Conformation-Restricted Partially and Fully Fused BODIPY Dimers as Highly Stable Near-Infrared Fluorescent Dyes

Jun Wang, Qinghua Wu, Shaowu Wang,* Changjiang Yu, Jin Li, Erhong Hao, Yun Wei, Xiaolong Mu, and Lijuan Jiao*

Laboratory of Functional Molecular Solids, Ministry of Education; Anhui Laboratory of Molecule-Based Materials; School of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui, China, 241000

S *Supporting Information*

ABSTRACT: A set of highly stable conformation-restricted partially and fully fused BODIPY dimers (α,β-cyclohexadiene-fused and α,β-benzene-fused dimers) were synthesized from a one-pot condensation of 2-formylpyrroles with α,β-cyclohexadiene-fused bipyrrole **3**. Effective expansion of π-conjugation over these fused BODIPY dimers was observed by X-ray analysis, density functional theory (DFT) calculations, and electrochemical and optical measurements, as demonstrated by their strong absorption and emissions in the near-infrared (NIR) range (650 to 820 nm).

H ighly π-conjugated systems have received much research attention and have found various applications in such highly diverse research fields as molecular electronics, nonlinear optics, and near-infrared (NIR) dyes due to their unique electronic and physical properties.[1] BODIPYs (4,4′-difluoro-4-bora-3a,4a-diaza-s-indacenes) are fascinating dyes with remarkable properties, including large molar absorption coefficients, high fluorescence quantum yields, and excellent stability.[2] These favorable properties have resulted in applications as fluorescent probes, imaging dyes, photodynamic therapy agents, and organic electronics/photovoltaics.[3] Among these, BODIPYs with absorption/emission at the NIR region are highly demanded for many applications.[4,5] The most straightforward method to expand the π-conjugation of BODIPY is via the direct dimerization/oligomerization of the BODIPY moiety at either the α- or β-position of the core. However, most of the single-bond linked dimers, like the β,β'-linked dimers **A** (Figure 1)

developed by Ziessel[6a] and Bröring,[6b] the α,α'-linked dimers disclosed by Bröring,[7] and the *meso,meso-* and *meso,α-*linked ones reported by Akkaya and others,[8] generally give a twisted nonplanar conformation due to the steric congestion caused by neighboring substituents. For the single-bond linked pyrrolic-unsubstituted BODIPY dimer **B** prepared by Shinokubo,[6c] flexibility of the conformation remains a problem.

Thus, it is more favorable to install additional ring(s), especially some aromatic ring(s) between the BODIPY units, to form so-called "conformation-restricted" BODIPY dimers or oligomers. However, the synthesis of these ring-fused systems, especially those that are fully fused, remains a challenge. Currently, only limited fully fused BODIPY dimers have been reported in the literature: the β,β'-benzene-fused dimer **C** (Figure 1) developed by Nagata and Uno[9a] as promising candidates for NIR-selective dyes, the α,β-benzene-fused BODIPY dimer **D** (Figure 1) prepared by Wakamiya and Yamaguchi[9c] as stable NIR dyes, and the α,β-pyrazine-fused BODIPY dimer (as a subunit within an NIR BODIPY trimer) disclosed by Hiroto and Shinokubo[9d] via the oxidation of the corresponding β-aminoBODIPY. The former two dimers (**C** and **D**) were obtained via comprehensive total synthesis. Herein, we report the efficient synthesis of a set of highly conjugated conformation-restricted fully fused (α,β-benzene-fused) BODIPY dimers **1a−c** and partially fused (α,β-cyclohexadiene-fused) dimers **2a−c** containing the same β,β'-single-bond linkage. These dimers show intensive absorption and emissions in the NIR region (650 to 820 nm) with good photostability.

The readily available α,β'-cyclohexadiene-fused bipyrrole **3**[10] was chosen as the key synthetic precursor in our synthesis, as the two pyrrole units have been constrained by an ethane linker. Condensation with formylpyrrole derivatives such as 2,4-
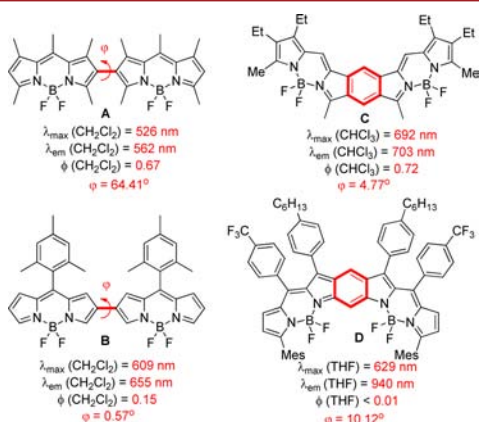
**Figure 1.** Reported β, β-linked BODIPY dimers **A**[6a]/**B**[6c] and fused BODIPY dimers **C**[9a]/**D**.[9c]

dimethyl-3-ethyl-5-formylpyrrole **4a** would generate conformation-restricted α,β-cyclohexadiene-fused BODIPY dimer **2a** after the subsequent BF_3 complexation. We anticipated that the cyclohexadiene linkage in **2a** could be easily oxidized using suitable oxidants to generate the desired fully fused α,β-benzene-fused BODIPY dimer **1**.

Interestingly, the BF_3 complexation of the condensation mixture of **3** and **4a** at 90 °C in toluene directly gave the fully fused BODIPY dimer **1a** in 10% isolated yield without resorting to any additional oxidation step (Scheme 1). On the other hand,

Scheme 1. Synthesis of Conformation-Restricted Fully Fused and Partially Fused BODIPY Dimers 1a−b and 2a−b
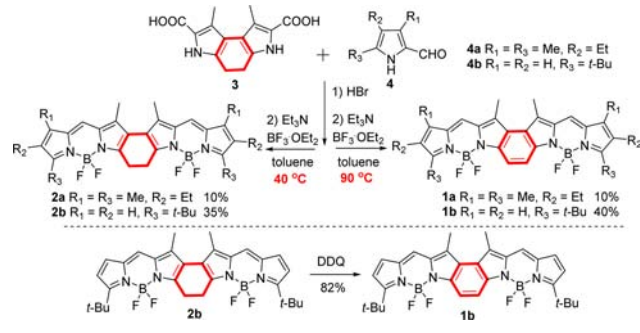
simply decreasing the reaction temperature to 40 °C for this BF_3 complexation reaction generated the designed partially fused (α,β-cyclohexadiene-fused) BODIPY dimer **2a** in a similar yield. We attributed the low yields of **1a** and **2a** to the poor solubility associated with these dimers' large planar structures, which facilitates the aggregation process.

To increase the solubility of the dimer, two bulky *tert*-butyl groups were introduced onto the dimer by substituting **4a** with 2-*tert*-butyl-5-formylpyrrole **4b** for this condensation reaction. The subsequent BF_3 complexation gave exclusively the α,β-benzene-fused BODIPY dimer **1b** at 90 °C and the α,β-cyclohexadiene-fused BODIPY dimer **2b** at 40 °C. Indeed, the installation of bulky *tert*-butyl substituents provides dimers **1b** and **2b** with good solubility in common organic solvents, like chloroform, toluene, and THF, and leads to a great improvement of the isolated yield of these dimers (up to 40%). This resulting partially fused **2b** was smoothly converted to the fully fused **1b** using DDQ as the oxidants, from which **1b** was isolated in 82% yield.

To further extend the π-conjugation of these BODIPY dimers, we further applied the readily available α-formylthiophene-fused pyrrole **4c** for the condensation with **3**. The subsequent BF_3 complexation gave exclusively **2c** in 36% yield at 40 °C and **1c** in 39% yield at 90 °C (Scheme 2). The further oxidation of **2c** by DDQ gave the fully fused **1c** in 81% yield. BODIPY dimers **1a−c** and **2a−c** were fully characterized by ^1H and ^{13}C NMR and

Scheme 2. Chemical Structure of BODIPY Dimers 1c and 2c and Their Key Synthetic Precursor 4c

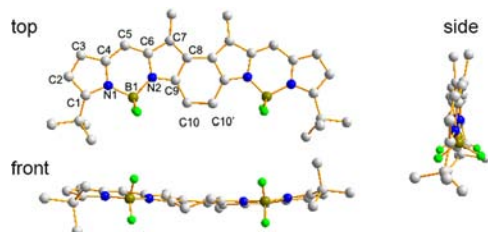HRMS analysis. Dimers **2b** and **1a** were further confirmed by X-ray analysis (Figures 2 and 3).

Figure 2. X-ray crystal structure of **2b**. C, light gray; N, blue; B, dark yellow; F, green.
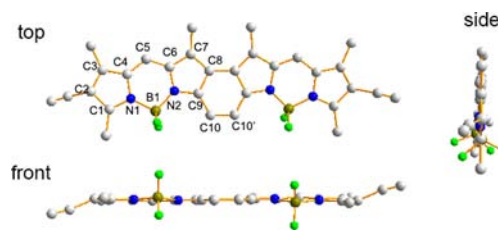

Figure 3. X-ray crystal structure of **1a**. C, light gray; N, blue; B, dark yellow; F, green.

The crystals of BODIPY dimers **2b** and **1a** suitable for X-ray analysis were obtained by the slow evaporation of their dichloromethane solutions. Dimer **2b** (Figure 2) revealed a 14.5° dihedral angle between the mean planes of the two pyrrole units adjacent to the cyclohexadiene ring, which is significantly smaller than that of dimer $\mathbf{A}^{6a}$ (64.4°, Figure 1). The bond distance of the ethane linker is 1.52 Å, typical of saturated C−C bonds. Dimer **1a** (Figure 3) showed a nearly planar structure over the two BODIPY units with the dihedral angle between the two pyrrole units adjacent to the benzene ring around 1.2°. In **1a**, the bond distances (Å) of C1−N1 (1.337(6)), C2−C3 (1.366(3)), and C4−C5 (1.365(9)) were shorter than those of C9−N2 (1.365(7)), C7−C8 (1.406(3)), and C5−C6 (1.391(0)), respectively. This is similar to that of BODIPY dimer $\mathbf{D}^{9c}$ and indicates the enhanced azafulvene character in both of the terminal pyrroles due to the presence of the benzene ring. Further, these results constitute a significant deviation from the aromatic benzene geometry observed in the benzene unit in **1a**, where the bond distances of C8−C8′, C8−C9, C9−C10, and C10−C10′ are 1.444(1), 1.426(6), 1.410(7), and 1.356(9), respectively. Both **2b** and **1a** exhibited well-ordered crystal stacking structures connected by multiple intermolecular C−H⋯ F H-bonds between F atoms and various H atoms (Figures S1− S6) with an interplanar distance of 4.06 and 3.58 Å, respectively.

To investigate the influence of the benzene-ring formation on the π-conjugation of these BODIPY dimers, a comparative DFT calculation was performed on dimers **1a** and **1b**. In agreement with X-ray analysis, the DFT calculation results also clearly showed the substantial bond alternation in the newly formed benzene unit. As shown in Figure S7, the natural population analysis (NPA) of **1a** by B3LYP/6-31G(d) showed markedly different atomic charges on the benzene subunit (C8: −0.089, C9: + 0.231, C10: −0.220). Similar results were also obtained for **1b**. Based on the structural features, the benzene-ring formation after oxidation significantly alters the electronic structure. The calculated LUMO and HUMO for **2a** (Figure 4) distributed over the whole conjugated π-system containing both the two
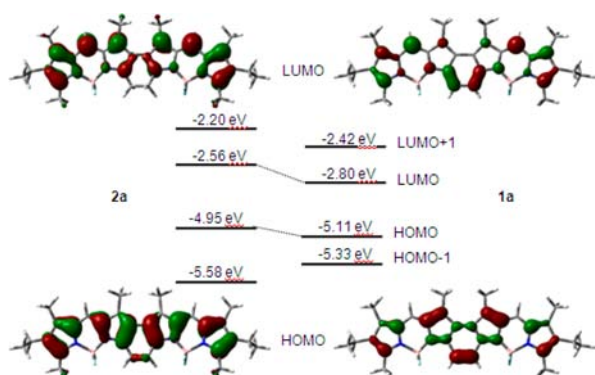
Figure 4. Pictorial presentation of HOMO and LUMO and a plot of energy levels for **2a** and **1a** (B3LYP/6-31G(d)).

BODIPY units and the β,β'-linkage (C8 and C8'). In contrast, the LUMO of **1a** (Figure 4) and **1b** (Figure S9) is mainly delocalized over two BODIPY units and the C9, C9', C10, and C10' atoms with little distribution over C8 and C8' atoms. In particular, the oxidative benzene-ring formation is effective at decreasing the LUMO level (0.24 eV from **2a** to **1a**, 0.27 eV from **2b** to **1b**).

The cyclic voltammetry of these dimers was investigated in deoxygenated dichloromethane at rt containing tetrabutyl-ammonium hexafluorophosphate (TBAPF$_6$) as the supportive electrolyte (Figure S10). The oxidation in cyclic voltammetry of these dimers showed multiple irreversible electron transfers, and the two reduction steps indicate the dimeric nature of the compound by electronic communication between the sub-units.[7a,11] Dimers **2a**, **2b**, **1a**, and **1b** each displayed an irreversible reduction wave with E_{red}^1 at −1.12, −0.98, −0.82, and −0.66 V, respectively. The LUMO energy levels for dimers **2a**, **2b**, **1a**, **1b** (−3.37, −3.51, −3.66, and −3.83 eV, respectively) were estimated from the onset potential of the first reduction waves (Table 1). The results indicate that the benzene-fused

Table 1. Electrochemical Data Acquired in Dichloromethane Solution Containing 0.1 M TBAPF$_6$ as the Supporting Electrolyte at Room Temperature (Glassy Carbon Electrode as a Working Electrode, and the Scan Rate at 50 mV s^{-1}) and HOMO−LUMO Gaps Determined from Spectroscopy[a]

dyes	E_{red}^1 (V)	E_{red}^2 (V)	$E^\circ_{B/B}$ (V)	E_{red}^{onset} (V)	LUMO (eV)	HOMO (eV)	E_g (eV)
2a	−1.12	–	−1.52	−1.03	−3.37	−5.59	2.22
2b	−0.98	–	−1.41	−0.89	−3.51	−5.72	2.21
1a	−0.82	−1.24	–	−0.74	−3.66	−5.92	2.26
1b	−0.66	−1.12	–	−0.56	−3.83	−6.08	2.24

[a] $E^\circ_{B/B}$ = reversible reduction potential; E_{red}^1 = irreversible reduction peak potentials; E_{red}^2 = irreversible reduction peak potentials; E_{red}^{onset} = the onset reduction potentials; $E_{LUMO} = -e(E_{red}^{onset} + 4.4)$; E_g = band gap, obtained from the intercept of the absorption spectra; $E_{HOMO} = E_{LUMO} - E_g$.

structure after oxidation is indeed effective to decrease the LUMO level (around 0.3 eV), which is important for stability toward air oxidation.

The optical properties of these resulting BODIPY dimers were first investigated in toluene. Dimers **2a** and **2b** each showed absorption maximums of 670 and 654 nm with broad shoulders at around 620 and 605 nm, respectively (Figure 5a, Table 2). In comparison with the unsymmetrical 3,5-dimethyl-4-ethylBODI-
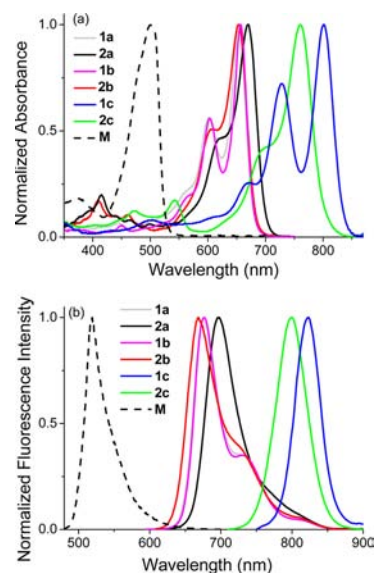
Figure 5. Overlaid normalized absorption (a) and fluorescence emission (b) spectra of BODIPY dimers **1a−c**, **2a−c**, and the unsymmetrical 3,5-dimethyl-4-ethylBODIPY **M** in toluene.

Table 2. Photophysical Properties of 1a−c, 2a−c, and 3,5-Dimethyl-4-ethylBODIPY M at RT in Toluene

dyes	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	ε (M^{-1} cm^{-1})	ϕ^a	Stokes shift (cm^{-1})
2a	670	696	52 500	0.72	558
2b	654	670	57 600	0.41	365
2c	760	800	191 000	0.27	658
1a	654	677	129 000	0.81	531
1b	657	676	107 000	0.70	428
1c	802	823	182 000	0.04	318
M	510	521	40 500	0.58	190

[a]Fluorescence quantum yields were obtained using Indocyanine Green (ICG) as a reference compound (ϕ = 0.12 in DMSO) for **1c** and **2c**; 1,3,5,7-tetraphenyl-azadipyrromethene (ϕ = 0.34 in chloroform) for **2a−b** and **1a−b**; and Fluorescein (ϕ = 0.90 in 0.1 M NaOH solution) for **M**. The standard errors are less than 5%.

PY **M**, dimers **2a−b** each showed a >100 nm red shift in their absorption maximums with comparable molar absorptivity. A similarly large red shift was observed in **1a−b** which had an intense absorption peak around 650 nm and a smaller one around 600 nm. The molar absorptivity of **1a−b** is around two to three times that of the monomer **M**. A further red shift of the absorption maximums to 760 and 800 nm was observed for **2c** and **1c**, respectively, with a dramatically enhanced molar absorptivity (more than four times that of monomer **M**).

As shown in Figure 5b and Table 2, all BODIPY dimers **1** and **2** had intense fluorescence emissions in the NIR region (670 to 820 nm) with comparable fluorescence quantum yields (0.27−0.81) to that of monomer **M**, except for **1c**. The intense fluorescence observed in most of these BODIPY dimers is in great contrast to that of the reported α,β-benzene-fused BODIPY dimer **D**[9c] which showed negligible fluorescence. These dimers exhibited small Stokes shifts due to the rigidity of their structures.

We further investigated the solvent-dependent photophysical properties of these BODIPY dimers. The increase of the solvent polarity from toluene to acetonitrile (Table S3 and Figures S11−16) led to a slight blue shift of the absorption and emission bands of these dimers. In comparison with **2b−c**, the fluorescence

quantum yields of **1a**−**c** and **2a** are more sensitive to the polarity of the solvents (Table S3). For example, the fluorescence quantum yield of **1a** was reduced from 0.81 in toluene to 0.03 in acetonitrile. This indicates the possible presence of an intramolecular charge transfer (ICT) process in these dimers, and ICT from solvent induced symmetry breaking in the excited state is presumably in effect in the solvent-dependent photophysical properties.[8e,g,12]

The photostabilities of these BODIPY dimers were investigated in toluene under continuous irradiation with a 500 W Xe lamp. As shown in Figure S19, dimers **1a**−**b** and **2a**−**b** showed excellent photostabilities during the period of strong irradiation (25 min): >98% of **1a**−**b** and **2a**−**b** remained, while only 40% of the well-known commercialized Methylene blue was left under this condition. Similarly, dimers **1c** and **2c** showed better photostabilities than that of the commercialized NIR dye ICG (Figure S20).

In conclusion, we have synthesized a new family of highly conjugated conformation-restricted partially fused and fully fused BODIPY dimers (α,β-cyclohexadiene-fused **2** and α,β-benzene-fused BODIPY dimers **1**) from a one-pot condensation of 2-formylpyrroles and α,β-cyclohexadiene-fused bipyrrole **3**. These BODIPY dimers are highly photostable and show excellent electrochemical and optical properties, including intensive absorption and emission in the 650−820 nm range.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02717.

> Experimental details, tables, and additional spectra (PDF)
> Crystallographic data (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: swwang@ahnu.edu.cn.
*E-mail: jiao421@ ahnu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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