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Regioselective Synthesis of 5-Monostyryl and 2-Tetracyanobutadiene BODIPY Dyes

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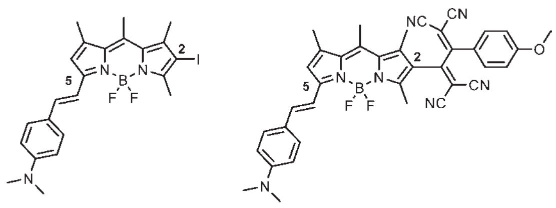
ABSTRACT



Several unsymmetrically 2,5-disubstituted BODIPY dyes were obtained from 2-substituted derivatives (iodo, ethynylaryl) using a regioselective Knoevenagel condensation reaction with dimethylaminobenzaldehyde. The unsaturated, unsymmetrical 2-ethynyl-5-styryl-BODIPY undergoes a regioselective [2 + 2] cycloaddition reaction with tetracyanoethylene leading to the 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) derivative. This shows rich redox activity with two reversible oxidation and three reversible reduction waves at +0.72 V, +1.04 V; −0.32 V, −0.78 V, and −1.50 V, respectively.

In the past ten years, the π-extended styryl derivatives of 4,4′-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene, BODIPY, dyes have been widely studied due to their remarkable optical/electrochemical properties.[1] They have found widespread applications in biological labeling[2] and cell imaging,[3] as logic gates[4] and ion sensors,[5] and in dye-sensitized solar cells[6] and solution-processed bulk heterojunction solar cells.[7] In general, the formation of mono or distyryl BODIPY dyes using a Knoevenagel condensation reaction has started with a symmetric BODIPY dye. In many cases, an excess of aldehyde has been used to convert the starting BODIPY dye fully to its distyryl derivative. Sophisticated dyes bearing preorganized functions have been prepared thereby.[8] However, a supplementary fine-tuning of the absorption and emission wavelengths is crucial for molecular design and engineering of fluorophores for specific applications. Thus, panchromatic dyes have been synthesized recently by the use of successive Knoevenagel reactions in a controlled fashion to provide oligomeric BODIPY dyes.[9] Herein, we disclose the regioselective preparation of

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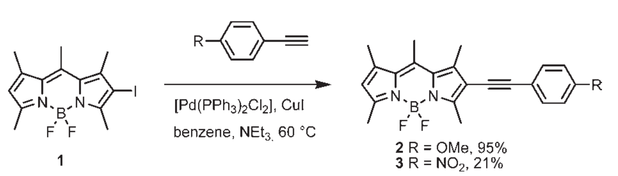
5-substituted dyes starting from BODIPY derivatives displaying a bulky group in the 2-position by using a Knoevenagel reaction with dimethylaminobenzaldehyde.

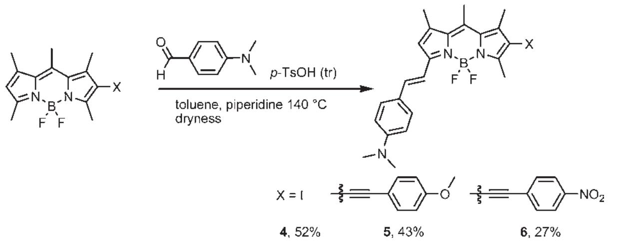
Initially, the BODIPY derivatives **2** and **3** were prepared by a Sonogashira cross-coupling reaction of the 2-iodo derivative **1** with the corresponding ethynyl derivatives shown in Scheme 1.[10] Compounds **1**, **2**, and **3** are a representative panel of dyes with substituents of varying electronic influence: the iodine atom is considered as both an electron donor (by conjugation) and an electron acceptor (by induction); the *p*-methoxybenzene-ethynyl as a donor group; and the *p*-nitrobenzene-ethynyl as an electron-withdrawing group.

Scheme 1. Synthesis of the Precursor Ethynyl-BODIPY



The Knoevenagel condensation reaction of compounds **1**−**3** with dimethylaminobenzaldehyde was carried out under standard conditions,[11] and the condensation was found to occur principally at the 5-position of the BODIPY core, leading to the 5-monostyryl BODIPY derivatives **4**−**6** in 27 to 52% yield (Scheme 2). Compound **6** was obtained in a relatively low yield, due to the decrease of nucleophilicity of the 5-methyl group induced by the conjugated nitro function.

Scheme 2. Synthesis of Monostyryl BODIPY



All these compounds were isolated by column chromatography. The chemical structures of the monostyryl BODIPY dyes were confirmed by ^{1}H NMR and 2D COSY NMR, in particular by the shift in the peak due to the β-pyrrolic proton at the 6-position of the BODIPY from 6.0 to 6.6 ppm, due to the formation of the styryl group at the 5-substitution position. This was consistent with published work on various mono and distyryl BODIPY dyes.[8,9c]

A single-crystal, X-ray study confirmed the expected structure (Figure 1) and the regioselective formation of the monostyryl function on the side opposite to the iodo residue. The molecular conformation of the monostyryl **4** is closely similar to that of monostyryl BODIPYs described in the literature.[12] The BODIPY core remains planar, with the double bond slightly twisted away from the BODIPY plane with a torsion angle (C6−C5−C1′−C2′) of 8.67° and the phenyl ring slightly twisted (by 8.06°) relative to the double bond (C1′−C2′−C1C−C6C). The distance between atoms C1′ and C2′ is 1.342 Å, that between C3 and I1 is 2.060 Å, and that between C4C and N3 is 1.386 Å, respectively. These values are in keeping with C=C, C—I, and C—N bonds, respectively.[1b,c,11]

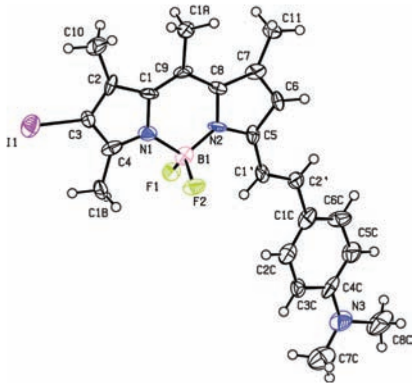


Figure 1. ORTEP view of compound **4**. Displacement ellipsoids are drawn at the 30% probability level.

Reaction of **5** with tetracyanoethene was conducted in the manner recently described by Diederich et al. for the reaction of TCNE with electron-rich alkyne derivatives.[13] Such groups undergo selectively a [2 + 2] cycloaddition reaction with TCNE, followed by the formation of an intermediate cyclobutene, which subsequently undergoes ring opening, leading to the 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) derivative **7** shown in Scheme 3. The reactivity of various donor-substituted alkynes with TCNE has comprehensively been reported.[14]

Scheme 3. Synthesis of TCBD-BODIPY **7**

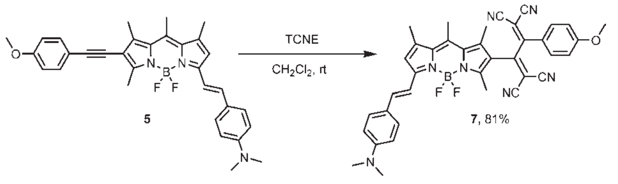


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Table 1. Optical Data for the BODIPY Derivatives[a]

compound (solvent)	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ (%)	τ (ns)	k_r (10^7 s^{-1})	k_{nr} (10^7 s^{-1})	ΔS (cm^{-1})[b]
4 (Dioxane)	606	80 300	658	66	3.3	20.0	10.3	1304
4 (Dioxane + H$^+$)	566	106 000	587	20	2.5	8.0	32.0	632
4 (EtOH)	602	94 000	699	14	2.1	6.7	41.0	2305
4 (EtOH + H$^+$)	563	114 700	574	13	1.3	10.0	66.9	340
4 (CH$_3$CN)	600	92 300	705	9	2.5	3.6	36.4	2482
4 (CH$_3$CN + H$^+$)	561	94 700	573	17	1.2	14.2	69.2	373
5 (Dioxane)	620	92 400	660	66	2.6	25.4	13.1	978
5 (Dioxane + H$^+$)	582	70 100	628	12	2.1	5.7	41.9	1259
5 (EtOH)	617	88 200	691	21	2.1	10.0	37.6	1736
5 (EtOH + H$^+$)	580	76 200	625	3	2.1	1.4	46.2	1241
5 (CH$_3$CN)	613	71 600	721	9	1.1	8.2	82.7	2444
5 (CH$_3$CN + H$^+$)	576	73 700	612	2	–	–	–	1021

[a] Quantum yield determined in dilute solution (1×10^{-6} M) using rhodamine 6G ($\Phi = 0.78$ in water, $\lambda_{exc} = 488$ nm), or cresyl violet as reference ($\Phi = 0.51$ in EtOH, $\lambda_{exc} = 578$ nm).[22] All ϕ are corrected for changes in refractive index. k_r and k_{nr} were calculated using the following equations: $k_r = \Phi_F/\tau$, $k_{nr} = (1 - \Phi_F)/\tau$. [b] ΔS = Stokes shift.

The reaction also appears to be regioselective, and no addition to the styryl double bond is seen. The inertness of double bonds toward TCNE has already been reported.[15] The purple, amorphous product **7** was easily purified by flash chromatography, with an excellent yield. This selective cycloaddition reaction generates a push–pull–pull chromophore, which displays a pronounced internal charge transfer transition (ICT). In addition, the TCBD residue imports good solubility to the dye **7** in common solvents due to the nonplanarity of the molecule, which efficiently prevents the formation of aggregates.[16]

The optical properties of the monostyryl BODIPY dyes **4**, **5** and TCBD dye **7** in various solvents are summarized in Table 1. In solution, the UV–vis absorption spectra of both styryl compounds are similar to those of monostyryl BODIPYs previously described.[17] A strong absorption band between 500 and 700 nm is observed with an absorption coefficient in the 70 000–110 000 M^{-1} cm^{-1} range, corresponding to the $S_0 \rightarrow S_1$ transition of the BODIPY core. For **4** and **5**, the absorption maximum is centered at 603 ± 3 and 617 ± 3 nm, respectively. A weak solvent dependence is observed for both molecules in absorption (Figure 2).

In contrast, the fluorescence emission spectra of both compounds are strongly dependent on the dipole moment of the solvent. For **4**, the emission maximum shifts from 658 nm in dioxane to 705 nm in acetonitrile. For **5**, the emission maximum shifts from 660 nm in dioxane to 721 nm in acetonitrile. The bathochromic shifts with a concomitant decrease of fluorescence quantum yield (ϕ) and lifetime (τ) are observed for both molecules in solvents of stronger dipole moment. For **5**, the quantum yield (ϕ) and lifetime (τ) decrease from dioxane ($\phi = 0.66$, $\tau = 2.6$ ns) to CH$_3$CN ($\phi = 0.09$, $\tau = 1.1$ ns), accompanying an increase in the nonradiative decay constant k_{nr} ((1.3 to 8.3) $\times 10^8$ s^{-1}) and a decrease of the radiative decay constant k_r ((25.4 to 8.2) $\times 10^7$ s^{-1}). The same trends are observed for dye **4** and can be attributed to the acceleration of internal conversion as the energy gap between ground state and excited state decreases. The protonation of **4** and **5** by passing HCl vapor into their solutions was used to "switch off" the ICT transition between the dimethylanilino group and the BODIPY moiety. In absorption, the protonation results in a hypsochromic shift of about 40 nm for **4** and **5**, which is independent of the solvent polarity. In emission, the protonation also results in a large hypsochromic shift. The emission maximum is centered

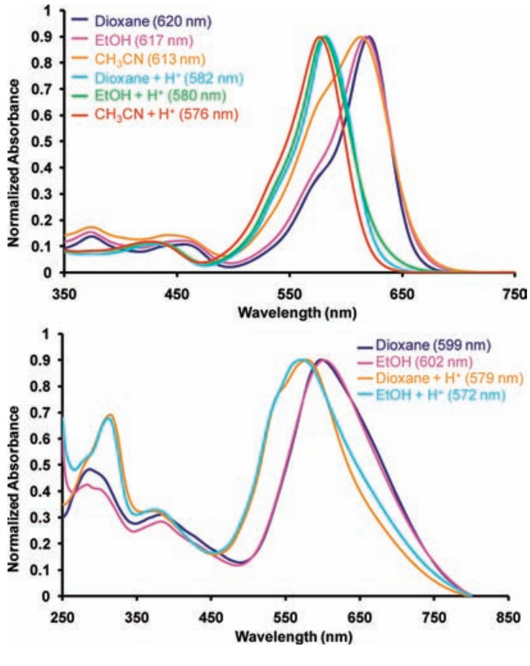

Figure 2. Top: absorption spectra of **5**. Bottom: absorption spectra of **7**.

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at 573 ± 7 nm for **4** and 620 ± 8 nm for **5**. For both molecules, a small hypsochromic shift is observed in more polar solvents. However, instead of resulting in a higher fluorescence quantum yield,[1c] protonation here produces rather low quantum yields (ϕ) for **4** (ϕ decreases from 0.20 to 0.13) and **5** (ϕ decreases from 0.12 to 0.02), due to a faster nonradiative decay k_{nr}. A decrease of the lifetime in more polar solvents is also observed for both molecules. The solvent dependency of the spectra of protonated **4** and **5** can be attributed to the ICT character of the major absorption. We presume that after protonation the amino group becomes the acceptor group, while the iodine atom of **4** and the ethynylanisole moiety of **5** act as donor groups. The electronic signature moves from a push/π/push situation to a pull/π/push case.[1b] Nonetheless, the CT character in both cases is rather modest, probably due to the weak electronic acceptor nature of the ammonium center. In the absorption spectra of the protonated form of **4**, the pronounced shoulder seen at 530 nm is assigned to an intramolecular CT transition, while the lowest energy absorption band centered around 560 nm can be attributed to the BODIPY $S_0 \rightarrow S_1$ ($\pi\pi^*$) transition.

For the TCBD dye **7**, the absorption spectra show a large broad band between 500 and 800 nm, with a maximum centered at 600 nm ($\varepsilon \approx 45\,000$ M^{-1} cm^{-1}). Weak solvatochromism is observed in solvents with higher dipole moments. Upon protonation, a hypsochromic shift of about 20 nm is observed in all solvents. In all cases, the fluorescence of the chromophore is completely quenched, probably due to a photoinduced oxidative electron transfer (PET) from the BODIPY* to the cyano residue.[18] A strong driving force of $\Delta G_0 \approx -720$ meV has been calculated using the Rehm–Weller equation and by disregarding the electrostatic effects.[19] The optical transition $E_{00} \approx 2.08$ eV has been estimated using the absorption profile and the steady state emission of the analogous derivative **5**.[20]

The electrochemical properties of **5** and **7** were investigated in deoxygenated CH_2Cl_2 solution at rt (Figure 3). The data are shown in Table 2. For **5**, on the oxidation scans, two irreversible steps at +0.56 and +0.86 V were observed, corresponding to successive one-electron oxidations of the dimethylamino group and the BODIPY core, respectively. In the reduction scans, the reversible step at −1.15 V can be attributed to the one-electron reduction of the BODIPY core.[21] For **7**, interestingly, the oxidation scans show two reversible steps at +0.72 and +1.04 V corresponding to the oxidation of the dimethylamino group and BODIPY moiety, respectively. The presence of the TCBD group makes the oxidation of the amino group and BODIPY core more difficult by 160 and 180 meV, respectively. In the reduction scans, three well-resolved reversible steps were observed, corresponding to two successive one-electron reductions of the two dicyanovinyl (DCV) moieties at −0.32 V and −0.78 V and the third reversible one-electron reduction of the BODIPY moiety at −1.50 V. The reduction of the BODIPY core is more difficult by 350 meV due to the successive reduction of the TCBD residues.

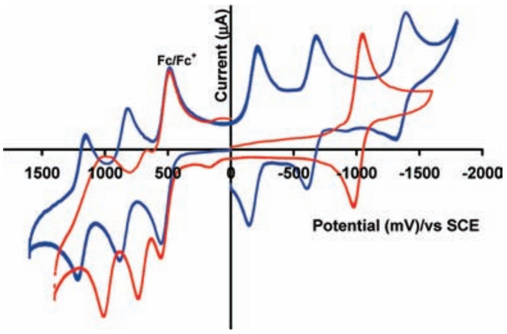

Figure 3. Cyclic voltammograms in dichloromethane at rt for **5** (red) and **7** (dark blue). Potentials were standardized using added ferrocene (Fc) as an internal reference.

Table 2. Selected Electrochemical Data[a]

dye	$E°_{ox}$ [V] ($\Delta E°$ [mV])	$E°_{red}$ [V] ($\Delta E°$ [mV])
5	+0.56 (irrev); +0.86 (irrev)	−1.15 (70)
7	+0.72 (70); +1.04 (70)	−0.32 (70); −0.78 (60) ;-1.50 (60)

[a] Cyclic voltammetry carried out in deoxygenated CH_2Cl_2 solutions, containing 0.1 M $TBAPF_6$, at a solute concentration range of 1.5×10^{-3} M, at 20 °C. Potentials were standardized using added ferrocene (Fc) as an internal reference and converted to SCE assuming that $E_{1/2}$ (Fc/Fc^+) = +0.38 V (ΔE_p = 70 mV) versus SCE. Error in half-wave potentials is ±15 mV. When the redox process is irreversible, the peak potential (E_{ap} or E_{cp}) is quoted.

In short, we have succeeded in the regioselective preparation of monostyryl derivatives and the selective addition of TCNE on the triple bond side. The interesting electrochemical properties, strong CT absorption band in the 500–700 nm range, and good solubility in common solvents, make the TCBD/BODIPY dye **7** an interesting candidate for incorporation in optoelectronic devices. Further investigations concerning generalization of the synthetic methods and applications to solar cells are currently in progress.

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

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