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COMMUNICATION

Asymmetric core-expanded *aza*-BODIPY analogues: facile synthesis and optical properties

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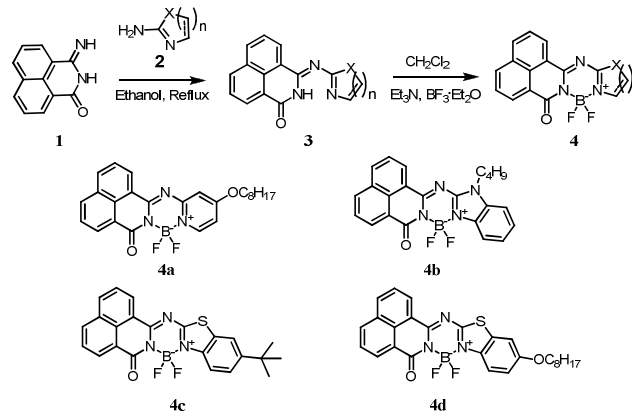
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Significant large Stokes shifts and enhanced solid state emission were achieved in a novel series of asymmetric core-expanded *aza*-BODIPY analogues, 4a-4d, synthesized by a facile and scalable two step reaction in high yields.

Boron dipyrromethene (BODIPY) dyes have attracted considerable research attention due to their unique optical property and comprehensive application.¹ Although BODIPYs are strongly emissive in solution, they are almost nonemissive in the solid state, owing to the self-absorption enhanced by the small Stokes shifts and intermolecular π - π interactions caused by the symmetric and planar structure.² Low-symmetrization of the structures causes more energetically distinguished ground and excited states and inhibit the strong π - π stacking interactions, hence open the door to realization of effective solid-state emission.³⁻⁴ For this reason, new types of asymmetrical BF₂ complexes have been developed, some of which have shown moderate emission in the solid state.⁵ However, their fluorescence efficiencies in the solid state are still low, due to their flexible structure in most cases, which enhance non-radiative decay process in solution.⁵ Furthermore, in contrast to a classic symmetry BODIPY system, which can be synthesized straightforward from pyrrolic derivatives, a facile and scalable synthesis of low symmetric BODIPY analogues for practical use is still a great challenge.

no oxidation step necessary. In contrast to the conventional BODIPY, the replacement of a pyrrole ring by a pyridine to form core-modified dyes, bearing five-membered ketoisindoline ring and six-membered pyridine ring, display intense vibrational bands with effective emission in solution and in the solid state.^{4,6} This indicates that optical properties of BODIPY can be finely tuned by core-modification. Inspired by the above-mentioned excellent features, we present, herein, the synthesis and spectroscopic properties of novel core-expanded *aza*-BODIPY analogues, consisting of a six-membered keto-pyridine unit in place of the five-membered pyrrolidone and six-membered pyridine ring or five-membered-ring-containing imidazole or thiazole unit (Scheme 1).



Scheme 1 Chemical structure and synthesis procedures of core-expanded *aza*-BODIPY analogues.

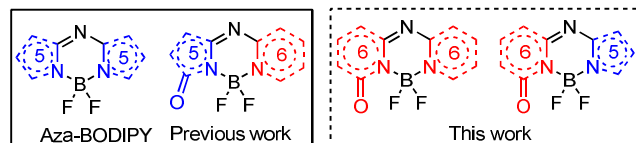


Fig. 1 Chemical structure of *aza*-BODIPY and core-modification *aza*-BODIPY analogues.

Recently, we developed a facile and large-scale synthetic method for rigid and asymmetrical BODIPY analogues (Fig 1), through the reaction of aminopyridine and imino-ketoisindoline, followed by coordination with BF₂.⁴ This method possesses many advantages including the following: (a) readily available, cheap and remarkably diversified starting materials; (b) easy synthesis in high yields, and

The core-expanded *aza*-BODIPY analogues **4a–4d** were synthesized from a reaction of heteroaromatic amines **2** and imino-ketoazaphenylene **1**, followed by coordination of trifluoroboron in overall 30% yield. These dyes were characterized by high resolution mass spectrometry and NMR analysis. In the ¹H NMR spectra, the proton signal of N–H of the azaphenylene unit observed at around 13.5 ppm completely disappeared after coordination with BF₂ (ESI,

S1, Section IV). The structures of **4c** and **4d** were further confirmed by X-ray single crystal analysis.

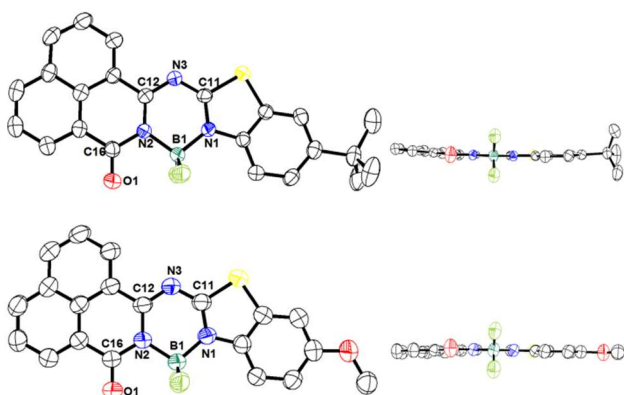


Fig. 2 Front (left) and side (right) ORTEP views of the molecular structures of **4c** (top) and **4d** (bottom) with the thermal ellipsoids set at 50% probability. Solvent molecule, hydrogen atoms and alkyl chain are omitted for clarity. Selected bond lengths [Å], for **4c**: B1–N1 1.554(4), B1–N2 1.581(4), O1–C16 1.216(3), N2–C12 1.365(3), N1–C11 1.329(3), N3–C12 1.319(3), N3–C11 1.343(3); for **4d**: B1–N1 1.555(4), B1–N2 1.574(4), O1–C16 1.218(3), N2–C12 1.373(3), N1–C11 1.329(4), N3–C12 1.311(4), N3–C11 1.342(4).

Crystals of **4c** and **4d** suitable for X-ray analysis were obtained by slow diffusion of hexane into their DCM solutions. The boron atoms on **4c** and **4d** adopt a tetrahedral geometry and the plane defined by F–B–F atoms is perpendicular to that of the central C₂N₃ core. The C16–O1 bond lengths of **4c** (1.216(3) Å) and **4d** (1.218(3) Å) are typical C=O (ca. 1.22 Å) bond lengths. The bond distances of B1–N2 and N2–C12 (azaphenylene nitrogen) are ca. 0.03 Å and 0.04 Å longer than the B1–N1 and N1–C11 (thiazole nitrogen) bond distances, respectively, due to the asymmetrical molecular structures. The indacene plane containing azaphenylene and thiazole units is highly planar with average root-mean-square (rms) deviation of 0.417 for **4c** and 0.052 for **4d**, respectively (Fig. 2). These molecules also showed partially overlapping head-to-head or head-to-tail π – π stacking interactions (ESI, Fig. S1). A well-ordered molecular packing is favorable and a critical factor as electron-transporting materials.⁷

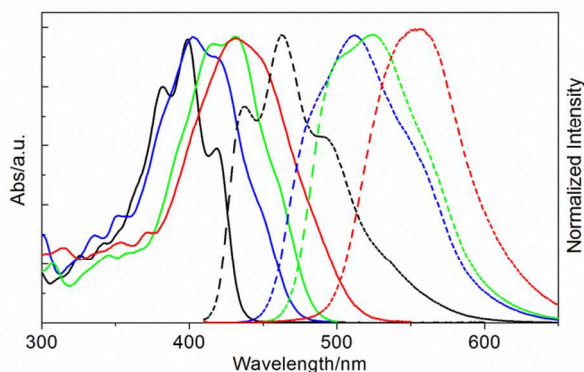


Fig. 3 Absorption (solid lines) and emission (dashed lines) spectra of **4a** (black lines), **4b** (blue lines), **4c** (green lines) and **4d** (red lines) in dichloromethane.

The photophysical properties of **4a–4d** were measured in several solvents of different polarity and full details on these were summarized in the ESI, Fig S1–S8, Table S1. These core-expanded dyes **4a–4d** exhibited broad absorption and emission bands relative to the conventional BODIPY dyes (Fig. 3). The half-maximum ($fwhm_{abs}$) of **4a–4d** are around 75 nm and ca. three-folds broader than normal BODIPY (containing aza-BODIPY), which suggest stronger vibrational coupling of the S₀–S₁ transition for **4a–4d**. In dichloromethane, **4a** showed a major absorption peak at 399 nm and a shoulder at 378 nm. The replacement of pyridyl unit by imidazole to form **4b** caused red-shift of the absorption and emission maxima to 401 and 512 nm, respectively. In the cases of **4c** and **4d**, further red-shift of the absorption by 30 nm and 32 nm and the emission by 61 nm and 90 nm, respectively, were observed relative to that of **4a**. The extinction coefficient of **4a–4d** is 39700, 26200, 31700 and 34800 M⁻¹ cm⁻¹, respectively. The maximum absorption and emission band of **4a–4d** do not show any clear trend as a function of the solvent polarity.

The Stokes shifts of core-expanded dyes (3464–5400 cm⁻¹) are larger than those of classical BODIPYs (ca. 500 cm⁻¹), indicating geometrical rearrangement on excitation.^{1a} This is also reflected in the increasing band-width of the fluorescence spectra of core-expanded dyes ($fwhm_{em}$ 73–90 nm in DCM) compared to classical BODIPYs ($fwhm_{em}$ ca. 30 nm in DCM).⁸ A larger Stokes shift can eliminate spectral overlap between absorption and emission and allow the reliable detection of fluorescence while reducing interference.⁹ Dye **4a** displays strong emission with absolute fluorescence quantum yield of 0.45, while relatively weak emission quantum yields of 0.21, 0.15, 0.04 are observed for dyes **4b–4d** containing thiazole or imidazole moiety, respectively, which can be ascribed to the enhanced intramolecular charge transfer (ICT) process. The fluorescence intensity of **4b–4d** was further quenched in polar solvents due to ICT states, which enhanced the rate of nonradiative decay (ESI, Table S1).¹⁰ The lower emission efficiency is also reflected by the rates of nonradiative decay k_{nr} : thiazole unit leads to 4- and 23-fold enhancement for **4c** and **4d** with respect to **4a** in dichloromethane, respectively (ESI, Table S1). The fluorescence decay profiles can be described by a single-exponential fit with lifetimes in the 0.23–3.16 ns range in DCM.

Table 1. Spectroscopic properties of **4a–4d** in DCM and in the solid states.

		λ_{abs} [nm]	λ_{em} [nm]	$\Delta\nu_{em-abs}$ [cm ⁻¹]	Φ_F ^[a]	τ_F ns
4a	CH ₂ Cl ₂	399	463	3464	0.45	3.16
	film		532		0.16	
	powder		496		0.25	
4b	CH ₂ Cl ₂	401	512	5406	0.21	1.59
	film		535		0.08	
4c	CH ₂ Cl ₂	429	524	4226	0.15	1.18
	film		543		0.07	
	powder		536		0.05	
4d	CH ₂ Cl ₂	431	553	5119	0.04	0.23
	film		613		0.005	
	powder		583		0.03	

[a] Φ_F , absolute fluorescence quantum yield

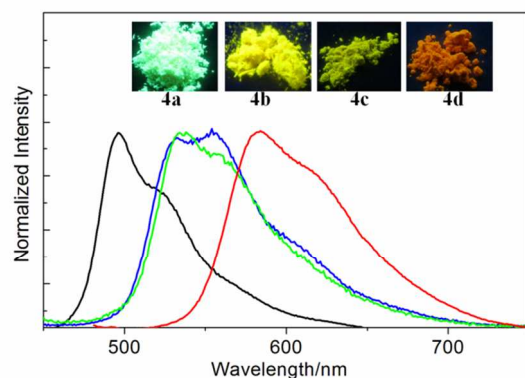


Fig. 4 Emission spectra of **4a** (black line), **4b** (blue line), **4c** (green line) and **4d** (red line) in powder. Inset: pictures of **4a–4d** powder excited at 365 nm using a UV lamp.

The emission spectra and absolute quantum yields (Φ_F) of the core-expanded dyes in film and powder were measured in Horiba Jobin Yvon Fluorolog-3 spectrofluorimeter with integrating sphere (Fig. 4), and the main photophysical properties are summarized in Table 1. The core-expanded dyes display moderate solid-state fluorescence with quantum yields of 0.25 (**4a**), 0.08 (**4b**), 0.05 (**4c**), and 0.03 (**4d**) in powder and 0.16 (**4a**), 0.08 (**4b**), 0.07 (**4c**), and 0.005 (**4d**) in film, respectively. This suggests that the asymmetrical structures enhance the solid-state emission intensity, compared to non-emissive normal BODIPY. The quantum yield of **4c–4d** is, however, much lower than that of **4a**. This result is consistent with the fluorescence behavior in solution, probably due to strong intramolecular charge transfer, leading to nonradiative S_1 decay. Although ICT is useful for increasing Stokes shift, resulting in fluorescence enhancement in the solid state through eliminating self-absorption, strong ICT is also a quenching factor due to an enhancement of the rate of nonradiative decay. Therefore, the balance of these two factors should be considered in order to further pursuit solid-state-fluorescent BODIPY analogues.

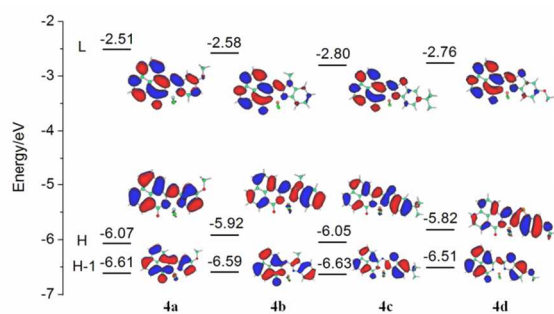


Fig. 5 Energy level diagram for the frontier π -MOs of **4a–4d** using the B3LYP functional with 6-31G(d) basis sets. The angular nodal patterns are shown at an isosurface value of 0.02 a.u.

To investigate the influence of core-expansion on the electronic properties of **4a–4d**, molecular orbital calculations were performed using DFT method at the B3LYP/6-31G(d) level.¹¹ Based on the TDDFT calculations, the main absorption bands of **4a–4d** can be attributed to transitions from the HOMO to the

LUMO (ESI, Table S2). There is *ca.* 30 nm red-shift of the absorption maximum of **4c–4d** with respect to that of **4a**, as the stabilization of the LUMO and destabilization of HOMO lead to the narrower energy gap. The MO distribution of the HOMO and LUMO of **4a** are almost delocalized in the whole indacene plane containing azaphenalene and pyridine units, so there is only limited scope for charge-transfer character in the HOMO→LUMO transition. For the dyes **4b–4d**, there are significant MO coefficients across the entire system for HOMO, while contributions to the LUMO distribution are mainly from azaphenalene moiety (Fig 5). It is obvious that intramolecular charge transfer occurs from the thiazole or imidazole moiety to the azaphenalene moiety, though there is still a marked overlap between the occupied and virtual orbitals. Attachment of alkoxy group on thiazole unit further increase the ICT features, leading to fluorescent quenching and large Stokes shift. The MO distribution can well explain the fluorescent behavior of the dyes.

Usually, the maximum absorption wavelengths of the conventional BODIPY **5**¹² and aza-BODIPY **6**¹³ are around 500 and 713 nm, with calculated energy gap 3.00 and 2.12 eV, respectively. Despite the core is expanded, **4a–4d** display large blue-shift absorption maxima in range of 399–431 nm with calculated energy gap 3.06–3.58 eV. The distances of C(1)–C(2) and C(4)–C(5) of **4c** are 1.465 Å and 1.475 Å in crystal structure, and are 1.459 Å and 1.476 Å for **4d**, respectively, the distances approach the single-bond limit for C(sp²)–C(sp²) (Fig 6). Similar trend is also observed in optimized structure of **4a** and **4b**. These structural features reveal that these bonds block electronic delocalization and the plane containing ketoazaphenalene and pyridine (or imidazole or thiazole) unit is not entire π -conjugated system, leading to short-wavelength absorption.

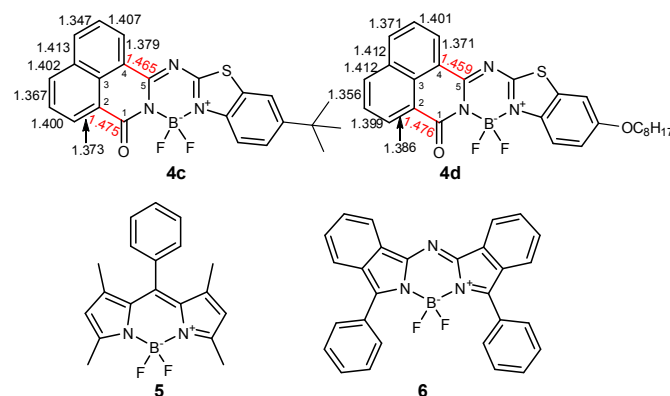


Fig. 6 Bond distances and structure of **4c–4d**, BODIPY **5** and aza-BODIPY **6**.

The electrochemical properties were studied by cyclic voltammetry in *ortho*-dichlorobenzene with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. **4a–4b** exhibit one reversible reduction waves and **4c** display two reversible reduction waves. One irreversible first reduction wave and one reversible oxidation waves are observed for **4d** (Table S3 and Fig. S12 in ESI†). The estimated LUMO values are -3.26 eV for **4a**, -3.30 eV for **4b** and -3.53 eV for **4c** according to the equation $E_{\text{LUMO}} = -e(E_{1/2}^{\text{red}} + 4.4)$, these LUMO values are lower than that for the widely used electron-transport material Alq₃ (tris 8-hydroxyquinoline aluminum) which has a LUMO value of -3.0 eV.¹⁴ The HOMO values, which are calculated from $E_{\text{HOMO}} = E_{\text{LUMO}} - E_g$, range from -6.01 eV to -6.18

eV, these values are also lower than that of Alq₃ (−5.7 eV). These features make the compounds **4a–4c** promising for use as electron-transport materials in OLEDs.

In summary, a novel series of asymmetric core-expanded *aza*-BODIPY analogues, in which the inner pyrrolic five-membered ring was replaced with larger six-membered ring units, have been synthesized by a facile two step reaction. These dyes exhibit broad absorption and emission spectra with significantly large Stokes shift in solution and moderately intense solid-state emission. Such features are clearly promising for new organic optical materials. Strong solvent polarity dependence is observed in the quantum yields of **4b–4d** due to the ICT process, which deceases the fluorescence quantum yields both in solution and in the solid state. Low LUMO values indicate their potential application as electron-transport materials. Therefore, the core-expansion is a promising method for modifying electronic structures and properties of BODIPY. Considering the facile synthesis method and excellent properties of this system, further core-modified analogues and their dimers are interesting and the synthetic research along with this direction is currently under way.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental details, additional spectroscopic properties, description of the computational methods and NMR spectra]. See DOI: 10.1039/b000000x/

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GRAPHIC ABSTRACT

A novel series of asymmetric core-expanded aza-BODIPY analogues, through a facile and scalable two step reaction in high yields, are reported.

