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Modulating the singlet oxygen generation property of *meso*–β directly linked BODIPY dimers†

Weidong Pang,[a] Xian-Fu Zhang,*[b] Jinyuan Zhou,[a] Changjiang Yu,[a] Erhong Hao[a] and Lijuan Jiao*[a]

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We report the synthesis, X-ray analysis and singlet oxygen generation properties of a set of *meso*–β directly linked BODIPYs with the *meso*–aryl group (φ_1) and *meso*–BODIPY component (φ_2) free to rotate or constrained.

BODIPYs (such as A in Fig. 1) known as the "little-sister" of porphyrin, have attracted interest in a diversity of research fields. They have been utilized as labeling reagents, laser dyes, fluorescent switches, light harvesters, sensors and sensitizers due to their tunable photophysical properties, versatility and rich chemistry.[1] Oligomeric, including some bridge-linked non-orthogonal dimeric BODIPYs have been reported.[2,3] Unlike the well-developed porphyrin dimers, only several types of directly linked BODIPY dimers have been synthesized:[4–7] the α–α linked BODIPY dimers **B** reported by Bröring and co-workers,[4] the β–β linked BODIPY dimers **C** reported by Ziessel,[5a] Shinokubo[5b] and Bard,[5c] the *meso*–*meso* linked BODIPY dimers **D** developed by Thompson[6] and Akkaya,[7] and the first and only *meso*–β linked BODIPY dimer **E** reported by Akkaya and coworkers[7] while we were working on this paper.

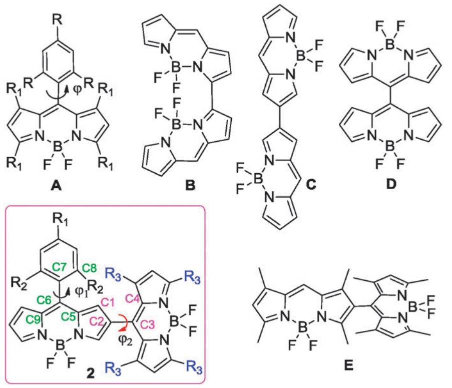
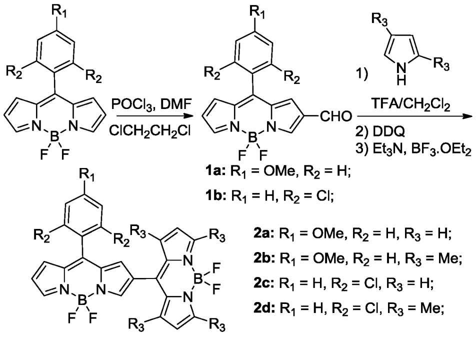


Fig. 1 Chemical structures of some representative BODIPYs (**A**), dimeric BODIPYs (**B**, **C**, **D** and **E**) and our BODIPY dimers **2**. The alkyl groups on the *meso*–aryl group and dipyrrin unit hinder the rotation of the *meso*–aryl ring in BODIPYs **A**.

The relative rotation of the *meso*–aryl group to the mean plane of the dipyrrin (defined as the dihedral angle φ) in *meso*–aryl BODIPYs **A** has been known to be able to greatly affect the excited-state dynamics of the dyes.[8] For example, Lindsey[8a] and Samuel[8b] have separately demonstrated its important effect on the photophysical properties of the excited state and the non-radiative decay of the dyes.

Recently, we have developed an efficient synthesis of β–formylBODIPYs[9] that can be easily applied for the further functionalization of BODIPY chromophore.[10] Herein, using these β–formylBODIPYs as a platform, a set of *meso*–β directly linked BODIPY dimers **2a–d** (Scheme 1) were synthesized and characterized *via* X-ray diffraction. Carefully controlled orthogonalities associated with their dihedral angles (Fig. 1, φ_1 and φ_2) in BODIPY dimers **2b** and **2d** were achieved through convenient substitutions at the *meso*-aryl and/or pyrrolic positions in the BODIPY subunits, which restricted the free rotation of the *meso*-aryl group and *meso*–BODIPY component in these two BODIPY dimers. We rationalized that a comparative study of these two orthogonal BODIPY dimers **2b** and **2d** with their non-orthogonal analogue dimers **2a** and **2c** would be instructive.

BODIPY dimers **2a–d** were straightforwardly synthesized in good yields from the acid-catalyzed condensation of β–formylBODIPYs **1** with pyrrole or 2,4-dimethylpyrrole,



Scheme 1 The synthesis of dimeric BODIPYs **2a–d**.

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[a] *Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, School of Chemistry and Materials Science, Anhui Normal University, Wuhu, China 241000. E-mail: jiao421@mail.ahnu.edu.cn*
[b] *Chemistry Department, Hebei Normal University of Science & Technology, Qinhuangdao, Hebei, China 066004. E-mail: zhangxianfu@tsinghua.org.cn; Fax: (+86) 1062770304*

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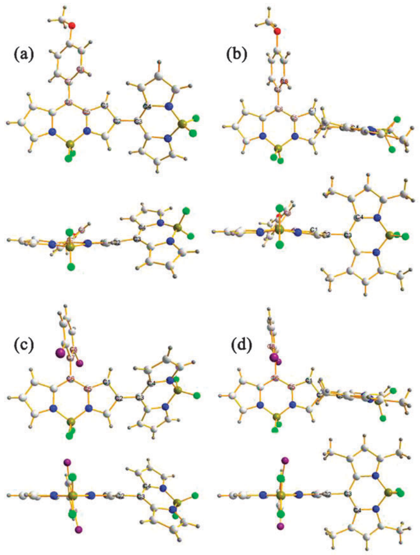

Fig. 2 Top view (top) and side view (bottom) of the X-ray structures of dimeric BODIPYs **2a** (a), **2b** (b), **2c** (c) and **2d** (d). Dihedral angles (φ_1: C5-C6-C7-C8; φ_2: C1-C2-C3-C4) between the two BODIPY units for **2a** are φ_1 = 38°, φ_2 = 34°; for **2b** φ_1 = 54°, φ_2 = 84°; for **2c** φ_1 = 84°, φ_2 = 39° and for **2d** φ_1 = 87°, φ_2 = 89°, respectively. C, light gray; H, gray; N, blue; B, dark yellow; F, light green and Cl, violet.

followed by DDQ oxidation and the subsequent BF_3 complexation reactions (Scheme 1), and were characterized by NMR, HRMS and X-ray analysis.

Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the dichloromethane solutions of these compounds. The two different C_9BN_2 BODIPY subunits in these dimeric BODIPYs remain essentially unperturbed, as shown in Fig. 2, although the planarity of these two is less pronounced than that in their corresponding monomers.[9b] Other bond lengths, angles and distances within each of these two C_9BN_2 BODIPY subunits are very similar to that of their corresponding monomers (Table S1 in ESI†). The C–C and C–N bond lengths within the two C_9BN_2 BODIPY subunits showed no clear distinction between single and double bonds, indicating the strong delocalization within each of the BODIPY subunits. The B–N and B–F bond lengths are typical (1.51–1.56 and 1.36–1.39 Å, respectively) in these BODIPY dimers and the angles around the boron atom are close to the tetrahedral angle of 109.6°.

These four dimeric BODIPY dyes differ by virtue of the substitution patterns at the *meso*–aryl or pyrrole units. *Meso*–aryl substituents greatly affected the dihedral angles (φ_1) between the *meso*-aryl group and the mean plane of the C_9BN_2 BODIPY subunits, similar to that described for most monomeric BODIPYs. BODIPY dimers **2a** and **2b** without *meso*–aryl substituents gave smaller dihedral angles between the *meso*–aryl group and the mean plane of one BODIPY subunit (φ_1 = 38° and 54° for **2a** and **2b**, respectively), while BODIPY dimers **2c** and **2d** with two chlorine atoms at 2,6-positions of the *meso*–aryl group in one BODIPY subunit gave a "near-perpendicular" dihedral angles (φ_1 = 84° and 87° for **2c** and **2d**, respectively). This may be attributed to the steric hindrance effect from two chlorine atoms in **2c** and **2d**, which restrict the rotation of *meso*–aryl group relative to the mean plane of the BODIPY core.

The pyrrolic substituents, especially the 1,7-positional substituents on the newly formed BODIPY core greatly affected the intramolecular interactions between the two BODIPY subunits. Dihedral angles close to 90° were observed between the two C_9BN_2 BODIPY subunits in **2b** (φ_2 = 84°) and **2d** (φ_2 = 89°). By contrast, **2a** and **2c** lacking pyrrolic substituents on the newly formed BODIPY subunit showed smaller dihedral angles between the two BODIPY subunits (φ_2 = 34° and 39° for **2a** and **2c**, respectively). This difference may be attributed to the presence of pyrrolic alkyl substituents in **2b** and **2d**, which restrict the relative rotation between the two BODIPY subunits.

The starting conformations in these dimeric BODIPYs also affected their photophysical properties, as summarized in Table 1. As shown in Fig. 3, BODIPY dimers **2a–d** showed characteristic absorption spectra similar to that of their corresponding starting BODIPY monomers **1**[9b] and other BODIPY chromophores. BODIPY dimers **2a** and **2c** with smaller dihedral angles between the two BODIPY subunits showed a very broad absorption band with an around 30 nm red-shift of the absorption maximum and the appearance of an additional band in comparison to those of monomers **1a** and **1b**. This broadened and red-shifted absorption band may be attributed to the formation of a ground-state charge-transfer complex through excitonic coupling, as described in the literature.[6,11,12] In comparison with **2a** and **2c**, less exciton couplings were observed for BODIPY dimers **2b** and **2d**. We attributed it to the perpendicular dihedral angles (φ_2) between the two BODIPY subunits in these two dimers, which reduced the efficiency in the exciton coupling between them.[6,7]

In comparison to those of the corresponding BODIPY monomers, much weaker fluorescence emission was observed in organic solutions for the orange-colored BODIPY dimers **2a–d** under ambient or hand-held UV lamp irradiation, indicating competing excited states in these dimers. These results are similar to that of the recently reported β–β[5b] and

Table 1 Comparative spectroscopic properties of dimeric BODIPYs

BODIPYs	λ_{abs}[a] (nm)	λ_{ems}[a] (nm)	φ_f[a,b]	τ(ns)[c]	χ^2[c]
2a	521	563	0.007	2.84	1.11
2b	507	540	0.002	2.41, 5.60	1.06
2c	538	568	0.002	1.37, 4.63	1.08
2d	507	542	0.002	1.08, 3.85	1.11

[a] In dichloromethane. [b] The fluorescence quantum yields were calculated using fluorescein in 0.1 M NaOH aqueous solution (φ = 0.90) as the standard. [c] In toluene.

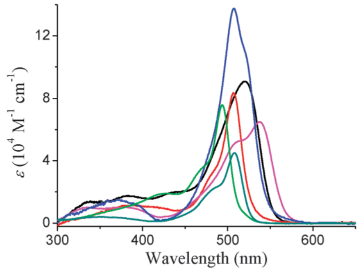

Fig. 3 Overlapped absorption spectra of BODIPYs **1a** (green), **1b** (dark cyan) and BODIPY dimers **2a** (black), **2b** (red), **2c** (magenta) and **2d** (blue) in dichloromethane.

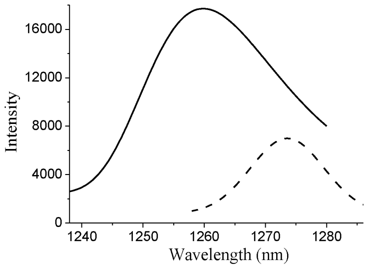

Fig. 4 Singlet oxygen phosphorescence with sensitization from dimeric BODIPYs **2b** (solid) and **2d** (dashed) in toluene at equal absorbances at the wavelength of 509 nm with InGaAs as the detector. Plots were based on the average of 10 times collection.

meso–*β*[7] directly linked BODIPY dimers. The fluorescence lifetime was measured by a time-correlated single photon counting method excited by a CdS portable diode laser (50 ps pulse width) and the emission was monitored at the maximum emission wavelength. The time evolution of the luminescence is described by either a single or double exponential decay for these BODIPY dimers under an experimental resolution of 100 ps.[13] The excimer formation shortens the lifetime of monomer moieties, for which the value is 2.84, 2.41, 1.37 and 1.08 ns for **2a–d**, respectively. The excimer lifetime is 5.60, 4.63 and 3.85 ns for **2b–d**, respectively.

To test a possible use of these dyes as singlet oxygen photosensitizers, we studied their ability to generate singlet oxygen.[4c,7] The singlet oxygen phosphorescence for BODIPY dimers **2a–d** (Fig. 4 and Fig. S6†) was obtained in toluene, excited at a wavelength of 509 nm and detected with a near-IR-sensitive detector. When excited at equal absorptivity concentrations for all compounds, BODIPY dimer **2b** gave the strongest singlet-oxygen phosphorescence emission at the signature wavelengths (with a maximum at around 1260 nm). A relatively weaker singlet-oxygen phosphorescence emission centred at around 1274 nm was observed for BODIPY dimer **2d**. By contrast, weak singlet oxygen phosphorescence emissions were observed for **2a** and **2c** (Fig. S6†). In addition, they were entrapped in the emissions of excited-state charge-transfer species[12] in these two BODIPY dimers, due to the lack of pyrrolic substituents in the newly formed BODIPY component to stabilize the excited-state charge-transfer species in **2a** and **2c**.

The relative efficiency of these four BODIPY dimers in generating singlet oxygen was further investigated in distilled toluene by using 1,3-diphenylisobenzofuran (DPBF) as a trap molecule (Fig. 5 and Fig. S7–10†). Consistent with the singlet-oxygen phosphorescence emission, the highest efficiency was also observed for orthogonal *meso*–*β* linked dimer **2b** under comparable conditions and the second most efficient one was **2d**. In contrast, BODIPY dimers **2a** and **2c** showed much lower efficiency in the singlet oxygen generation. Our results confirmed the calculation by Akkaya regarding the great effect of orthogonality of the BODIPY dimer on their efficiencies in the singlet oxygen generation.[7]

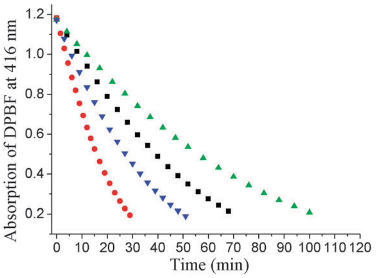

Fig. 5 Comparative DPBF (initial concentration at 5 × 10^{-5} M) degradation profiles in toluene by BODIPY dimers **2a** (■), **2b** (●), **2c** (▲) and **2d** (▼) (1 × 10^{-6} M). Filtered light > 455 nm used.

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