Short communication

Synthesis and aggregation-induced emission of a pyrene decorated chiral BODIPY chromophore

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ABSTRACT

BODIPY chromophore with pyrene moieties was designed and synthesized successfully in the present paper. Optical results demonstrate that the pyrene-terminated dye **3** presents a bigger Stokes shift and slightly smaller fluorescence quantum yield in the red region than BODIPY dye **1** bearing no substituent at 2,6-positions. Dye **3** possesses absorption and emission maximum at 530 and 585 nm in THF solution, respectively. With the addition of different water volume fractions, the gradually bathochromic shifts are observed in the absorption and emission spectra, simultaneously. Under UV irradiation, the corresponding emission images of solutions/aggregates are visual, showing the aggregation-caused quenching effect of orange fluorescence. In addition, theoretic computational studies on related pyrene decorated chiral BODIPY compounds have also been carried out.

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Since 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) dyes were firstly synthesized by Treibs and Kreuzer in 1968, research on BODIPY chemistry has received extensive attention in the field of functional materials such as fluorescent dyes, light harvesting antennas and photovoltaic cells [1–3]. In recent years, numerous scientific efforts have been made to study the red or NIR BODIPY dyes, which might have the abundant advantages such as high fluorescence quantum yields, large absorption coefficients and narrow emission spectra [4–6]. Furthermore, pyrene derivatives are one of the significant organic functional intermediates as they have found widespread applications in molecular self-assembly, smart material and organic electronic owing to their good π-conjugated system, intriguing photophysical and electrochemical properties [7–10]. However, the fluorescent materials marrying BODIPY and pyrene groups in a single molecule are less explored [11–13] in the case of extending the π-conjugated systems of their respective derivatives by contrast.

In our previous work, a family of stable and soluble thiazole fluorescent molecules having the same triphenylamino chromophores have been described [14]. However, those dyes do not reveal red or NIR characteristics. Considering that the fluorescence response for the longest π-conjugated compounds in that case is observed at 509 nm having the

absorption maximum at 425 nm, we report herein the synthesis (Scheme 1), red fluorescent characteristic and aggregation-induced emission (AIE) of a pyrene decorated chiral BODIPY chromophore with the emission maximum at 585 nm. The aim of combing BODIPY and pyrene donor–acceptor substituent is to finely tune its electronic structure and thoroughly explore the red or NIR molecular dyes. To the best of our knowledge, this is the first report on 2,6-disubstituted pyrene-terminated BODIPY functional dye.

Our synthetic strategy was based on the routes shown in Scheme 1, in which the dye **3** was prepared from 1-pyrenylboronic acid and the starting material **2** [15] by Suzuki–Miyaura cross-coupling reactions in a high yield of 91% [16]. As shown in Fig. SI1–2 (Supporting Information), compound **3** has been characterized by ^{1}H NMR and EI-TOF-MS spectra, and the results clearly demonstrate the formation of the expected compound. The introduction of a (S)-2-methylbutoxyl group on the benzene ring can effectively increase the solubility in conventional organic solvents and easily form chiral BODIPY chromophore.

As illustrated in Fig. 1, normalized UV–Vis absorption and fluorescence emission spectra of dyes **1** and **3** have been measured at room temperature for comparison. Compared with the absorption peaks of dye **1** in dichloromethane, the π–π* transition shows bathochromic shift of about 30 nm in dye **3** owing to the introduction of pyrene groups. However, the molar extinction coefficient of dye **3** ($\varepsilon = 56\ 500\ \text{L mol}^{-1}\ \text{cm}^{-1}$) is less than that of dye **1** ($\varepsilon = 124\ 000\ \text{L mol}^{-1}\ \text{cm}^{-1}$) as depicted in Table 1. It is noted that the strong absorption peaks at high-energy band (328 and 342 nm) for compound **3** are assigned as the interring electronic transitions among the pyrene

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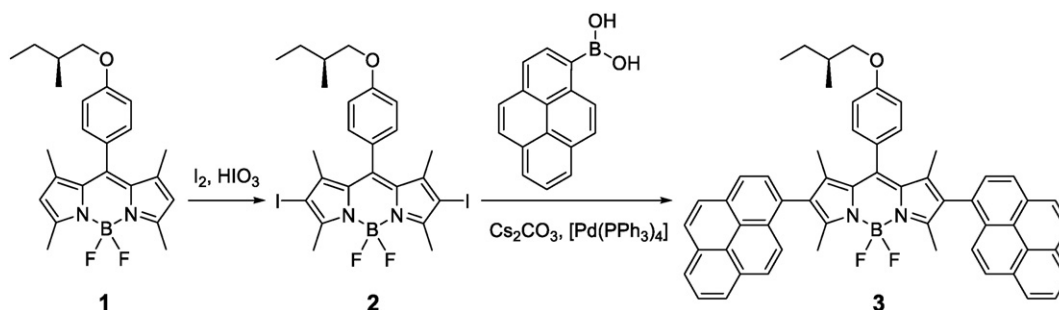
Scheme 1. Synthesis of pyrene decorated chiral BODIPY dye **3**.

units, which is consistent with previous reported pyrene chromophores [10–13]. Fluorescence emissions of dye **1** and **3** can be found at $\lambda_{max} =$ 520 and 585 nm upon excitation at $\lambda_{ex} =$ 500 and 530 nm, respectively, where dye **3** presents a bigger Stokes shift than BODIPY dye **1** bearing no substituent at 2,6-positions. More importantly, compound **3** shows a strong orange fluorescence peak with the luminescence quantum yield of 50% by using rhodamine B as standard ($\Phi_{std} =$ 65%, see the Supporting Information). In addition, the quantum yield of 2,6-disubstituted BODIPY dye **2** is 6% because of the fluorescence quenching effect of two iodine atoms.

The photophysical behavior in the aggregated state was then investigated in aqueous mixtures. As can be seen in Fig. 2a, compound **3** with pyrene substituents on the 2,6-positions, possesses an absorption maximum at 530 nm in THF solution. Upon the addition of different water volume fractions (f_w), the band gradually shifts to 556 nm, thus a bathochromic shift of 26 nm is observed. At the same time, the above-mentioned high-energy absorption band also presents a bathochromic shift from 342 to 352 nm. With the enhancement of f_w, the emission bands exhibit a red-shifted phenomenon from 585 to 611 nm in the fluorescence spectra, while the emission peaks have reduced remarkably because of aggregation-caused quenching (ACQ) effect. Compared with the intensity at 585 nm in THF solutions ($f_w =$ 0%), the quenching percentage is 98% when $f_w =$ 90%. The appearances of the THF/water mixtures with water volume fractions ranging from 0% to 90% under daylight and UV light were shown in Fig. 2c. In THF solutions, dye **3** shows a pink color. When a large amount of water is added, the appearance of the solutions alters to light purple. Under UV irradiation, the corresponding emission images of solutions/aggregates are visual, showing the gradually decreasing orange fluorescence.

To further show the essential distinction, DFT computational studies are carried out where the fixed atom coordinates of dye **1**–**3** are used for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) gap (energy gap) calculations. DFT calculations are carried out with the Gaussian 09, revision C.01 program [17], using the B3LYP method and 6-31G* basis set. For computational simplicity, the (S)-2-methylbutoxyl group is replaced by the methyl groups since this replacement is not expected to alter the results and the trends significantly. DFT computational results given in Table 1 reveal that the resultant HOMO–LUMO gaps for BODIPY dye **1**–**2** are 3.00 and 2.90 eV, respectively, while that for the corresponding pyrene decorated chiral BODIPY chromophore **3** is much smaller at 2.77 eV, which are in agreement with their UV–Vis absorptions. Furthermore, compared with dye **1**, introducing two pyrene groups at 2,6-positions in dye **3** can effectively raise the HOMO level and the alteration of the LUMO level can be neglected in this case (see Fig. 3). In addition, the average length of the C–C bond between pyrene and pyrrole rings is 1.484(1) Å determined by fully optimized geometry of dye **3**. However, the free rotation of the C–C single bond is blocked to some extent (see the Supporting Information) owing to the steric hindrance effect of the pyrene unit and methyl groups from pyrrole ring on both sides, which might influence the photophysical behavior in the solution/aggregated state.

In summary, we have designed and synthesized successfully a pyrene decorated chiral BODIPY chromophore, which showed absorption and emission maxima of up to 530 and 585 nm, respectively. The pyrene-terminated dye **3** presents a bigger Stokes shift and slightly smaller fluorescence quantum yield in the red region than BODIPY dye **1**. Pyrene substitution groups on the 2,6-positions of BODIPY core do not contribute much to the π-conjugated system from a theoretical and experimental perspective. However, ACQ effect with red-shifted emission and large Stokes shift of aggregated states is induced. Further work is underway on the preparation of new BODIPY dyes with AIE-active, which may be used for fabricating cell-compatible fluorescent nanoparticles as high-efficient fluorescent reagent.
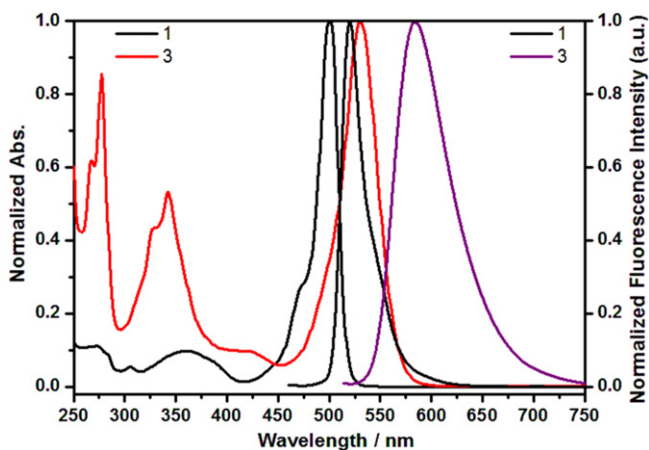

Fig. 1. Normalized UV–Vis absorption and fluorescence emission spectra of BODIPY dye **1** and pyrene functionalized BODIPY dye **3** in their CH$_2$Cl$_2$ solutions at room temperature.

Table 1
UV–Vis absorption and fluorescence emission data, optical and calculated HOMO–LUMO energy gaps for related BODIPY compounds **1**–**3**.

Compd	UV–Vis $\lambda_{max}(\varepsilon)$ [nm (L·mol^{-1} cm^{-1})]	Fluorescence		Stokes shift [nm]	E_g^{opt}[b] [eV]	E_g^{calcd}[c] [eV]
		λ_{max}[nm]	Φ_s[a]			
1	501 (124 000)	520	0.87	19	2.39	3.00
2	532 (131 000)	557	0.06	25	2.24	2.90
3	530 (56 500)	585	0.50	55	2.18	2.77

[a] Photoluminescence quantum yields.
[b] Optical energy gaps determined from the UV–Vis absorptions in dichloromethane solution.
[c] Theoretical computations.