4**, **5**, **2T-1**, **2T-2**, **2T-3**, and **2T-4**. * Stands for the residual peak of the solvent ($CDCl_3$).

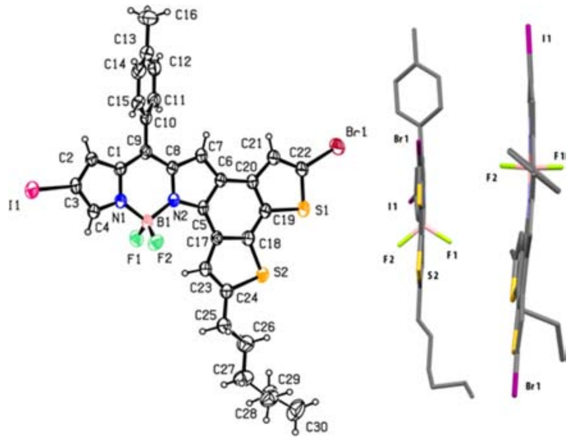


Figure 2. (Left) ORTEP view for **2-T4** showing the atom-labeling scheme. Thermal ellipsoids are plotted at the 30% level. B1−N1, B1−N2, B1−F1, B1−F2, N1−C1, N2−C8, N1−C4, and N2−C5 bond lengths are 1.552(7), 1.534(7), 1.395(7), 1.382(7), 1.384(6), 1.392(6), 1.340(6), and 1.370(5) Å, respectively. (Right) Views orthogonal to the previous one to highlight the planarity of the molecule and the projection of the hexyl chain out of the mean plane.

ppm, indicating that the intramolecular oxidative reaction had given the γ-fused form of **2T-4** (Figure 1).

This deduction was, however, contradicted by the fact that the ^{13}C NMR spectrum of **2T-4** showed a through-space coupling of 8.8 Hz, previously ascribed to C−F coupling,[15] for the peak near 123.0 ppm, indicating that the reaction may have involved position 3 or α to give the α-fused form of **2T-4**.

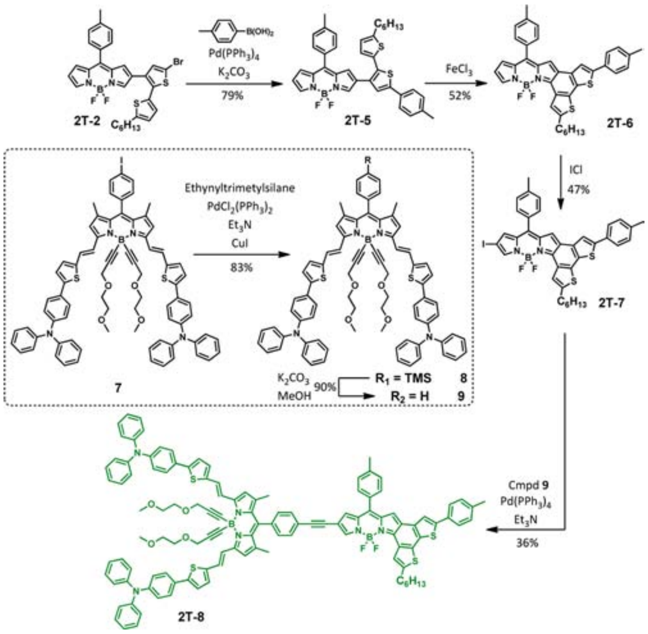
Fortunately, single crystals of **2T-4** could be obtained, and an X-ray structure determination showed that indeed it was at the α-pyrrolic position of the BODIPY that the ring closure occurred, confirming that the α-position of the BODIPY dyes is the most reactive site toward oxidative coupling reactions (Figure 2). As usual, the *meso* substituent and the BODIPY core are twisted (52.2°) away from coplanarity, consistent with the absence of electronic delocalization. The BODIPY core together with the α-fused dithienyl unit comprises a nearly flat 22-atom entity (albeit slightly concave; see Figure 2) with an rms deviation of 0.086 Å, the maximum deviation concerning the iodinated carbon (>0.17 Å). The boron atom lies within the mean plane and has the usual tetrahedral geometry (N−B−N from 106.5° to 112.4°) while the disordered hexyl group extends out of the plane (Figure 2).

Some efforts were made to selectively substitute the halogen centers on **2T-4** via Pd cross-coupling reactions under mild conditions, but neither Sonogashira nor Suzuki coupling gave significant chemoselectivity. These unsatisfying results prompted us to review our synthetic strategy to obtain the dyad **2T-8** (Scheme 2). First, the bromine on **2T-2** was substituted using a standard Suzuki coupling with *p*-benzoyl boronic acid, leading to **2T-5** in 79% yield. Next, oxidative ring closure afforded **2T-6** (52%) which could be halogenated with ICl (**2T-7**, 47%). Sonogashira cross-coupling between **2T-7** and BODIPY **9** afforded the deep-green dyad **2T-8** in an acceptable yield (36%).

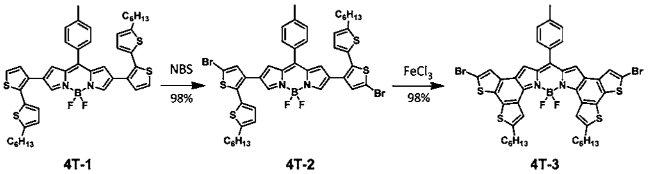
The preparation of the bis-thienyl BODIPY **4T-3** was preferentially achieved by Suzuki coupling using the bis-bromo derivatives **6b** and **3a**, affording **4T-1** in 77% yield. Bromine “stoppers” were inserted quasi-quantitatively using NBS at 0 °C on the α-position of the bis-thiophene moieties, giving **4T-2**, before performing cyclization with $FeCl_3$ to afford **4T-3** in excellent yields (Scheme 3).

The NMR spectra of **4T-3** were similar to those of the unsymmetrical compound **2T-4**, showing a triplet at 123.6 ppm (8.4 Hz) in the ^{13}C spectrum and the same low field shifts of the γ-pyrrolic protons from 6.83 to 8.23 ppm (Figure 3) in the ^{1}H. Again, cyclization afforded the bis α-fused BODIPY.

Scheme 2



Scheme 3



The electronic absorption spectra in toluene for key dyes are shown in Figure 4. BODIPY **4** and **6b** exhibit standard absorption spectra with high extinction coefficients, and narrow bands with a shoulder on the high energy side due to vibronic coupling with the C−C frame vibration of 1300 cm^{-1} typical of dipyrromethenes. On grafting two flexible dithienyl modules, the shape of the main absorption transition is broader (fwhm ≈ 2600 cm^{-1}) and bathochromically shifted with a significant decrease of the extinction coefficient (Table S1).

This may be a reflection of the conformational flexibility of the dithienyl side chains. After ring closure, the shape of the $S_0 \rightarrow S_1$ main transition for **4T-3** (Figure 4) is similar to that of those for the unsubstituted derivatives **4** and **6b**, but the extinction coefficient increases to 163 000 M^{-1} cm^{-1} and the absorption is shifted by 163 nm to lower energy. This is mainly due to the rigidification of the structure and the additional bathochromic shift to the increase of the delocalization pathway. The fluorescence of the nonfused BODIPY is weak (less than 10%) probably due to the free rotation of the tolyl group (Table S1). No fluorescence was observed for **4T-3** in solution at rt due to intersystem crossing (ISC) to a low lying triplet state favored by the presence of sulfur atoms. Preliminary results with **4T-3** in degassed and frozen methyl-THF showed a triplet emitting state around 990 nm, revealing the existence of a pronounced ISC.

Despite the weak luminescence at rt, we were able to show that these dyes could be used as input centers for an intramolecular cascade energy transfer when linked to a fluorescent module such as in the hybrid BODIPY molecule **2T-8**. This compound exhibits several absorption bands between 320 and 720 nm due to the linear combination of the absorption of the individual fragments **9** and **2T-7** (Figures 5 and S1). In fact, selective irradiation at 580 nm in the α-fused BODIPY showed the unique emission of the **2T-8** module at 764 nm (Figure 5), therefore creating a virtual Stokes shift of approximately 3500 cm^{-1}. The quantum yield

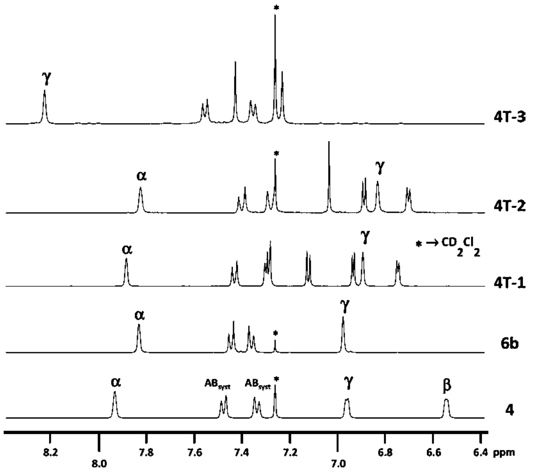


Figure 3. ^1H NMR superposition of **4**, **6b**, **4T-1**, **4T-2**, and **4T-3**. * Stands for the residual peak of the solvent ($CDCl_3$).

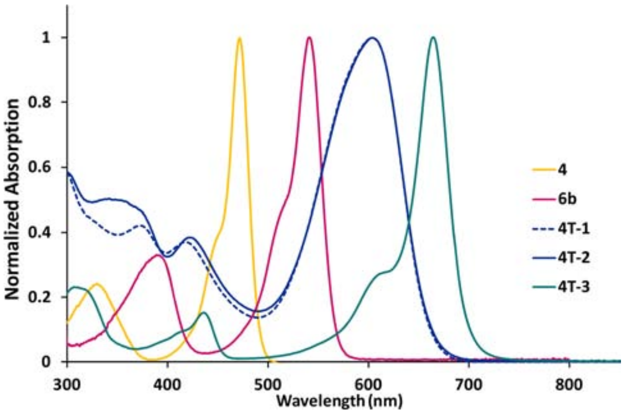


Figure 4. Normalized absorption of **4**, **6b**, **4T-1**, **4T-2**, and **4T-3** in toluene at 25 °C.

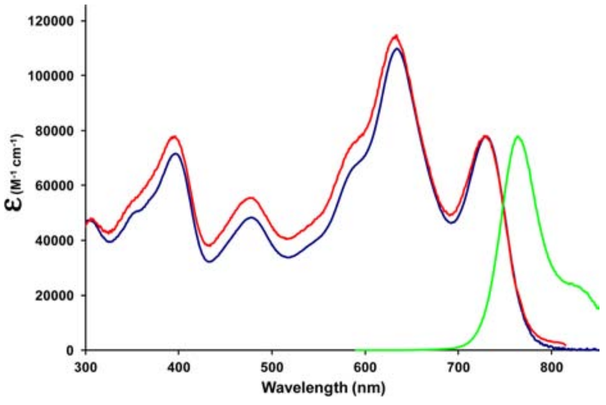


Figure 5. Absorption (blue trace), normalized emission (green trace), and excitation spectra (red trace) of **2T-8** in toluene at 25 °C.

for dye **9** is 6% in toluene whereas in the dyad the same module has a QY of 4%, allowing the conclusion that that more than 70% of the excitonic energy is transferred from fragment **2T-7** to fragment **9** in the dyad **2T-8**.

In short, we have shown here a means of access to new families of near-IR dyes using an innovative approach consisting in the oxidative coupling induced by $FeCl_3$ of prepositioned lateral arms. Cyclization occurs exclusively in the α,α'-position of the BODIPY core and is compatible with reactive functional groups on the thiophene residues. The convenience of this method is also due to the possibility to selectively anchor energy donor and acceptor or reactive fragments at precise positions. Fusion of the lateral moieties is useful to shift the absorption to the red, to markedly enhance the extinction coefficient, and to sharpen the absorption bands. The presence of thiophene rings in the fused framework renders the dyes weakly fluorescent or nonfluorescent possibly due to deactivation in a triplet state by intersystem crossing. Characterization and exploitation of the triplet state are currently under investigation.

■ ASSOCIATED CONTENT

S Supporting Information

Materials and instrumentation, synthetic procedures, NMR traces, UV−visible spectroscopy, and X-ray data are reported. 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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