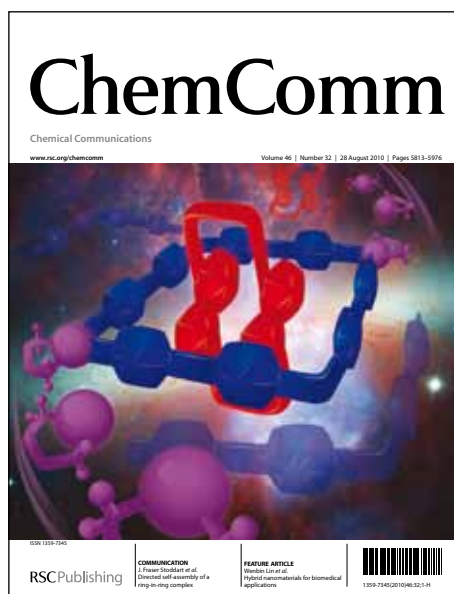


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ARTICLE TYPE

Dual emissive Borane-BODIPY dyads: Molecular conformation control over electronic properties and fluorescence response towards fluoride ion

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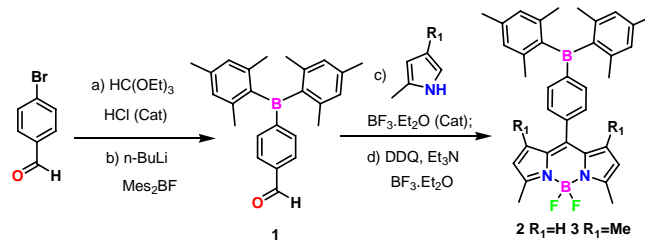
Facile synthesis of two new dimesitylboryl appended BODIPYs are reported. The two dyads have similar fluorescent chromophores but differ in their molecular conformations. They exhibit dual fluorescence, intramolecular energy transfer between boryl and BODIPY chromophores and different fluorescence responses (emission enhancement and quenching) upon fluoride binding.

Triarylboranes¹ and tetracoordinate boron-dipyrromethenes (BODIPYs)² have been continuously gaining much attention owing to their excellent photophysical properties. Because of its inherent Lewis acidity, the three-coordinate boron in triarylborane has been extensively used as a receptor for biologically, environmentally and industrially important anions like fluoride and cyanide.³ On the other hand, highly luminescent BODIPYs have been widely used as a fluorescence reporter for various cations, anions, and also as a fluorescent label for various biologically important molecules.^{2,4} Although the triarylborane and BODIPYs are known for past five decades, surprisingly covalently linked triarylborane-BODIPY molecules are not documented until 2008.⁵ It is important to note that only a few borane-BODIPY dyads are known in literature, and most of them were prepared by adopting heavy metal catalyzed C-C bond forming reactions.^{5,6} An important objective of this project is to devise a facile synthetic route for the simplest and compact borane-BODIPY dyads.

Recently, Akkaya *et al* have demonstrated that upon excitation BODIPYs redistribute more charge at the *meso*-carbon than other parts of the indacene unit.⁷ We reasoned that by introducing an electron deficient borane receptor at *meso*-position, one can redistribute the excited state charge on *meso*-carbon to borane centre. Further, conformation and relative orientation of the two fluorescent chromophores can be controlled by introduction of methyl groups on pyrrole units. In this communication, we present the results aimed at the development of simple synthetic approach for the synthesis of borane-BODIPY dyads **2** and **3**. In addition, we also report the molecular

conformation dependent photophysical properties of **2** and **3** in presence/absence of fluoride ion.

The key precursor **1** was readily prepared by successive reactions of 1-bromo-4-(diethoxymethyl)benzene with *n*-BuLi, Mes₂BF and then subsequent hydrolysis with 2% HCl in THF (Scheme 1). Dyads **2** and **3** were prepared by the condensation reaction of **1** with pyrrole (2-methylpyrrole for **2** and 2,4-dimethylpyrrole for **3**), followed by oxidation with DDQ and subsequent addition of Et₃N and BF₃·Et₂O in DCM (Scheme 1). The structure of dyads **2** and **3** were confirmed by NMR (¹H, ¹³C, ¹¹B and ¹⁹F) spectroscopy, mass spectrometry and single crystal X-ray diffraction studies.

Scheme 1 Synthesis of **2** and **3**.

DFT calculations (See ESI)⁸ were carried out for **2** and **3** with the objective to investigate their molecular conformations and possible electronic communication between chromophores. The dihedral angle between the *meso*-phenyl ring and the BODIPY core is an important factor which determines the nature of electronic communication between the borane and the BODIPY. The dihedral angle in **2** (53.9°) is much less than the angle found in **3** (88.6°) (Fig 1). The strategic placement of additional two methyl groups on pyrrole moiety of **3** forces the phenyl ring to be orthogonal and the dyad molecule in conformationally locked state (Fig 1). The structural parameters of DFT optimised structures closely resemble those (Fig. 2) obtained from single crystal X-ray analysis (See ESI for refinement details), except that there is a slight difference in the values of the dihedral angles. This may be due to the solid state packing and the associated intermolecular hydrogen bonding (see ESI).

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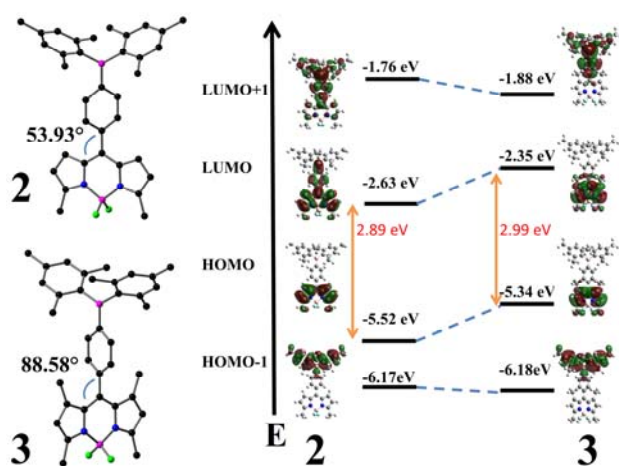


Fig 1 DFT B3LYP/6-31G(d) optimised structures of **2** and **3** and selected MOs of **2** and **3** (Isovalue 0.02). C = Black, B = Magenta, N = Blue, F = Green

The locked molecular conformation has a significant effect on the MOs of compound **3** (Fig 1). In compound **3**, the orthogonal phenyl moiety prevents electronic mixing of the borane and BODIPY units. As a result the HOMO-1 and LUMO+1 orbitals are mainly concentrated on the borane unit but the HOMO and LUMO orbitals are concentrated on the indacene unit. Non-orthogonal orientation of meso-phenyl moiety in **2** allows the moderate mixing of the π systems of borane and indacene units in LUMO and LUMO+1 but not in HOMO and HOMO-1. Thus, absorption characteristics of **2** and **3** are expected to be similar to the additive spectrum of respective free boryl and BODIPY units, whereas the emission properties may be modified (e.g. energy transfer) due to proximity effect.

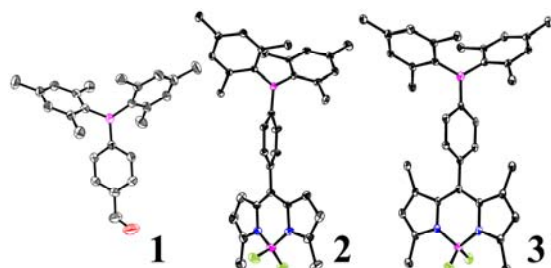


Fig 2 ORTEP plots of **1**, **2** and **3** (30% probability ellipsoids, Hydrogens omitted for clarity). C = Black, B = Magenta, N = Blue, F = Green, O = Red.

The preliminary photophysical studies on **2** and **3** were carried out. Both **2** (512 and 350 nm) and **3** (502 and 335 nm) have similar type of absorption characteristics (see ESI). The higher energy band is dominated by borane centered $\pi \rightarrow p_{\pi}^*$ transition and the lower energy band arises from $S_0 \rightarrow S_1$ transition centered at indacene unit. The absorption bands in **2** are slightly red shifted (10 nm) compared to those in **3**. This bathochromic shift in **2** can be attributed to the electronic communication between the boryl and BODIPY units in the dyad **2**. The distribution of MO coefficients in **2** and **3** (Fig 1) clearly indicate the presence of minimal electronic interaction in **3**. In emission studies, DCM solutions (and in other solvents) of **2** and **3** show two emission bands (~410 and ~520 nm) when excited at the

boryl absorption dominated band (250-350 nm) (Fig.3). For **2**, the intensity of the emission bands are nearly equal, in case of **3** the intensity of the ~410 nm band is significantly less than lower energy band at ~515 nm. To check whether there is any intermolecular contribution to the dual emissions of **2** and **3**, concentration-dependent emission behaviour of both the compounds were carried out in the concentration range 10^{-4} M to 10^{-6} M. Both the compounds showed no concentration dependent change in the relative intensity of the emission peaks (see ESI). The NMR spectra of **2** and **3** did not show any detectable impurities that may be responsible for the dual emission phenomenon (see ESI). The excitation spectra (see ESI) duplicates perfectly the absorption spectrum of the respective dyads. These findings strongly suggest that the dual emission peaks are from a single species and have only intramolecular origin.

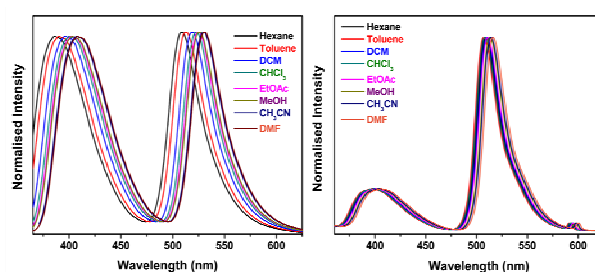


Fig 3 Normalised fluorescence spectra of **2** (left) and **3** (right) in different solvents (λ_{ex} = 350 nm)

The peak positions and intensity of emissions of both the dyads remain nearly constant for λ_{ex} : 250-350 nm, while, the intensity of ~410 nm band decreases and the ~515 nm peak increases for λ_{ex} : 355-500 nm (See ESI). The absorption and emission spectra of **2** and **3** were compared with those of model molecules **4**, **5** and **6** (see ESI). **4** showed absorption and emission peaks in dichloromethane at ~335 and ~400 nm. **5** showed absorption peaks at 350 (weak band) and 500 nm (strong) and emission peak at 525 nm, whereas **6** showed absorption peaks at 300-400 (weak band) and 500 nm (strong band) and emission peak at 520 nm. Thus, dual emission bands in **2** and **3** are identified with the emissions of boryl and BODIPY units. The pertinent question is the origin of BODIPY emission when excited in the boryl band. The absorption of BODIPY unit in the boryl band region is weak and this cannot explain the intense BODIPY emission when excited in boryl dominated band. This may be due to singlet-singlet energy transfer from borane (donor) to BODIPY (acceptor) unit. The principal requirements for Forster energy transfer between donor and acceptor are overlap of spectra of donor emission and acceptor absorption, favourable orientation, and proximity between donor and acceptor¹⁰. These conditions are met in compounds **2** and **3**. The dual emission results indicate that the energy transfer efficiency is not 100%. The dual emission of **2** and **3** is in complete contrast to those observed in other borane-BODIPY dyads.^{5,6} where only BODIPY emission was observed upon excitation at boryl band. The absence of boryl emission is attributable to unit efficiency of energy transfer.

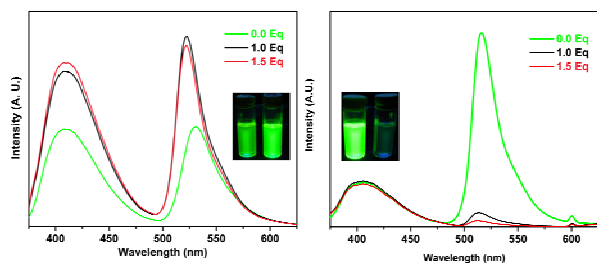


Fig 4 Spectral changes in the emission spectrum of **2** (left) and **3** (right) in DCM ($\lambda_{\text{ex}} = 350$ nm) upon addition of TBAF. Insets: pictures of the solution under UV lamp before and after TBAF addition.

It is well known that fluoride ion binds strongly to boron.^{1,3} In the case of triarylboranes (Ar_3B), fluoride binding leads to a new entity, namely, Ar_3BF^- . The energy levels, absorption and emission properties of the Ar_3BF^- may be entirely different from those of Ar_3B . In the case of **2** and **3**, fluoride binding would not only affect the electronic structure of the boryl unit but also the conformation and relative orientation of boryl and BODIPY units, thereby potentially modifying the energy transfer efficiency. Thus, we used fluoride (F^-) as a probe to get further insight into the dependence of the energy transfer efficiency of **2** and **3** on their molecular conformations. Experiments showed that addition of TBAF (0-1.5 equiv) to dichloromethane solutions of **2**, resulted in a gradual enhancement of both the bands of the dual emission upon excitation of the boryl dominated band at 330 nm giving rise to brighter green emission (Fig 4). The absorption spectrum of the fluoride-bound **2** was similar to that of **2** (except 5 nm blue-shift in the lower energy band (see ESI)). This indicated that the quantum yield of the boryl emission is higher for the fluoride-bound **2** (Q_{F}^- : 49.5% and 74.3% for **2** and **2** $\cdot\text{F}^-$ respectively) and the energy transfer efficiency remained unchanged (the relative intensity of the emission peaks remain constant). As expected, compound **3** behaves in the opposite way. In the case of **3**, upon addition of TBAF to the DCM solutions and excitation of the boryl absorption dominated band at 330 nm, it was observed that the intensity of the boryl band at 405 nm increased slightly but the BODIPY band at 515 nm disappeared almost completely at ~ 1 eq of fluoride (Fig.4) (Q_{F}^- : 42.51% and 18.13% for **3** and **3** $\cdot\text{F}^-$ respectively). Independently, it was verified that TBAF does not quench BODIPY emission ($\lambda_{\text{ex}} = 500$ nm) in **3** or the model compound **6**. The addition of F^- quenches both the absorption and emission bands ($\lambda_{\text{ex}} = 330$ nm) in **4**.¹² Thus, the selective disappearance of BODIPY emission in fluoride-bound **3** when boryl unit is excited is interpreted as indication of drastic decrease in energy transfer efficiency of PhBMes_2 unit in **3**. A comparison of computational results obtained for **2**, **3**, **2** $\cdot\text{F}^-$ and **3** $\cdot\text{F}^-$ (See ESI) support the above inferences. Dual emissive BODIPYs are scarce in literature¹¹, and to our knowledge, compounds **2** and **3** are the first examples that display such an unusual dual emission among known borane-BODIPY dyads. The change of emission intensity upon addition of TBAF to **2** or **3** is linear upto 1 equivalent of F^- and is negligible beyond 1 equiv. This confirms the formation of 1: 1 complex of **2** $\cdot\text{F}^-$ and **3** $\cdot\text{F}^-$.

In summary, we have developed a facile synthetic procedure for simple and the most compact borane-BODIPY dyads. The two

molecules reported here display dual emission and unusual emissive properties upon fluoride binding, which are explained on the basis of molecular structures and conformation dependent energy transfer. Detailed studies on the structures, conformation and photophysical properties of a series of borane-BODIPY dyads are under investigation.

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Notes and references

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- † Electronic Supplementary Information (ESI) available: [Synthetic Methods and characterization data for all compounds, DFT results, X-ray crystallographic data and Photophysical data]. For ESI see DOI: 10.1039/b000000x/
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