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Synthesis of Highly Functionalized BOPHY Chromophores Displaying Large Stokes Shifts

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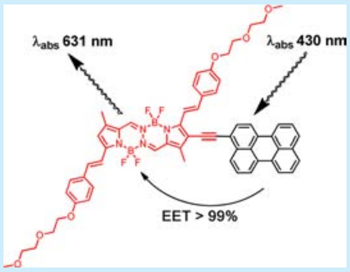
Supporting Information

ABSTRACT: BOPHY dyes bearing bromo (in 5,5′-position) and iodo (in 4,4′-position) were synthesized. Double Knoevenagel reactions allow the extension of conjugation, resulting in an absorption above 625 nm. Selective cross-coupling reactions promoted by palladium(0) and microwave irradiation allow linking of a perylene module. These dyes are highly fluorescent, and the intramolecular cascade energy transfer from the perylene moiety to the BOPHY framework is almost quantitative, providing large virtual Stoke shifts (>5100 cm^{-1}).



Standard fluorescent dyes, such as naphthalimides, coumarins, fluoresceins, cyanines, rhodamines or BODIPYs, are cornerstones for various spectroscopic or microscopic methods that hold a prominent position in biological studies. Although robust, the singular fact that all these fluorescent scaffolds were first developed many decades ago encourages a search for new fluorescent scaffolds to enrich the pool of fluorophores for downstream applications. The availability of boron(III) complexes has recently united the fields of fluorescence imaging, organic electronics and light harvesting.[1,2] Workhorses in this field have been 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) and its derivatives,[3] the BORANILS[4] and more recently the bis(difluoroboron)-1,2-bis{(1*H*-pyrrol-2−2-yl)methylene}hydrazine (BOPHY) dyes.[5] The attractiveness of these mono- and dinuclear boron complexes relates to their easily tailored spectroscopic and electronic properties. In the BODIPY case this can be achieved by increasing the delocalization on the dipyrromethene core,[6] by switching pyrrole for isoindole modules,[7] or by fusion of the main core with additional heteroaromatic rings.[8,9] The synthesis of these latter architectures requires stepwise synthesis and tedious chemistry partially connected to the fact that regioselective functionalization is often needed.[9] Another option is the replacement of the central carbon atom by a nitrogen atom leading to aza-BODIPY. This variant also involves tedious synthesis but provides dyes with useful properties in the near-infrared.[10] Within the BOPHY family, absorption is usually limited to the 400−470 nm region,[5a] although one case is known with absorption extending to 530 nm.[5b] This is a case where functionalization of the BOPHY was achieved by a single Knoevenagel condensation. Despite such widespread efforts, it is often true that limited amounts of the functionalized dyes are available for materials science applications.

The design, synthesis and characterization of dinuclear or polynuclear boron(III) complexes[11] are driven by the fact that panchromatic dyes can be formed in which intramolecular cascade energy or electron transfer are effective. Such systems are also seen as possibly paving the way to solar concentrators, fluorescence intensifier and multivalence systems where their blocked or cooperative behavior may be used to encode preprogrammed functions.

Herein, we describe the first functionalizations of BOPHY in the 4,4′, 5,5′ positions, as well as double-Knoevenagel condensations on the methyl residues in the 5,5′ substitution positions and iodination at the 4,4′-positions which enable attainment of absorption above 620 nm (Ar = −PhNMe$_2$ in Figure 1).

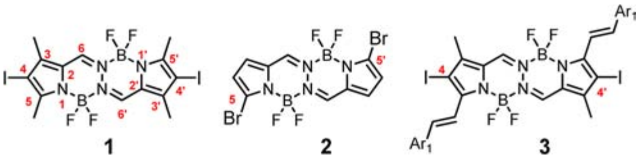


Figure 1. Molecular structures of key building blocks.

We selected first the tetramethyl building block **1** and second the dibromo derivative **2**. Both were prepared by preliminary condensations of 3,5′-dimethylpyrrole-2-carboxyaldehyde or pyrrole-2-carboxyaldehyde with hydrazine monohydrate, providing the ditopic Schiff base ligands (Scheme S1). With the tetramethyl compound, complexation with BF$_3$·OEt$_2$ affords the BOPHY in 53% yield, and treatment with ICl at RT in polar solvents provides the diiodo BOPHY **1** in 84% isolated

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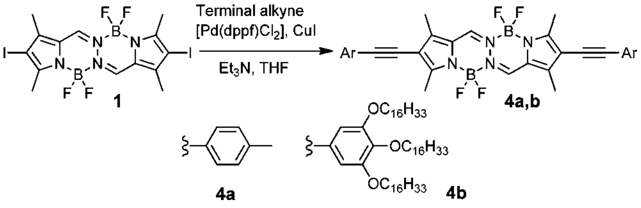
yield. After bromination of the Schiff base ligands, boron complexation of the product provided BOPHY **2**. The synthetic routes were inspired by previous work on the BODIPY framework.[12]

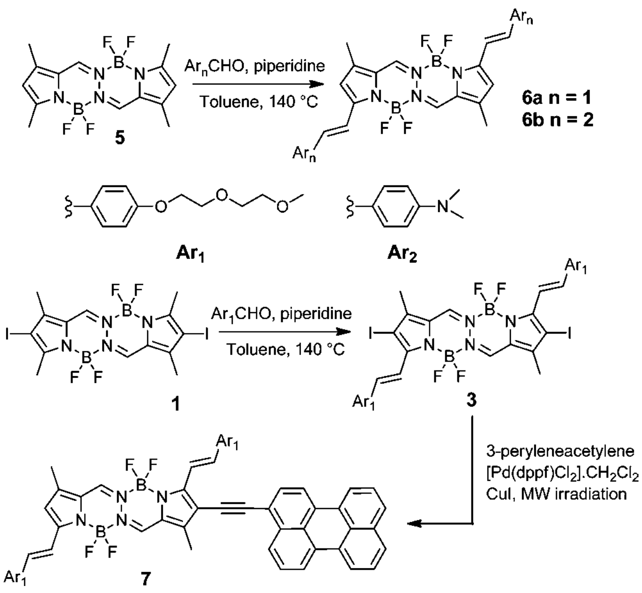
It was soon found that **2** was resistant to palladium-catalyzed cross-coupling reactions, whereas **1** is suitable for formation of such C−C bonds. Interestingly, cross-coupling dye **1** with a variety of terminal alkynes does occur with [Pd(dppf)Cl$_2$]·CH$_2$Cl$_2$ (3 mol %) as catalyst [dppf = 1,1′-bis(diphenylphosphino)ferrocene], CuI (6 mol %) as reductant and triethylamine as base (Scheme 1).

Scheme 1. Synthesis of 4,4′-Bis-Coupled BOPHYs



Drawing an analogy with BODIPY systems,[13] we considered that both solubility enhancement and a shift of optical absorptions to lower energies might be achieved by conversion of the 5,5′-methyl substituents to vinyl derivatives through Knoevenagel reactions. The previously developed protocol[14] of high temperature (>140 °C) using piperidine in toluene and trace amounts of *p*-TsOH as activator (Scheme 2), resulted in the first demonstration of double condensation on a BOPHY, leading to the extended distyryl dyes **6a** and **6b** in 56 and 65% isolated yields, respectively. We then turned our attention toward the use of the diiodo derivative **1** under the same conditions, obtaining the highly functionalized dye **3** in 35% isolated yield.

Scheme 2. Synthesis of Bis-Styryl BOPHYs



With the diiodo precursor it is possible to cross-link polyaromatic structures providing materials useful for intramolecular energy transfer. A major disadvantage of Pd-catalyzed cross coupling reactions on BOPHY systems bearing styryl functions is that under conventional conditions the framework is rapidly degraded. A partial solution found is the use of microwave irradiation at a moderate temperature (about 65 °C) and with a short irradiation time (30 min) using [Pd(dppf)Cl$_2$].CH$_2$Cl$_2$ (10 mol %) and CuI (10 mol %) in THF/triethylamine under anaerobic conditions. Unfortunately, double cross-coupling was not effective, but large amounts of the monodehalogenated compound were formed, ultimately providing the mono cross-coupled dye **7** in modest yields (about 16%, Scheme 2). Such dehalogenation processes have previously been observed with similar dyes.[15] The unsymmetrical nature of these dyes is readily seen by proton NMR, with the observation of a singlet for the *β*-pyrrolic proton at 6.81 ppm and two imino singlets 6,6′ at 8.10 and 8.01 ppm in CD$_2$Cl$_2$.

The molecular structure of BOPHY **6a** functionalized on the periphery by a pair of a methyl groups at C2/C7 and a styryl group extended by a polyethylene glycol chain at C4/C9 was determined by single-crystal X-ray diffraction and is shown in Figure 2. Details of the crystal data as well as the structure refinement are summarized in the Supporting Information. The molecular structure, with its elongated substituents, appears bent and disordered to a certain extent, drifting away from a speculative C_{2h} symmetry, but still with a pseudo inversion center in the middle of the N−N bond of the tetracycle. The dihedral angle between the two moieties of the tetracycle is 39.0°.

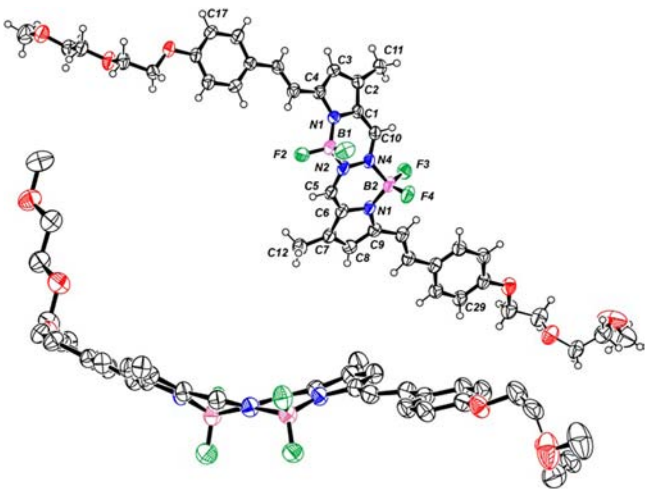


Figure 2. ORTEP view of compound **6a**. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are shown as small spheres of arbitrary radii. On the bottom is shown a view along the BOPHY median N−N bond, highlighting the slightly twisted, propeller-like shape of the overall structure and the concavity of the central platform.

Electronic absorption and emission spectra of dyes **1** and **4a** in THF are shown in Figure S16. The shape of the absorption spectra are similar to unsubstituted BOPHY dyes,[5a] with λ_{max} at 475 nm (ε = 59 300 M^{-1} cm^{-1}) and λ_{max} at 493 nm (ε = 71 500 M^{-1} cm^{-1}) for **1** and **4a**, respectively. For the diiodo derivative **1**, the fluorescence is heavily quenched due to the heavy atom effect while for **4a** a strong fluorescence is observed at 527 nm (ϕ_F = 63%). Unlike the BODIPY dyes, the emission profile is not the mirror image of the absorption profile and the higher energy emission at 496 nm is more intense than the lower energy transition. This is indicative of reorganization in the

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excited state.[16] The consequence is that the Stokes shifts are larger ($\Delta_{SS} \approx 1300$ cm^{-1}) compared to their standard BODIPY analogues ($\Delta_{SS} = 600$ cm^{-1}).[3] No solvent effect is observed by replacing THF by toluene.

The substitution of the methyl groups in the 5,5′-positions by styryl functions (dyes **6a** and **6b**) gives rise to a clear bathochromic shift in the absorption and emission spectra in THF (Figure 3). Compared to dye **1**, the longest wavelength absorption maximum ($\pi-\pi$ *) is red-shifted by 104 and 150 nm, respectively, for dyes **6a** and **6b**. Another more energetic transition appearing at 320 and 360 nm is assigned to the styryl functions, at similar energy to that of BODIPY distyryl derivatives.[17] For compound **6a**, the fluorescence quantum yield is 47% in THF with a maximum emission at 611 nm whereas ϕ_F drops to 13% in THF for dye **6b**. The excitation spectrum for both compounds matches the absorption spectrum, a result in keeping with the absence of both impurities and aggregates. The iodination of the 4,4′-position in **3** has only a minor influence on the absorption and fluorescence spectra (red-shift of 3 and 22 nm respectively compared to **6a**), but the fluorescence quantum yield drops to 6%. The presence of an iodo substituent favors intersystem crossing to the triplet state, resulting in the drop in the fluorescence quantum yield (Table 1).[18]

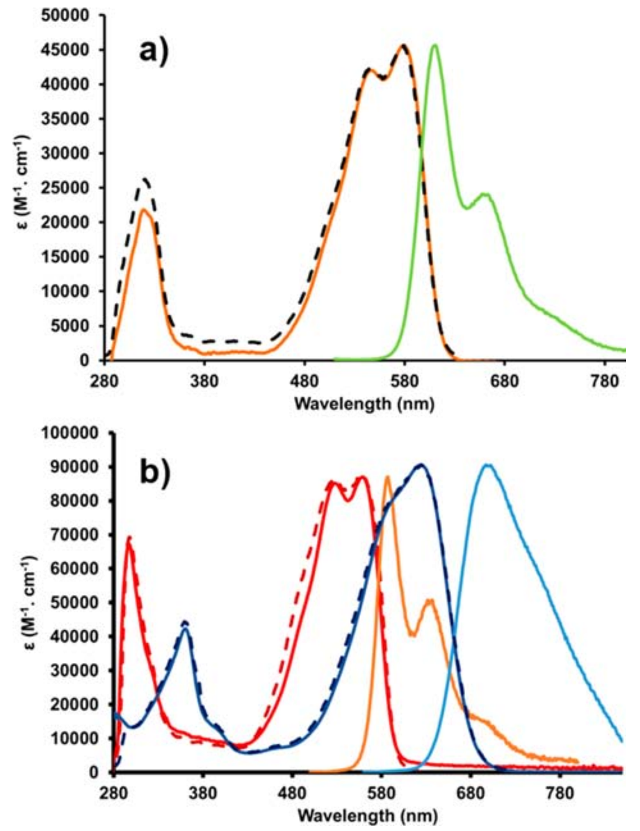

Figure 3. (a) Absorption (orange line), excitation (black dashed line) and emission (green line) spectra of **6a** in THF. (b) Absorption (dark blue), excitation (dashed blue) and emission (light blue) spectra of **6b** in THF. Absorption (dark red), excitation (dashed red) and emission (orange line) of **6b** protonated with $HCl_{(g)}$ in THF.

Protonation of **6b** in THF with $HCl_{(g)}$ results in a hypsochromic shift of 66 nm of the main transition and an increase of the QY by 215% (Table 1). At the same time, the styryl $\pi-\pi$* absorption is shifted by 64 nm and the steady state emission became structured (Figure 3). As expected, linking 3-ethynylperylene in the 4-position resulted in a strong supplementary $\pi - \pi$* absorption band of about 30 000 M^{-1} cm^{-1} in the 400−500 nm wavelength range (Figure 4).[19] Interestingly, irradiation in the perylene absorption band at 430 nm resulted in very little residual perylene emission (1% at 515 nm) and strong emission of the BOPHY framework at 631 nm with a quantum yield of 23%. This almost quantitative energy transfer is the consequence of a perfect spectral overlap between the emission of perylene and the absorption of the BOPHY framework. The virtual Stokes shift is defined as the difference between the wavenumber of the absorption maximum of the donor and the wavenumber of the emission

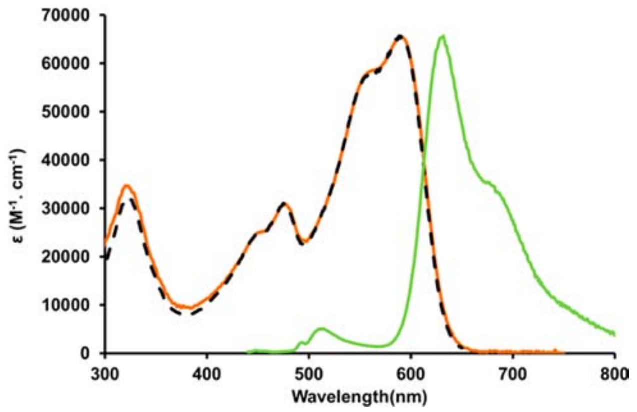

Figure 4. Absorption (orange line), excitation (black dashed line) and emission (green line) spectra of **7** in THF.

Table 1. Selected Spectroscopic Data for the Novel BOPHY Dyes

compds	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_F (λ_{ex}, nm)[a]	τ (ns)	k_r (10^8 s^{-1})[b]	k_{nr} (10^8 s^{-1})[b]	Δss (cm^{-1})	fwhm (cm^{-1})[c]
1	475	59 300	496	0.17 (@420)	0.67	2.54	12.4	890	3260
2	459 (439)	51 500	482	0.25 (@410)	1.51	1.66	4.97	1040	3410
4a	493	71 500	527	0.63 (@450)	2.00	3.15	1.85	1310	3140
4b	495	73 600	531	0.02 (@460)	0.18	1.30	63.6	1370	3280
6a	579	45 600	611	0.47 (@500)	1.83	2.57	2.90	900	2900
6b	625	90 600	698	0.13 (@570)	0.82	1.59	10.6	1673	2850
6b + HCl_g	559	87 000	587	0.41 (@490)	1.46	2.81	4.04	853	3180
3	582	82 300	633	0.06 (@525)	0.28	2.14	33.6	1380	3270
7	590	65 700	631	0.24 (@560)	1.36	1.76	5.59	1100	3050

[a] Quantum yields were determined using either Rhodamine 6G[22] for dyes **1**, **2**, **4a** and **4b** and BODIPY-tetraOMe[7] for dyes **3**, **6a**, **6b**, and **7** as actinometry reference. [b] k_r calculated from $\phi_F = k_r\tau$; $k_{nr} = (1 - \phi_F)/k_r$. [c] Full width at half-maximum of absorption.

maximum of the acceptor (perylene and BOPHY respectively in 7). This allows calculation of a virtual Stokes shift of 5100 cm^{-1}. A rate of electronic energy transfer could be estimated at 1.8×10^{10} s^{-1}, from the quantum yields obtained by irradiation in the perylene absorption, and knowledge of the excited state lifetime of the perylene in the absence of the BOPHY unit.[20]

All these new dyes are redox active, and cyclic voltammograms (CV) of **1**, **4a** and **6a**,**b** and are shown in Figures S17 and S18. The new dye **4a** substituted by two tolyl groups displays an irreversible oxidation at a similar potential to that of dye **1** (+1.39 V vs Fc_2). The irreversible reduction of **4a** is facilitated by 260 mV, as would be expected from the σ-withdrawing effect of the alkyne substituent (Figure S17).[21]

The distyryl derivative **6a** displays two reversible oxidation waves, the first being shifted anodically by 290 mV and the second shifted by only 70 mV with respect to the naked BOPHY **1**. The reduction is facilitated by 480 mV compared to **1**, a result in keeping with the decrease of the optical transition E_{00} previously determined from the intersection between the absorption and emission traces (2.07 eV for **6a**, compared to 2.42 eV for dye **1**). Switching from a short polyethyleneglycol chain to a stronger donor group such as dimethylamino facilitates the first oxidation by 510 mV, and several processes are observed in keeping with the successive oxidations of the dimethylamino groups, the styryl functions and the BOPHY core.[17] Compared to dye **6a**, the reduction is more difficult by 290 mV, a result in line with the increase of the electron density along the BOPHY core. As would be expected by protonation of the dimethylamino groups, the CV is simplified due to the impossibility of oxidizing protonated amines, while the successive oxidations of the distyryl fragments and BOPHY core remain at similar potentials compared to the reference compound **6a**. Note that during the protonation process the reduction potential of the BOPHY dye at −1.22 V remains unchanged (Figure S18).

In summary, we have successfully designed and synthesized distyryl-BOPHY dyes bearing in some cases reactive iodo groups in the 4,4′-substitution positions. In these positions, alkyne residues could be introduced by standard cross-coupling reactions. Tolylacetylyene and 3-ethynylperylene substituents were introduced to study their influence on the optical and electrochemical properties. With the perylene moiety, a very efficient cascade energy transfer was deduced from the steady state emission, consistent with a virtual Stokes shift above 5100 cm^{-1}. Our protocols involved synthetic conditions compatible with the presence of iodo substituents on the core and should assist in developing new functional organic materials that contain charge transporting modules suitable for application in organic electronics. These novel highly absorbing and redox active dyes have LUMO/HOMO orbital levels well suited as potential photoactive layers in bulk heterojunction solar cells.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and spectra data for all new compounds. Absorption, emission spectra for **1** and **4a**, CV for **1**, **4a**, **6a**, and **6b**, and crystal packing for **6a**. 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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