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ARTICLE TYPE

Spiranic BODIPYs: a ground-breaking design to improve the energy transfer in molecular cassettes†

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Boosted excitation energy transfer in spiranic *O*-BODIPY/polyarene cassettes, when compared with the parent non-spiranic (flexible) system, is highlighted as a proof for the ability of a new structural design to improve the energy transfer in molecular cassettes.

The development of multichromophoric systems able to achieve efficiently excitation energy transfer (EET) from donor to covalently-linked acceptor chromophores (i.e., molecular cassettes) has gained a great interest in the last years, since they are extremely useful in the development of advanced materials for outstanding photonic technologies (including optoelectronic), such as solar harvesting, fluorescence microscopy or biomolecular probing.¹

BODIPYs constitute a recognized family of modulable organic fluorophores with noticeable utility in the development of photonic tools.² The usually large molar-absorption coefficients (ϵ) and high fluorescence quantum yields (ϕ) of BODIPYs have promoted their application as fluorescent dyes for bioimaging,³ chemosensing^{2e,4} and lasing,^{2d,5} among others.^{2,4a} However, the small Stokes shifts (around 600 cm⁻¹) of these dyes may cause re-absorption of the emitted light or effects from excitation-light scattering, which are important limits in those applications, mainly in advanced bioimaging technologies based on multicolor labeling.⁶ This handicap can be solved by developing efficient energy-transfer cassettes with large pseudo-Stokes shifts, based on BODIPY as the acceptor chromophore.^{3c,df,4b,c,5a,b} Moreover, green-emitting cassettes (standard BODIPY emission) are interesting for constructing valuable tunable narrowband ultraviolet (UV) laser pulses in the 250-300 nm region (by frequency doubling) for biological applications.⁷

The development of BODIPY cassettes requires a fine molecular engineering, since the involved chromophores (BODIPY and donor/s) must retain their identity in the molecular structure (electronically non-conjugated), and must be photophysically and structurally proper to achieve an EET mechanism.⁸ Thus, orbital overlap is needed for the Dexter mechanism (electronic exchange by short-range interaction),⁹ whereas rigid and twisted unsaturated linkers are demanded for the through-bond energy transfer (TBET, which seems to involve electronic exchange as well).^{3c,4c} On the other hand, Förster resonance energy transfer (FRET), also known as through-space, requires short distances,

spectral overlap of donor emission and acceptor absorption, and adequate orientation on the involved transition dipole moments to enable dipole-dipole coupling (long-range interaction).^{10,4c} In this complex framework, Ziessel et al. have cleverly constructed efficient BODIPY cassettes (**1** in Fig. 1),^{2b,11} by tethering, directly or through ethynyl bridges, two donor polyarenes to the BODIPY boron, which acts as key linking site avoiding electronic conjugation.

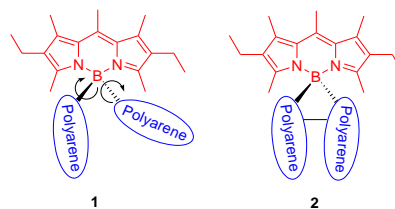


Fig. 1 BODIPY/polyarene cassettes by boron functionalization: Conformational motion vs. spiranic design.

However, the conformational motion of **1** could influence negatively on the fluorescence and EET efficiency of these interesting BODIPY cassettes (e.g., when flexible bridges linking the chromophores are involved). This prompted us to study a new design for them, which is attained by linking together the polyarene moieties of **1** to build up the spiranic system **2** (Fig. 1). In this design, the mentioned motion should be significantly restricted, while the acting donor and acceptor chromophores are arranged almost orthogonally. To test this strategy, we have studied comparatively the cassette properties of *O*-BODIPYs **3** and **4**¹² (Fig. 2), which are straightforwardly obtained from commercial BODIPY PM567, and 2-naphthol and 1,1'-bi(2-naphthol) (BINOL) (see ESI†).

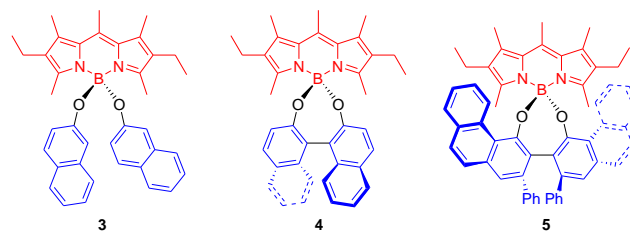


Fig. 2 Studied *O*-BODIPY cassettes.

Satisfactorily, the absorption spectra of **3** and **4** (Fig. 3) were almost the sum of the absorptions of the individual chromophores involved in their molecular structures, as shown by their comparison with the spectra recorded for PM567, 2-naphthol and BINOL in the same conditions (see Fig. S1 in ESI†). Therefore, no noticeable electronic coupling between chromophores exists in **3** and **4**, at least at their ground states, as it was expected by the role of the linking boron in these BODIPY cassettes.¹¹ Theoretical calculations conducted on **4** (B3LYP/6-31+g*, see ESI†) support also the claimed electronic isolation of chromophores, by predicting the involvement of molecular orbitals placed exclusively at the polyarene moiety, or at the BODIPY, for the main electronic transitions associated to each absorption band, UV or visible (Vis), (see Fig. S2 in ESI†). Therefore, the cassette-required selective excitation of chromophores should be possible in **3** and **4**.

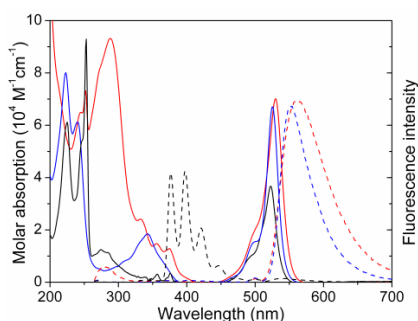


Fig. 3 Absorption spectra (bold) and fluorescence spectra (dashed) of **3** (black), **4** (blue) and **5** (red) upon UV irradiation (250 nm) in hexane (see ESI†).

The excitation of the BODIPY chromophore in **3** or **4** (Vis irradiation) leads to the typical fluorescent BODIPY signature, also with high fluorescence quantum yield (up to 89% for **4**; see Table S1 in ESI†). However, exciting the polyarene (UV irradiation) provides opposite results for each test compound. Thus, single polyarene emission is recorded for **3** (just naphthalene-like emission without detection of BODIPY fluorescence), whereas the UV polyarene emission is totally quenched in favor of a bright BODIPY-emitting Vis signal in the case of spiranic **4** (see Fig. 3). In fact, the fluorescence quantum yield of **4** was almost the same upon direct excitation of the BODIPY chromophore, than when exciting its polyarene moiety (Vis vs. UV irradiation; see Table S1 in ESI†), which indicates an EET efficiency of ~100%.¹³ This observation is extremely important taking into account that the EET efficiency of parent **3** was almost null (see Fig. 3, and Table S1 in ESI†). In other words: flexible **3** does not exhibit cassette behavior, whereas tight spiranic **4** does it efficiently.

The observed EET process should take place by the FRET mechanism, taking into account the feasible spectral overlap between the emission transition of the naphthalene-based donor and the more-energetic absorption transitions of the acceptor BODIPY (e.g., $S_0 \rightarrow S_2$),¹⁴ the spatial proximity of the involved chromophores and more important, the lack of orbital overlap avoiding the electronic exchange required by the Dexter or TBET mechanisms (note the spacing imposed by tetrahedral boron).

Indeed, the EET efficiency of **4** was practically the same when decreasing the temperature, even at 77 K (see Fig. S3 in ESI†), where the electronic exchange, an energy-activated process, is virtually nullified.¹⁵ However, the mentioned FRET requirements are also present in cassette-silent **3**, highlighting that a proper spatial arrangement of the acting chromophores, as the existing in **4** due to its spiranic design, is crucial to achieve an efficient EET in these *O*-BODIPY cassettes.

The conformational motion of the polyarenes of **3** must give place to a dispersion of the mutual orientations for the involved transition dipole moments. This mutual orientation is a key factor modulating the FRET efficiency (κ^2 term in the Förster formalism).¹⁰ Therefore, the orientation of dipoles provided by the conformationally-restricted structure of spiranic **4** must be highly proper for promoting the FRET process (the conducted theoretical calculations predict an almost-orthogonal mutual orientation of the bi(polyarene) and BODIPY moieties of **4**; see Fig. S4 in ESI†).

The mentioned conformational motion should also explain the lower fluorescence efficiency of **3**, when compared with **4**, upon the direct excitation of the BODIPY chromophore (56 vs. 89%), as well as the biexponential fit of its fluorescence-decay curve (see Table S1 in ESI†). In this line, it is widely accepted that rigidity is usually required for improving the fluorescence, whereas flexibility provides additional non-radiative relaxation pathways (cf. tight **4** vs. flexible **3** in Table S1 in ESI†). The extraordinary conformational motion of *O*-BODIPY **3** (note the flexible oxygen bridges), also explains its cassette behavior (null) when compared with related (PM567/naphthalene) less-flexible *C*-BODIPY cassettes.¹¹

To support the workability of the new design for improving the FRET efficiency in BODIPY cassettes involving the boron as the key site for tethering the donor chromophores, we have synthesized and photophysically studied an additional spiranic *O*-BODIPY-cassette based on polyarene as the donor (**5** in Fig. 2). This compound was obtained easily from the corresponding commercial bi(phenanthrenol) (VAPOL) according to the same procedure used for **3** and **4** (see ESI†). As in the cases of **3** and **4**, the absorption spectrum of **5** (Fig. 3) was the sum of the individual spectra of their chromophoric fragments (almost the sum of the individual spectra of PM567 and VAPOL; see Fig. S1 in ESI†), showing the required electronic isolation for the involved chromophores (theoretical calculations support also this isolation; see Fig. S2 in ESI†).

The selective excitation of the polyarene of **5** gives place to BODIPY-chromophore emission (a residual UV signal coming from the polyarene can be now detected; see Fig. 3 and Table S1 in ESI†). As in the case of **4**, the fluorescence quantum yield of **5** was the same upon Vis or UV irradiation (i.e., upon BODIPY or polyarene excitation, respectively), which implies an EET efficiency of ~100%, regardless the used solvent, as calculated up to now.¹³ Nonetheless, the measurable detection of polyarene emission upon UV irradiation ($\phi = 0.006$; see Table S1 in ESI†), when compared with the emission of VAPOL alone in the same conditions ($\phi = 0.35$), allows now a more reliable determination of the EET efficiency of **5**,¹⁶ which stands ca. 98%. Noticeably, the high fluorescence quantum yield of starting PM567 is retained in cassette **5** (94%, see Table S1 in ESI†), suggesting

that the bulky VAPOL fragment is nicely accommodated in its molecular structure; i.e., without affecting the planarity of the BODIPY chromophore, as theoretically shown in Fig. S4 (ESI†).

In summary, we have reported the first examples of a new structural strategy to improve the EET efficiency in molecular BODIPY cassettes involving the boron atom as key site linking the acting chromophores. This design consists in a spiranic O-BODIPY which involves the boron as the spiranic shared atom. The goal of this simple design is to keep the conformational motion of the involved donor/acceptor chromophores restricted, and tightly fixed in an almost orthogonal arrangement to ensure an efficient EET via FRET. Another important goal is the straightforward synthetic access to these O-BODIPY cassettes from BODIPYs and donor-based diols, which assures an excellent potential for developing future smarter BODIPY cassettes for valuable fluorescence applications (bioimaging, lasing, chemosensing, optoelectronics, etc.). Thus, further experimental and computational studies are now in progress, directed to know the key structural factors ruling the EET efficiency in these spiranic O-BODIPY cassettes and related ones (C- instead of O-BODIPY, other donors instead of polyarene, etc.). Key factors to be studied are the conformational flexibility of the spiranic system, the relative arrangement of the acting chromophore dipoles, the electronic features of the atoms linking the boron center, or the possibility of using hybrid donors (i.e., two different chromophores integrated in the bi(arene) system) or donors different to polyarene. We are convinced that the herein communicated new structural design to boost the EET, from flexible molecular cassettes to tight spiranic ones, has a great potential for inspiring the future development of molecular cassettes in general, and not only those based on BODIPY.

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†Electronic Supplementary Information (ESI) available: Experimental, photophysical and computational details, characterization data, NMR spectra of new compounds, as well as Figures S1-S4 and Table S1. See DOI: 10.1039/b000000x/

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