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COMMUNICATION

The emission enhancement of the NIR distyryl Bodipy dyes by the indirect $S_0 \rightarrow S_2$ excitation and their application towards a Hg^{2+} probe†

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A new strategy for enhancing the brightness of the NIR distyryl Bodipy derivatives was proposed based on the indirect $S_0 \rightarrow S_2$ excitation, and applied to fluorescence turn-on detection of Hg^{2+}, by which the marked fluorescence enhancement (2.5-fold) and the high sensitivity for Hg^{2+} (up to 3 ppb) could be realized.

The development of functional dyes that emit in the near-infrared (NIR) region of the optical spectrum has received increasing attention in the last decade.[1–4] Besides their high significance for photophysical technologies, NIR fluorophores are of enormous importance for biological and medicinal applications.[2] The NIR spectral region is often referred to as the optical window in biological tissues because autoabsorption and autofluorescence of biomolecules are least between 650 and 1200 nm combined with low light scattering and deep tissue penetration of NIR radiation.[3] Thus, NIR fluorophores provide an excellent tool for bioimaging with substantially increased sensitivity compared to ultraviolet (UV) or visible (Vis) fluorophores. From the sensitivity point of view, an important criterion that evaluates the quality of a fluorophore is its brightness. An ideal fluorophore should feature sharp and intense absorption spectra combined with a high fluorescence quantum yield. However, because of their inherent low band gaps, NIR dyes often suffer from a dominant vibronic coupling between ground and excited states which promotes nonradiative deactivation pathways. As a result, most NIR dyes show low fluorescence efficiency.

Traditionally, cyanine dyes are the most widely used NIR chromophores in various applications.[4] However, whereas their absorption characteristics are very favorable, their fluorescence quantum yields often do not exceed moderate values (5–15%). As a promising alternative, borondipyrromethene (Bodipy) derivatives have gained huge popularity in many fields.[5] Bodipy dyes can be seen as rigid, cross-conjugated cyanines. The simple Bodipy core absorbs and emits in the 480–540 nm region. Long wavelength absorbing and emitting Bodipys are often obtained by extending the conjugation of the Bodipy chromophore *via* functionalization of the pyrrolic position. Among these, the distyryl modification of the Bodipy core by Knoevenagel reaction of the 3- and 5-methyls with aromatic aldehyde is a simple and efficient method, and the obtained distyryl Bodipys have the desirable characteristics including moderate to strong emission in the NIR region, good photostability and solubility in many solvent systems. As a result, they have been widely studied as fluorescent probes for metal ions,[6] building blocks for artificial photosynthetic models,[7] and photosensitisers for photodynamic therapy[8] and dye-sensitised solar cells.[9] However, there is still a need to improve the brightness of this type of dyes for their wider applications.

A prevalent method for enhancing the brightness of fluorophores is the exploration of multifluorophores with energy-donor–acceptor architectures, by which the amplified emission of acceptors could be observed when these systems are excited at the donor λ_{max} due to the efficient fluorescence resonance energy transfer (FRET), the so-called antenna effect.[10] Herein, we hope to present another strategy to enhance the brightness of certain single conjugated organic dyes by the indirect $S_0 \rightarrow S_2$ excitation by reference to a NIR di(methoxystyryl)-Bodipy fluorophore (**B1**) (Fig. 1). The obtained results demonstrated that, by this strategy, the molecule shows a 2.5-fold emission enhancement compared with the direct $S_0 \rightarrow S_1$ excitation. Furthermore, with **B1** as a platform, we also developed a PET (photo-induced electron transfer)-based fluorescence turn-on chemosensor, **B2**, by introducing a known Hg^{2+} binding group[11] to **B1**, and its highly sensitive fluorescence turn-on responses towards Hg^{2+} by the indirect excitation justified our idea.

In fact, the indirect $S_0 \rightarrow S_2$ excitation followed by the $S_2 \rightarrow S_1$ internal conversion is a way of dissipating excess electronic energy, and is important in the protection of biological molecules from

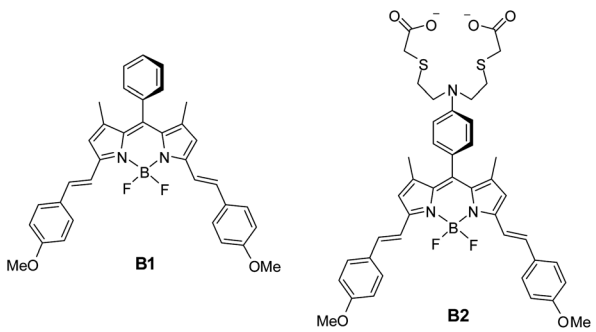

Fig. 1 Chemical structures of **B1** and **B2**.

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harmful UV radiation.[12] However, the known photophysical process has not previously been specifically exploited and applied in the sensing field, presumably because many excellent dyes, such as rhodamine, fluorescein, simple Bodipys, and cyanine derivatives, only display the weak $S_0 \rightarrow S_2$ transition, thus being less effective for absorbing high-energy photons. It was interesting to note that, in the absorption spectra of **B1**, despite the typical $S_0 \rightarrow S_1$ transition located at 640 nm, there exists an intense high energy absorption band located at 370 nm, which can be assigned to the $S_0 \rightarrow S_2$ transition (Fig. 2).[13] The assignment could be rationalized by density function theory (DFT) calculations at the B3LYP/6-31G(d) level of the Gaussian 03 program (Fig. S3, Table S1 and S2 in the ESI†), where two main electronic transitions ($S_0 \rightarrow S_1$, oscillator strength f_{ab} = 1.12; and $S_0 \rightarrow S_2$, oscillator strength f_{ab} = 1.54) were obtained. The calculated absorption bands were 613 nm and 360 nm, respectively, corresponding to the two absorption peaks at 640 nm and 370 nm obtained experimentally. Noteworthy is that the $S_0 \rightarrow S_2$ transition has a big oscillator strength f (f_{ab} 1.54), corresponding to the intense high energy absorption band located at 370 nm in absorption spectra of **B1**. Inspection of the molecular orbitals involved in the electronic transitions shows that in the S_1 state, the electronic delocalization is mainly on the Bodipy core, and less on methoxystyryl moieties; however, in the S_2 state, the electronic delocalization is mainly on the methoxystyryl moiety, and less on the Bodipy core (Fig. 3). Thus, the strong $S_0 \rightarrow S_2$ transition appears to be linked to the 3,5-substituted methoxystyryl moieties. In fact, the 3,5-dimethoxystyryl substituted Bodipy **B1** is a typical D–A–D (donor–acceptor–donor) system that usually has the big $S_0 \rightarrow S_2$ transition-related two-photo absorption action cross-section.[13,14] Thus, we speculated that the observed strong $S_0 \rightarrow S_2$ transition in **B1** is probably due to its D–A–D structural feature that leads to the obvious symmetric charge transfer upon excitation, and the enhancement of the corresponding transition dipole moment.[14] Similarly, the obvious $S_0 \rightarrow S_2$ transition could also be found in other 3,5-distyryl-Bodipys,[9,15] 3,5-di(4-methoxyphenyl)-Bodipy,[16] and 3,5-difuranylvinyl-Bodipys,[17] all of which possess the D–A–D motif.

Turning our attention now to the excitation spectrum of **B1**, the corrected fluorescence excitation spectrum recorded by monitoring fluorescence at 655 nm was nearly in agreement with the ground-state absorption spectrum (Fig. 2), suggesting that both the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions participate in the emission process. Importantly, the shorter wavelength excitation peak is more dominant in the excitation spectrum; thus, the fluorescence enhancement by the indirect excitation can be expected. In fact, when exciting **B1** at the $S_0 \rightarrow S_2$ transition (λ_{ex} = 370 nm), fluorescence was only observed from the S_1 state (λ_{em} = 655 nm), indicative of the rapid and almost quantitative $S_2 \rightarrow S_1$ internal conversion.[18] Moreover, compared with the direct $S_0 \rightarrow S_1$ excitation (λ_{ex} = 640 nm), the molecule shows a 2.5-fold emission enhancement, an important feature for practical applications.

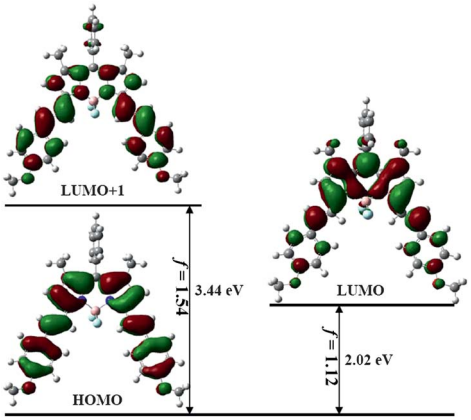

Fig. 3 The energy levels and interfacial plots of the orbitals for **B1**.

Because the photon number absorbed is dependent on the wavelength and it increases with a decrease in the wavelength, the observed emission enhancement of **B1** is probably a result of the fact that more numbers of the high-energy photon are absorbed by the indirect $S_0 \rightarrow S_2$ excitation than by the direct $S_0 \rightarrow S_1$ excitation, as well as the efficient $S_2 \rightarrow S_1$ internal conversion process, though the $S_0 \rightarrow S_2$ transition is less intense than the $S_0 \rightarrow S_1$ transition. In fact, the significant increase in core emission in light-harvesting molecules is mainly attributed to the large light-harvesting capability of the donor fluorophores located at the periphery of these molecules,[10] though the efficient energy transfer from the donor to the core is another important factor.

Because mercury is a deadly toxin to humans by causing cell dysfunction,[19] development of the highly sensitive and specific mercury probes, which are applicable to the common biological milieux, is an important goal.[20] As a preliminary illustration of the utility of the above-mentioned strategy, with **B1** as a platform we created the fluorescent probe **B2** as a Hg^{2+} probe by introducing a known Hg^{2+} binding group[11] to **B1** (Fig. 4). The detailed synthetic

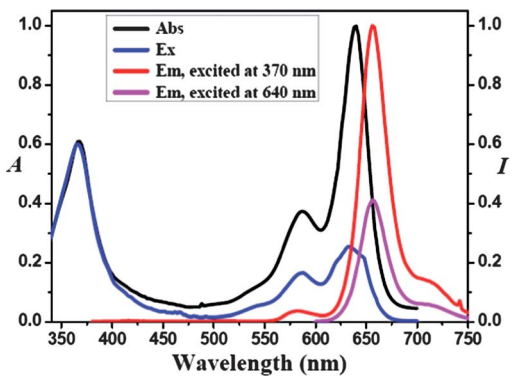

Fig. 2 The absorption, excitation and emission spectra of **B1** (5 μM) in EtOH.

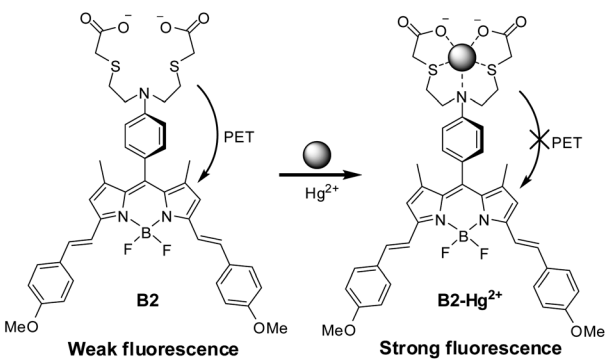

Fig. 4 The proposed sensing mechanism of **B2** to Hg^{2+}.

procedures are provided in the ESI†. In subsequent experiments, CH_3CN–HEPES buffer solution (10 mM, pH = 7.4, 1 : 1, v/v) was selected as a testing system to investigate the spectra response of **B2** to Hg^{2+}.

In the absorption spectra of **B2** (5 μM), despite the typical $S_0 \rightarrow S_1$ transition located at 640 nm, a strong $S_0 \rightarrow S_2$ transition located at 370 nm was also observed (Fig. S1, ESI†). The Hg^{2+} addition results in a slightly red shift of the long-wavelength band and an isosbestic point at 645 nm (Fig. S1, ESI†), suggesting that the binding of **B2** with Hg^{2+} produces a single component. However, unlike **B1**, **B2** displayed a considerably weak fluorescence at 655 nm (Fig. 5) due to the efficient PET quenching from the aniline-containing binding group to the Bodipy fluorophore.[11] The PET quenching process in **B2** could be rationalized by density function theory (DFT) calculations (Fig. S2, ESI†). As expected, upon addition of Hg^{2+}, the fluorescence intensity increased remarkably with the virtually unchanged emission shift, suggesting that the PET quenching is inhibited due to the binding of **B2** with Hg^{2+}. Importantly, when the high energy part of the absorption spectra of **B2** was excited (λ_{ex} = 370 nm), the fluorescence intensity of Hg^{2+}-bound **B2** was significantly higher (2.5-fold) than that obtained by direct excitation of Bodipy dye (λ_{ex} = 640 nm), thus confirming that the indirect exciton induced fluorescence enhancement still works well in the system. In addition, the binding process of Hg^{2+} to **B2** was found to be very fast at room temperature, and could be completed within several seconds.

The fluorescence titrations were conducted using a 5 μM solution of **B2** in CH_3CN–HEPES buffer solution (10 mM, pH = 7.4, 1 : 1, v/v) with the excited wavelength of 370 nm (Fig. 6). With the increase of the Hg^{2+} concentration, the titration reaction curve showed a steady and smooth increase, and the changes of the emission intensities became constant when the amount of Hg^{2+} added reached 2 equiv., and an approximately 30-fold fluorescence enhancement could be observed. The association constant for Hg^{2+} was estimated to be 2.1×10^5 M^{-1} (R^2 = 0.9996) on the basis of nonlinear fitting of the titration curve assuming a 1 : 1 stoichiometry (Fig. 6, inset). This 1 : 1 binding mode was supported by a Job plot (Fig. S3, ESI†). In addition, a typical calibration graph of the response to Hg^{2+} under the optimum experimental conditions could be obtained with a good linear relationship ranging from 0 to 5.0×10^{-6} M (Fig. S4, ESI†), and the detection limit (S/N = 3) for **B2** was calculated to be 0.015 μM (3 ppb).

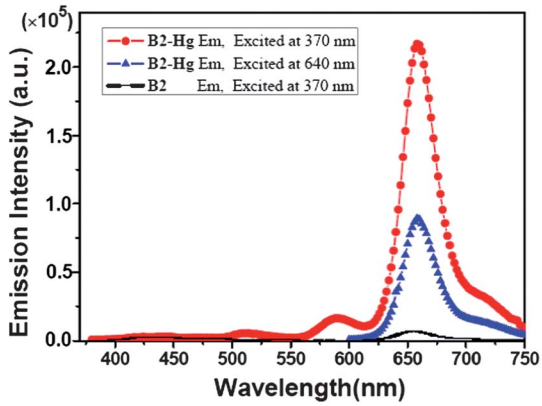

Fig. 5 Fluorescence spectra of **B2** (5 μM) in the absence and presence of 2 equiv. of Hg^{2+} with varied excitation. *Condition*: CH_3CN–HEPES buffer solution (10 mM, pH = 7.4, 1 : 1, v/v), slit: 1 nm/1 nm.

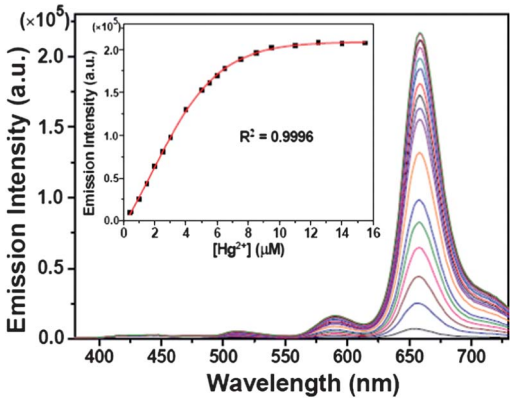

Fig. 6 Fluorescence spectra of **B2** (5 μM) in the presence of different amounts of Hg^{2+}. *Condition*: CH_3CN–HEPES buffer solution (10 mM, pH = 7.4, 1 : 1, v/v). slit: 1 nm/1 nm. $\lambda_{ex}/\lambda_{em}$ = 370/655 nm.

Further, the response of **B2** to other metal ions was also studied. As shown in Fig. 7, the addition of 30 equiv. of Na^+, K^+, Ca^{2+}, and Mg^{2+} as well as 3 equiv. of Cd^{2+}, Ag^+, Pb^{2+}, Mn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Cr^{3+}, and Fe^{3+} has no obvious effect on the fluorescence emission of **B2**, whereas Ag^+, Ni^{2+}, and Cd^{2+} responded with a slight increase in the fluorescent intensity at 655 nm. In sharp contrast, the addition of Hg^{2+} resulted in a significant enhancement of the emission intensity. Thus, **B2** was shown to be a promising fluorescent sensor for Hg^{2+}.

In addition, **B2** was also used for *in vitro* Hg^{2+} detection in HeLa cells. After HeLa cells were incubated with 10 μM of **B2** in phosphate-buffered saline (PBS) for 30 min at 37 °C, and then incubated with 20 μM of Hg^{2+}, their fluorescence images were taken using a confocal fluorescence microscope (Fig. 8). The HeLa cells incubated with only sensor **B2** (5 μM) exhibited almost no fluorescence due to the efficient PET quenching. By contrast, the cells stained with both the sensor and Hg^{2+} showed strong red fluorescence. The results establish that sensor **B2** was efficiently internalized within the HeLa cells and capable of sensing Hg^{2+} in cells. In addition, no change in the cell morphology is induced by incubating the dyes and Hg^{2+} for at

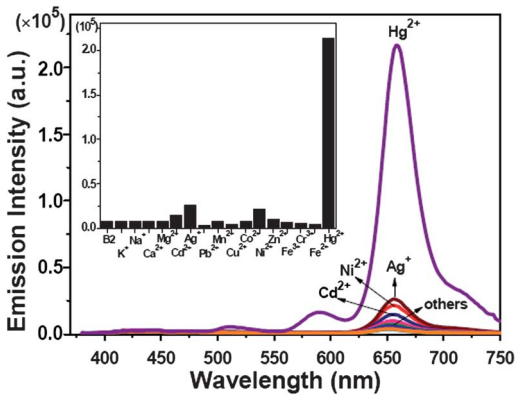

Fig. 7 The fluorescence spectra of **B2** (5 μM) upon addition of 3 equiv. of Hg^{2+} and various other metal ions, including of Na^+, K^+, Ca^{2+}, and Mg^{2+} (30 equiv.); Cd^{2+}, Ag^+, Pb^{2+}, Mn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Cr^{3+}, Fe^{3+}, and Hg^{2+} (3 equiv.), in CH_3CN–HEPES buffer solution (10 mM, pH = 7.4, 1 : 1, v/v). Slit: 1 nm/1 nm. $\lambda_{ex}/\lambda_{em}$ = 370/655 nm.

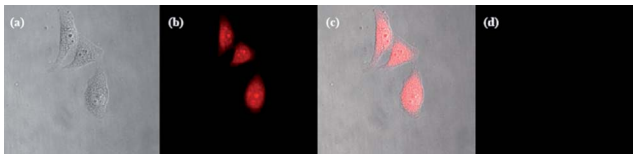

Fig. 8 Confocal fluorescence images of HeLa cells incubated with **B2** (10 μM), and then further incubated with Hg^{2+} (20 μM). (a) Brightfield and (b) fluorescence images; (c) the overlay of (a) and (b); (d) fluorescence image of cells treated with only probe **B2**. Emission was collected at 620–730 nm upon excitation using a 633 nm He–Ne laser.

least 12 h (Fig. S5, ESI†), suggesting the absence of significant cytotoxicity.

In conclusion, we have demonstrated a new strategy of the indirect $S_0 \rightarrow S_2$ excitation for enhancing the brightness of the near-infrared distyryl Bodipy derivative (**B1**). For the application of the strategy, **B2** was designed and synthesized by incorporating a Hg^{2+} receptor to the **B1** platform for fluorescence turn-on detection of Hg^{2+} based on the PET mechanism. The results obtained disclosed that by the indirect $S_0 \rightarrow S_2$ excitation, **B2** could detect Hg^{2+} with high sensitivity. In addition, **B2** was also applied to biological imaging of Hg^{2+} inside HeLa cells.

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