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

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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.

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-ketoazaphenalene 1, 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 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 pyrrolidine 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.

The core-expanded aza-BODIPY analogues 4a–4d were synthesized from a reaction of heteroaromatic amines 2 and imino-ketoazaphenalene 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 azaphenalene unit observed at around 13.5 ppm completely disappeared after coordination with BF2 (ESI,
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 C₇N₂ core. The C16–O1 bond lengths of 4c (1.216(3) Å) and 4d (1.216(3) Å) are typical C=O (ca. 1.22 Å) bond lengths. The bond distances of B1–N1 and N2–C12 (azaphenalene 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 azaphenalene 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.

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 (fwhm₀/₂) 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. This is also reflected in the increasing band-width of the fluorescence spectra of core-expanded dyes (fwhmₚ₀/₂ 73–90 nm in DCM) compared to classical BODIPYs (fwhmₚ₀/₂ ca. 30 nm in DCM). A larger Stokes shift can eliminate spectral overlap between absorption and emission and allow the reliable detection of fluorescence while reducing interference. 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). The lower emission efficiency is also reflected by the rates of nonradiative decay τₙᵣ and further red-shift of the fluorescence maxima 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.

<table>
<thead>
<tr>
<th>Dye</th>
<th>λₐₕ[,]nm</th>
<th>λₐₜ[,]nm</th>
<th>Δλₚₐₛ[,]cm⁻¹</th>
<th>Φₐ[,]%</th>
<th>τ[,]ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>CH₂Cl₂</td>
<td>399</td>
<td>463</td>
<td>3464</td>
<td>0.45</td>
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<tr>
<td></td>
<td>film</td>
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<td></td>
<td></td>
<td>0.16</td>
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<td></td>
<td>powder</td>
<td>496</td>
<td></td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>4b</td>
<td>CH₂Cl₂</td>
<td>401</td>
<td>512</td>
<td>5406</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>film</td>
<td>535</td>
<td></td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>powder</td>
<td>529</td>
<td></td>
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<td>0.08</td>
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<tr>
<td>4c</td>
<td>CH₂Cl₂</td>
<td>429</td>
<td>524</td>
<td>4226</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>film</td>
<td>543</td>
<td></td>
<td></td>
<td>0.07</td>
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<td></td>
<td>powder</td>
<td>536</td>
<td></td>
<td></td>
<td>0.05</td>
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<tr>
<td>4d</td>
<td>CH₂Cl₂</td>
<td>431</td>
<td>553</td>
<td>5119</td>
<td>0.04</td>
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<td>powder</td>
<td>583</td>
<td></td>
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<td>0.03</td>
</tr>
</tbody>
</table>

[a] Φₐ, absolute fluorescence quantum yield
The emission spectra and absolute quantum yields ($\Phi_q$) 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 S1 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 pursue solid-state-fluorescent BODIPY analogues.

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. 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 and aza-BODIPY 6 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.

The electrochemical properties were studied by cyclic voltammetry in ortho-dichlorobenezene with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. 4a–4b exhibit one reversible reduction waves and 4e 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 $E_{\text{LUMO}} = -eE_{\text{red}} + 4.4$, 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. The HOMO values, which are calculated from $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{F}}$, range from −6.01 eV to −6.18 eV.
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 decreases 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


11. M. J. Frisch, et al., Gaussian 09, see ESI for full reference and a detail description of the computational methods.


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.