Multichromophoric *COO*-BODIPYs: An advantageous design for the development of energy transfer and electron transfer systems†

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***COO*-BODIPYs are highlighted as cutting edge scaffolds for the easy access to a new generation of multichromophoric architectures with enhanced (photo)chemical stability, showing either boosted capability for excitation energy transfer, glow fluorescence and laser emission, or photoinduced electron transfer. The new finding paves the way towards the rapid development of smarter organic dyes for advancing photonics and optoelectronics.**

Molecular multichromophoric arrays (MMAs) allow the development of dyes with optical and optoelectronic properties which are not available from a single chromophore, expanding its capabilities into a specific photonic field, from advanced biomedicine to clean energy.[1] For instance, fluorescent MMAs enabling excitation energy transfer (EET), from light-absorbing donor chromophores to a light-emitting acceptor one, allow access to smarter fluorescent dyes for bioimaging,[1b-c,e,i,k] whereas MMAs able to harvest solar energy from different spectral regions (antennae) and transfer it to a final chromophoric system enabling photoinduced electron transfer (PET) are key for advancing solar cells and artificial photosynthesis.[1d,j]

BODIPY (boron dipyrromethene) fluorophores outstand for their excellent capabilities to absorb and emit visible (vis) photons, as well as for their rich chemistry.[2] BODIPY chemistry makes it possible to modulate optical signatures (*e.g.* shifting the vis spectral bands to the near infrared for biophotonics),[3] promote intersystem crossing (ISC; *e.g.* focused to the generation of singlet oxygen for photodynamic therapy),[4] gain specific biological properties (*e.g.* bio-recognition),[5] or enable chiral perturbation towards valuable chiroptical properties, such as circularly polarized luminescence,[6] among other interesting possibilities.[7] Moreover, BODIPYs can lase under proper excitation conditions,[8] which expands their use in photonics and optoelectronics.[9]

However, BODIPY fluorophores are also characterized by small Stokes´ shifts (*ca.* 600 cm^{-1}), which is an important handicap limiting their use in fluorescence-based applications (*e.g.* in bioimaging or lasing), due to the promotion of undesired effects coming from the re-absorption of the emitted and scattered light.[9] In this context, BODIPY-based MMAs combining fluorescence and EET help to apply BODIPY fluorophores in the development of smarter bright dyes for fluorescence-based applications by the consecution of proper *pseudo* Stokes´ shifts, but also by fitting the absorption and emission bands into the required working spectral regions.[10] On the other hand, non-fluorescent MMAs involving chromophoric BODIPY systems able to undergo a proper PET are key for advancing clean energy.[11,1f]

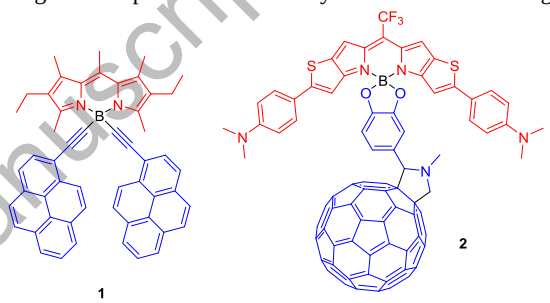


Fig. 1 Ziessel´s *C*-BODIPY MMA enabling EET and fluorescence (**1**), and D´Souza´s *O*-BODIPY MMA enabling PET (**2**).

Therefore, the establishment of advanced designs for the rapid development of BODIPY-based MMAs enabling EET and/or PET from simpler BODIPY dyes is of a great interest, the boron atom being a privileged reactive position for this purpose, avoiding also undesired electronic couplings between the involved chromophores.[2f] To date, two main designs have been extensively used for preparing at-boron-substituted BODIPY-based MAAs from simpler *F*-BODIPYs, the seminal *C*-BODIPY design developed by Ziessel *et al.* (*e.g.* **1**[12] in Fig. 1) using ethynyl- and aryl-based *C*-nucleophiles, and the synthetically simpler *O*-BODIPY design (*e.g.* **2**[13] in Fig. 1), which uses hydroxyarenes as *O*-nucleophiles.[2d] However, the higher conformational freedom of the B-O-C sigma bonds linking the acting chromophores in the *O*-BODIPY design can limit the efficiency of the MMA. This drawback can be solved in some cases by designing conformationally-restricted spiranic systems.[14] Another concern in these MMAs is the known (photo)chemical instability of the *O*-BODIPY dyes, especially under acidic conditions,[15] due to the high lability of the involved boron chelate. All these features constitute an important limit to the potential implementation of the *O*-BODIPY-based MMAs in real photonic applications (*e.g.* fluorescence bioimaging, which requires severe laser irradiation in aqueous media).

COO-BODIPYs constitute a subclass of *O*-BODIPY dyes involving two acyloxyl moieties pending from the boron atom (*e.g.* **4a** in Fig. 2).[2d] The introduction of the carbonyl group is known to enhance the electrophilic character of the boron atom when compared to standard *O*-BODIPYs, significantly increasing the (photo)chemical stability of the involved boron chelate.[16] Additionally, we have recently developed a straightforward procedure to prepare *COO*-BODIPYs from readily available *F*-BODIPYs and carboxylic acids, by using BCl_3 to promote the involved at-boron nucleophilic substitution in soft conditions.[16] Taking advantage of this simple procedure, we decided to develop unprecedented multichromophoric *COO*-BODIPYs as breaking model designs for the rapid development of efficient MMAs involving EET and/or PET processes. However, specific, unknown conformational and stereoelectronic features of the involved acyloxyl units could influence negatively on the photonic efficiency of such MMAs. To investigate this possibility, we selected multichromophoric *O*-BODIPY **3** and related *COO*-BODIPY **4a** (Fig. 2) to compare their capabilities as MMAs combining fluorescence and EET. The selection was done taking into account photonic and accessibility factors. Note that both dyes are based in the highly-fluorescent *F*-BODIPY dye known as PM567 (2,6-diethyl-4,4-difluoro-1,3,5,7,8-pentamethylBODIPY), able to emit vis light, and naphthalene-based chromophores able to absorb ultraviolet (UV) light.

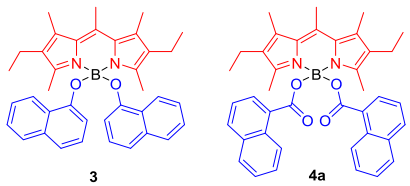
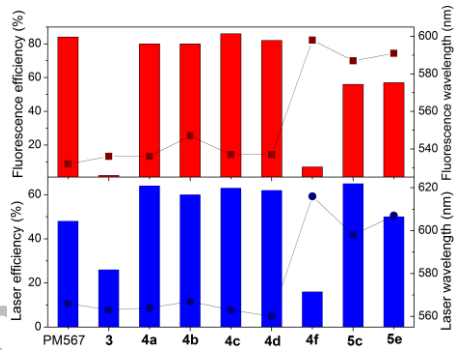


Fig. 2 Compared MMAs (based on *O*- *vs.* *COO*-BODIPY) combining EET and fluorescence.

To our satisfaction, **3** and **4a** could be straightforwardly obtained from PM567 and 1-naphthol or naphthalene-1-carboxylic acid, respectively, by using the said BCl_3-based methodology[16] (80% and 88% yield, respectively; see ESI†). Noticeably, this is the first time that such methodology is extended to the successful synthesis of a simple *O*-BODIPY dye. Importantly, array **3** turned out to be highly unstable in weakly acidic chloroform solution at room temperature (it was not even possible to record a clean ^{13}C NMR spectrum of this *O*-BODIPY dye in deuterated chloroform), whereas **4a** remained unchanged after treatment in more acidic media (*e.g.* 1 h in 1 M HCl).

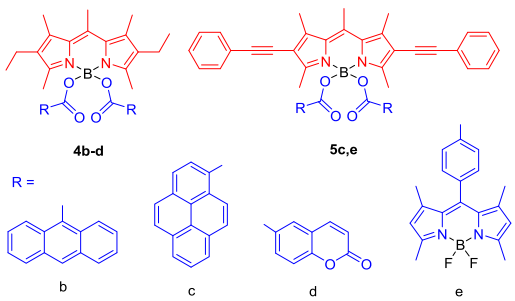
As expected, vis-exciting **4a** gives place to the typical bright *COO*-BODIPY fluorescence (fluorescence quantum yield, ϕ, up to 82%; see Fig. 3, and Fig. S1 and Table S1 in ESI†).[2d,16] However, **3** is significantly less fluorescent than **4a** (Fig. 3), showing also faster lifetimes (see Table S1 in ESI†). Therefore, the oxygenated groups at boron promote non-radiative deactivation channels in **3**, likely due to photoinduced intramolecular charge transfer (ICT), as reported for related polyalkylated *O*-BODIPYs.[17] Besides, theoretical support (wb97xd/6-311g*) shows the BODIPY chromophore of **3** severely distorted along its transversal axis (see Fig. S1 in ESI†). Oppositely, *COO*-BODIPY **4a** acts as a bright emitter owing to the lower electron-donor ability of its at-boron-pending oxygenated moieties, which restricts said ICT and also due to a lower conformational mobility imposed by the carbonyl groups. Indeed, the optimized geometry of **4a** features a fully planar BODIPY chromophore with the carbonyls disposed oppositely and symmetrically (see Fig. S1 in ESI†). Besides, the computed energy gap between the HOMO-1 and the HOMO of **4a** (placed at naphthalenes and BODIPY core, respectively) is higher than that computed for **3** (see Fig. S3 in ESI†), supporting less ICT for **4a**. On the other hand, significant differential emission due to a possible aggregative behaviour was not found for these dyes (*e.g.*, see Fig. S2 in ESI). In good agreement with these hypotheses and theoretical observations, under vis (532 nm) or UV (355 nm) laser irradiation, the lasing efficiency and photostability of *COO*-BODIPY **4a** in ethyl acetate solution is higher (more than 2- and



5-fold, respectively) than those recorded for *O*-BODIPY **3** pumped under otherwise identical experimental conditions (Fig. 3, and Table S2 and Fig. S4 in ESI†).

Fig. 3 Comparison of the fluorescence and laser (pumping at 532 nm) efficiency (columns) and wavelength (scatter) of MMAs **3**, **4a-d, 4f** and **5c,e** with respect to parent PM567, in ethyl acetate. For detailed data, see Table S1 (fluorescence) and Table S2 (laser) in ESI†.

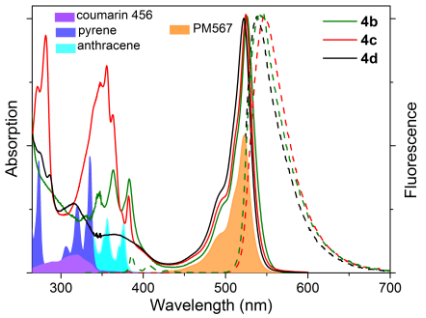
To prove the versatility of the *COO*-BODIPY design to rapidly develop fluorescent EET-based antennae involving different spectral regions, we selected MMAs **4b-d** and **5c,e** (Fig. 4), which could be straightforwardly prepared from the corresponding *F*-BODIPYs (PM567 for **4b-d** and 2,6-bis(phenylethynyl)-4,4-difluoro-1,3,5,7,8-pentamethylBODIPY[18] for **5c,e**) and carboxylic acids (commercial anthracene-9-carboxylic acid for **4b**, commercial pyrene-1-carboxylic acid for **4c** and **5c**, commercial 6-carboxycoumarin for **4d** and 8-(4-



carboxyphenyl)-1,3,5,7-tetramethylBODIPY[19] for **5e**), with yields ranging from 66% for **5e** to 97% for **4c** (see ESI†).

Fig. 4 Battery of *COO*-BODIPY-based MMAs combining EET and yellow (**4b-d**) or orange-red (**5c,e**) fluorescence.

In all cases, chromophoric integrity and isolation is maintained upon covalently binding the corresponding building blocks through the boron atom. Thus, the absorption spectra of **4a-d** are almost the sum of the absorptions of the individual chromophores involved in each MMA, as shown by the comparison of each



MMA spectrum with those recorded from related, simple monochromophoric marketed dyes (Fig. 5). The same occurs for **5c,e** (see Fig. S5 in ESI).

Fig. 5 Normalized UV-vis absorption spectra (bold lines) and fluorescence spectra upon UV-exciting the donor units (dashed lines) of PM567-based **4b-d** in cyclohexane (tetrahydrofuran was used for **4d** due to insolubility in cyclohexane), as well as UV-vis absorption spectra of monochromophoric PM567, coumarin 456 (7-hydroxy-4-methylcoumarin), pyrene and anthracene (filled spectra).

Theoretical calculations (wb97xd/6-311g*) also support the absence of electronic coupling between the involved chromophoric subunits (Fig. S6-S8 in ESI†), predicting that each main electronic transition involves molecular orbitals placed exclusively at each individual chromophore: BODIPY for the vis transition and arenes for the UV one (*e.g.* see Fig. S4 and Fig. S5 for the cases of **4b,c** and **5c,e**, respectively, in ESI†). Therefore, **4a-d** and **5c,e** should act as MMAs enabling EET from their arene donor chromophores to the BODIPY acceptor one.

To our satisfaction, only the BODIPY vis emission was recorded from **4a-d** and **5c,e** regardless of the excited chromophore (BODIPY or arene), with almost negligible emission from the arenes when selectively exciting with UV light (Fig. 5, and Fig. S5 in ESI†). Moreover, excitation spectra, monitored at the acceptor emission, matched the corresponding absorption spectra, displaying the bands of the involved acting chromophores (Fig. S9 in ESI†). Indeed, the calculated EET efficiencies (see ESI† for experimental details) are higher than 95% in all these MMAs (Table S1 in ESI†). On the other hand, MMAs based on the alkylated BODIPY core (**4a-d**) display high fluorescence quantum yields (ϕ >80%, Fig. 3), whereas those based on the π-extended BODIPY core (**5c,e**) show lower fluorescence efficiencies (ϕ around 60%, Fig. 3). The latter is in agreement with the promotion of non-radiative BODIPY de-excitation channels owing to charge separation upon the excitation, which is evidenced by higher Stokes shifts (up to 750 cm^{-1}) and lower fluorescence responses in polar media (see Table S1 in ESI†), as previously reported for related phenylethynylated BODIPY dyes.[20] As a matter of fact, the fluorescence efficiency of MMA **4c** is more than four times higher than that of a related MMA bearing the pyrenes directly tethered to the boron atom (*i.e.*, without the *COO* linker).[21]

Interestingly, acording to their photophysical behaviors, **4a-d** and **5c,e** became highly effective laser dyes when pumped at 532 nm in ethyl acetate solution, as reported for previous *COO*-BODIPYs,[16] but also when pumped at 355 nm in the same solvent, exhibiting laser emission peaked at *ca.* 570 nm with a pump threshold of 0.8 mJ/pulse, lasing efficiencies up to 65% (at 532 nm) and 57% (at 355 nm), and high photostability, enhancing significantly the laser action recorded from parent PM567 (a well-known laser dye) when pumped under otherwise identical experimental conditions (Fig. 3, and Fig. S4 and Table S2 in ESI†).

Finally, to prove the capability of the *COO*-BODIPY scaffold to rapidly develop valuable MMAs enabling PET, we designed **4f** (Fig. 6) as a molecular system able to undergo oxidative PET upon BODIPY excitation. This design was done computationally (wb97xd/6-311g*) by predicting the desired PET on virtual molecular structures involving available, electron-acceptor carboxyl-based moieties to be linked to PM567. As an example, the theoretical calculation of **4f** predicts the BODIPY HOMO to be intercalated within the rhodamine HOMO-LUMO energy gap (Fig. S10 in ESI†), making thermodynamically feasible a BODIPY-to-rhodamine PET competing with BODIPY-to-rhodamine EET upon BODIPY excitation.

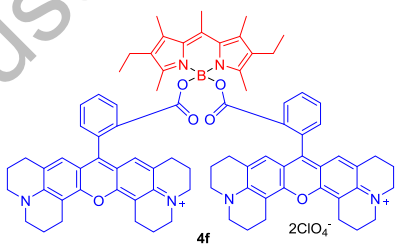


Fig. 6 *COO*-BODIPY-based MMA enabling PET (from the red to the blue moiety) upon BODIPY excitation.

As in the previous cases, **4f** could be straighforwardly obtained by BCl_3 activation (65% yield) from PM567 and the corresponding carboxylic acid (commercial rhodamine 640 perchlorate, see ESI†). As predicted computationall, the analysis of the absorption spectrum of **4a** (Fig. S11 in ESI†) supports the expected electronic isolation of the involved chromophores. Moreover, the fluorescence of **4f** upon BODIPY excitation was poor (ϕ *ca.* 7%; see Fig. 3), as a consecuence of the predicted PET competing with the expected EET. However, although the working PET diminishes the laser action of **4f**, it does not prevent it. Thus, by pumping **4f** in ethyl acetate solution at 532 nm, laser emission is detected at *ca.* 616 nm, but it required higher energy threshold (1.3 mJ/pulse) and exhibited lower efficiency and photostability than those recorded from the other herein studied *COO*-BODIPY dyes (Table S2 and Fig. S4 in ESI†).

Although the PET enabled in **4f** is not expected to be suitable for inducing an electric current, all the reported computational, synthetic and photonic results avail the *COO*-BODIPY design for the straightforwardly development of MMAs based on EET or PET for advancing photonic applications.

In summary, we have reported the first examples of a new design to develop BODIPY-based MMAs involving the boron atom as the key site linking the acting chromophores. The goals of this

simple design are: (1) easy and efficient synthetic access from available starting materials in a single step; (2) improved (photo)chemical robustness when compared with related *O*-BODIPY arrays; (3) boosted EET and fluorescence capability likely due to a preferred, optimal disposition of the acyl units in the array structure; (4) possibility of designing MMAs for PET. All these features assure the excellent potential of the multichromophoric *COO*-BODIPYs for developing future smarter dyes for advanced optical and optoelectronic applications (bioimaging, lasing, chemosensing, solar harvesting, etc.). In this context, further experimental and computational studies are now in progress in order to expand the design toward the development of more complex MMAs (*e.g.* triads involving three different chromophores) and directed to know the key structural factors ruling EET efficiency, fluorescence efficiency and/or PET efficiency in these systems, as well as to endow them with additional photophysical phenomena, such as ISC for photosensitizer-based applications (*e.g.* photoinduced water splitting or photodynamic therapy), circularly polarized luminescence for chiroptics, or lasing for advanced optics.

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

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