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meso-Alkynyl BODIPYs: Structure, Photoproperties, π-Extension, and Manipulation of Frontier Orbitals

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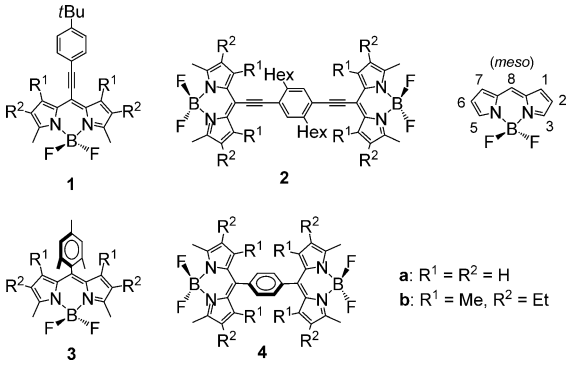
The importance of 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY,[1] Scheme 1) has increased at an accelerated pace: In addition to existing applications (fluorescent bioprobes[2] and laser dyes[3]), new practical approaches in areas



Scheme 1. Chemical structures of *meso*-alkynyl BODIPY monomers **1** and dimers **2**, and *meso*-aryl BODIPY monomers **3** and dimers **4**. The numbering of the carbons in an unsubstituted BODIPY is also shown.

such as photodynamic therapy (PDT)[4] and solar cells[5] have been explored recently using BODIPY-based compounds. The increased efforts have led to numerous BODIPY derivatives. The main purpose of modifications is to redshift and broaden the absorption and fluorescence in order to facilitate BODIPYs ability to use solar radiation and tissue-penetrating light effectively, and to obtain color variations. The simplest modification reported thus far includes the introduction of π-conjugating substituents such as ethynyl[6] and vinyl[7] groups. Additionally, annulation reactions have been reported to expand the π-conjugation effectively.[8] Most of the modifications have been undertaken at the 1–3 and 5–7 positions (Scheme 1); however, the 8 position (*meso* position) has not been exploited fully in the π-extension of BODIPYs. For example, an aryl group on the *meso* position cannot contribute to the π-extension owing to an orthogonal configuration. Other types of *meso*-modifications include a terminal ethynyl group,[9a] alkenyl group,[9b] formyl group,[9c] and oxidative annulation between an anthracenyl group at the *meso* position[9d] and the 1 and 7 positions. However, the first type of modification resulted in low thermal stability, while the rest led to significant quenching of fluorescence.

In this communication, we report the synthesis of BODIPY derivative **1** (Scheme 1) with an arylethynyl group at the *meso* position. In addition, a new type of BODIPY dimer **2** featuring a *p*-diethynylaryl linker was created. We investigated how π-conjugation between the BODIPY core and arylethynyl group works from various aspects, such as single-crystal X-ray structure analysis, photochemical measurements, cyclic voltammetry, and density functional theory (DFT) calculations. In this context, comparison with conventional *meso*-aryl-substituted BODIPY **3** (Scheme 1) assists us greatly to highlight the π-conjugation effect in **1** and **2**. We note that a *meso*-arylethynyl BODIPY similar to **1** has been synthesized independently very recently.[10]

The synthetic strategy for *meso*-alkynyl BODIPY monomer **1** is shown in Scheme 2. Sonogashira coupling of *tert*-butyliodobenzene with propargyl alcohol gave **5**, which was converted into precursor aldehyde **6** by means of oxidation with pyridinium chlorochromate. Condensation between pyrrole derivatives and aldehyde in the presence of a catalytic amount of trifluoroacetic acid (TFA), successive oxidation by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and complexation with $BF_3{\cdot}OEt_2$ gave BODIPY **1** (**1a**: 5%, **1b**: 17%). BODIPY dimer **2** was also obtained (**2a**: 24%, **2b**: 25%) by using a method similar to that for **1**. BODIPY dimer **2** was sufficiently soluble in typical organic solvents.

To reveal the structure of *meso*-alkynyl BODIPYs, single-crystal X-ray diffraction analysis was conducted for **1a** and **2a**:[11] Their thermal ellipsoid plots and packing structures are shown in Figure 1, and the crystallographic data are summarized in Table S1 in the Supporting Information. This is the first crystallographic report on *meso*-alkynyl BODIPYs. The dipyrrin moieties and arylethynyl groups are ap-

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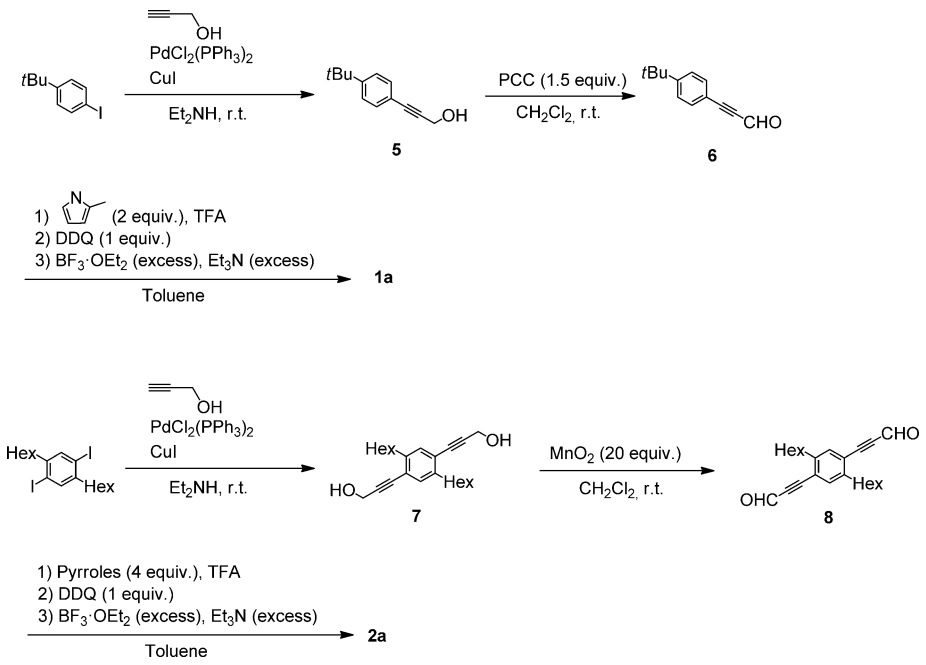

Scheme 2. Syntheses of **1a** and **2a**. Hex denotes *n*-C_6H_{13}. PCC = Pyridinium chlorochromate.

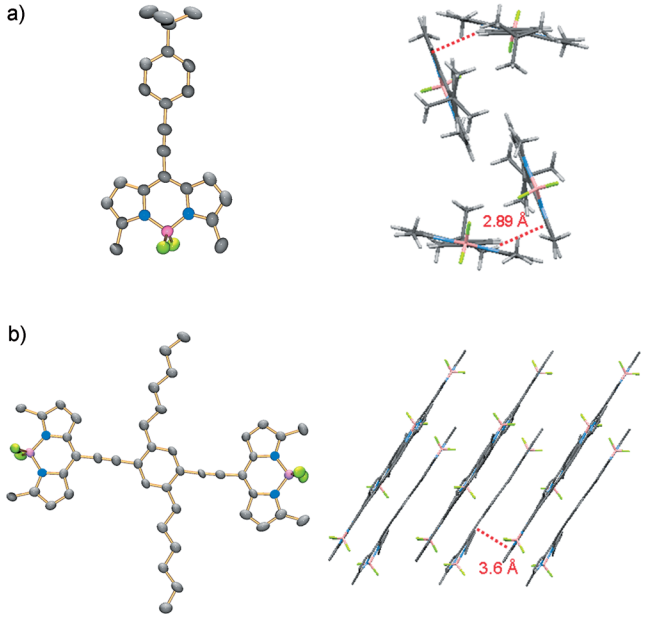

Figure 1. ORTEP drawings (50% probability level) and packing structures of a) **1a** and b) **2a**. Pink: B, gray: C, blue: N, and green: F. Hydrogen atoms are omitted for clarity.

proximately coplanar in **1a**. Similarly, the *p*-diethynylaryl linker and dipyrrin ligand lie on the same plane in **2a**. These structural features suggest that **1** and **2** should enjoy effective π-conjugation. The packing structure of **1a** adopts a herringbone-like alignment with short CH–π contacts between the aryl C–H bond and the pyrrole ring. On the other hand, the structure of **2a** features layer-by-layer piles. The interlayer distance is 3.6 Å, yet the molecules avoid effective overlaps so that there is no π–π interaction among the layers.

The electronic spectra and fluorescence spectra of *meso*-alkynyl BODIPYs **1a** and **2a** and the reference *meso*-aryl BODIPY **3a** in toluene are shown in Figure 2. Their numerical data are collected in Table 1. Compound **1a** showed an intense $^1\pi$–π^* absorption and fluorescence with maxima at 557 nm and 570 nm, respectively, which were redshifted by 44 nm and 46 nm from those of **3a**. This result indicates that effective π-extension can be achieved by the introduction of the arylethynyl group at the *meso*-position. Also noteworthy is the fluorescence quantum yield (ϕ_F) of **1a**. The value ($\phi_F = 0.86$) is as high as for ordinary BODIPYs, and importantly, is much greater than for any other π-expanded BODIPYs at the *meso* position, all of which suffer from significant quenching of fluorescence (e.g., *meso*-styryl BODIPYs show negligible fluorescence ($\phi_F < 0.01$)[9b]). As for arylethynyl BODIPYs, substitution at either 2 position or 3 position was reported.[6] Table 1 also lists the optical properties of such examples,

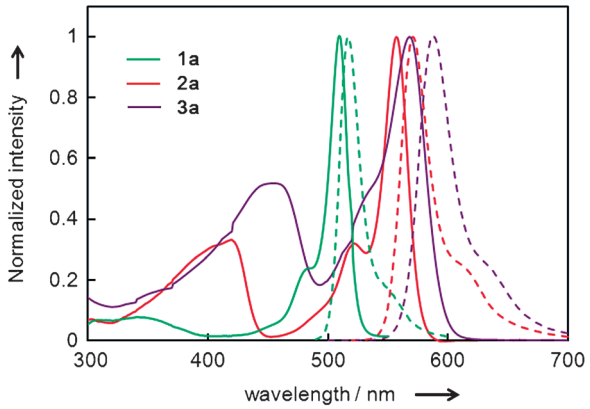

Figure 2. UV/Vis (solid lines) and fluorescence spectra (dashed lines) of **1a**–**3a** in toluene.

Table 1. Photochemical parameters of **1a**–**3a**, **9**, and **10** in toluene.

	$10^{-4}\ \varepsilon_{max}$ [$M^{-1}cm^{-1}$]	λ_{abs} [nm]	λ_{em} [nm]	Stokes shift [cm^{-1}]	ϕ_F
1a	6.1	557	570	409	0.86
2a	7.9	568	592	714	0.59
3a	8.9	513	524	409	0.95
9[a]	_[c]	566	577	337	0.91
10[b]	7.2	526	575	1620	0.47

[a] From ref. [6e]. [b] From ref. [6f], in dichloromethane. [c] No data reported.

9[6e] and **10**[6f] (Figure 3). This comparison suggests that *meso*-arylethynyl BODIPY **1a** undergoes π-extension comparable with those of **9** and **10**.

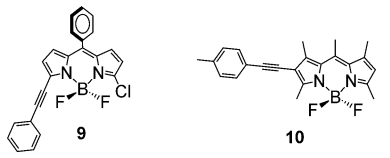

Figure 3. Chemical structures of previously reported arylethynyl BODIPYs **9** and **10**.

meso-Alkynyl BODIPY dimer **2a** has absorption and fluorescence maxima at 568 nm and 592 nm. These values are greater than those of **1a** by 11 nm and 22 nm. Furthermore, the absorption band of **2a** is broadened significantly. These facts indicate that **2a** enjoys more intense π-conjugation than **1a** upon dimerization. The high ϕ_F of **2a** (0.59) is also distinctive. BODIPY oligomers tend to have reduced ϕ_F values; for example, a BODIPY dimer tethered at the *meso* position with a phenylene linker, **4a** (Scheme 1), possessed a ϕ_F of merely 0.095 in the same medium, toluene.[12] Therefore, we can conclude that arylethynyl substituents have a good affinity with BODIPYs in terms of *meso*-substitution: π-extension and fluorescent ability are compatible.

To gain insight into the frontier orbital energy of the *meso*-alkynyl BODIPYs, cyclic voltammetry was conducted. The electrochemical reversibility of **1a** and **2a** was poor. On the other hand, **1b** and **2b** (Scheme 1) with additional alkyl groups on the BODIPY core had good electrochemical reversibility (Figure 4). Thus, hereafter, **1b** and **2b** are discussed with regard to referential *meso*-aryl BODIPY **3b**. The formal potentials ($E^{0'}$) of the BODIPYs are given in Table 2. *meso*-Alkynyl BODIPY **1a** showed reversible one-electron oxidation and reduction at $E^{0'}_{ox} = 0.63$ V and $E^{0'}_{red} = -1.46$ V, respectively. On the other hand, those of *meso*-aryl BODIPY **3b** emerged at $E^{0'}_{ox} = 0.58$ V and $E^{0'}_{red} = -1.84$ V. The oxidation is ascribable to electron subtraction from the HOMO, the highest π orbital of the BODIPY core, whereas the reduction can be ascribed to electron donation to the LUMO, the lowest π* orbital of the BODIPY core. The small change in the oxidation potential upon introduction of the arylethynyl group instead of the aryl group indicates that the HOMO level is not affected by the modification. In sharp contrast, the reduction potential underwent a significant positive shift of 0.38 V, indicative of substantial lowering of the LUMO by the introduction of the arylethynyl group in **1b**. The oxidation and reduction of **2b** appeared at $E^{0'}_{ox} = 0.66$ V and $E^{0'}_{red} = -1.38$ V. Judging from greater peak currents of **2b** as compared to those of **1b**, the oxidation and reduction of **2b** are attributed to one-step two-electron processes. We can recognize a positive shift of the reduction potential in **2b** compared to **1b**.

The photochemical investigation implied that *meso*-alkynylation afforded successfully π-extension, whereas the electrochemical measurement suggested that it lowered the

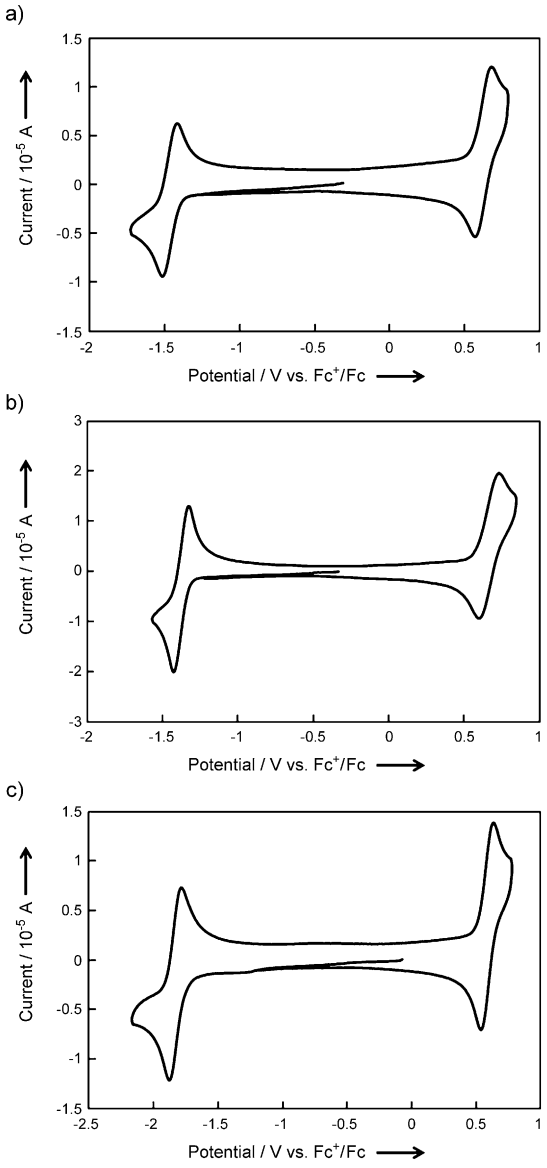

Figure 4. Cyclic voltammograms of a) **1b**, b) **2b**, and c) **3b** (0.5 mM each) in dichloromethane containing 0.1 M tetrabutylammonium perchlorate.

Table 2. Formal potentials of **1b**–**3b**.

	$E^{0'}_{ox}$ [V]	$E^{0'}_{red}$ [V]
1b	0.63[a]	−1.46[a]
2b	0.66[b]	−1.38[b]
3b	0.58[a]	−1.84[a]

[a] A one-electron process. [b] A two-electron process.

LUMO level while the HOMO level remained unchanged. To elucidate the electronic structure of the *meso*-alkynyl BODIPYs, DFT calculations were conducted. To reduce the cost of the calculations, compounds **1c**–**3c** that did not contain alkyl groups on the pyrrole rings were used (Figure 5 and Figure S1 in the Supporting Information). Figure 5 also shows the energy diagram for the frontier orbitals of *meso*-alkynyl **1c** and *meso*-aryl **3c**. The HOMO and LUMO of **3c** are π and π* orbitals of the BODIPY core: The aryl group

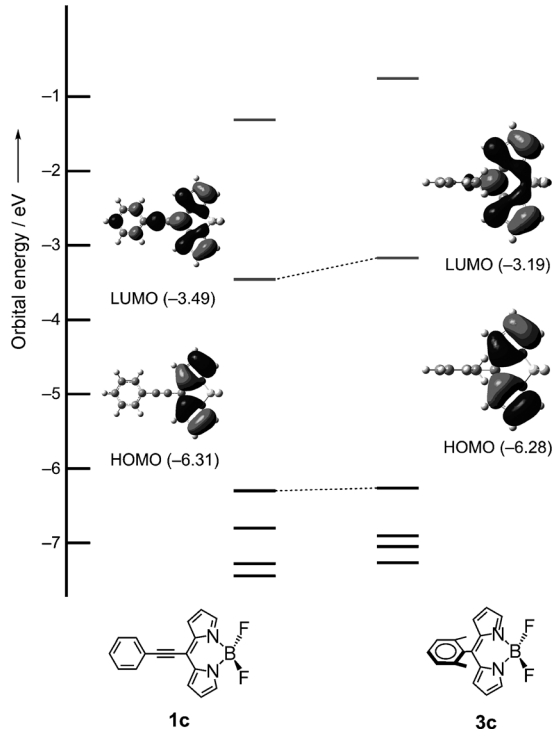

Figure 5. Energy diagram of the frontier orbitals of **1c** and **3c** estimated by DFT calculations. The black and gray solid lines indicate occupied and unoccupied orbitals, respectively.

does not contribute to the HOMO and LUMO, thus reflecting the orthogonality with the BODIPY core. Also noteworthy is a node of the HOMO at the *meso* carbon. The other carbon atoms of the BODIPY core have substantial orbital contributions, and the LUMO has no node on the carbons. Considering the node on the *meso* carbon, the phenylethynyl group of **1c** does not contribute to the HOMO. On the other hand, the LUMO of **1c** is delocalized over the whole molecule, which indicates the existence of effective π-conjugation between the phenylethynyl group and the BODIPY core. The π-conjugation is reflected appreciably in the molecular orbital energy. The energy level of the HOMO is almost the same in **1c** and **3c**, whereas significant stabilization is found in the LUMO of **1c**. This result is consistent with the electrochemical measurement, in which only the reduction potential undergoes a significant positive shift upon *meso*-alkynylation (Table 2). In other words, the *meso*-alkynylation can manipulate the LUMO level and maintain the HOMO level. This is hardly attained by modifications at the 1–3 and 5–7 positions because these carbons contribute substantially to both HOMO and LUMO. The smaller HOMO–LUMO gap in **1c** gives rise to the redshift of absorption and fluorescence.

Figure S1 in the Supporting Information shows the energy diagram for the frontier orbitals of **2c**. This compound features characteristics similar to **1c**: The HOMO and HOMO−1 lack a contribution from the *p*-ethynylphenyl linker, whereas the LUMO and LUMO+1 enjoy π-conjugation. As a result, a reduction of the LUMO and LUMO+1 level takes place.

In conclusion, BODIPY monomers **1** and dimers **2** bearing arylethynyl substituents at the *meso* position were synthesized. Both absorption and fluorescence were redshifted upon *meso*-alkynylation, thus indicating the existence of effective π-conjugation between the arylethynyl groups and BODIPY cores. Unlike other substitutions at the *meso* position, high fluorescence quantum yields were retained. Cyclic voltammetry revealed that the reduction potentials of **1b** and **2b** were shifted substantially in the positive direction, whereas their oxidation potentials were unchanged. DFT calculations rationalized the shift of the redox potentials. The HOMO of the BODIPY core had a node on the *meso* carbon, which prevented it from π-conjugation with the arylethynyl group. On the other hand, the LUMO of the BODIPY core included an orbital contribution from the *meso* carbon, which led to effective π-conjugation with the arylethynyl group, and resultant reduction of the LUMO level. *meso*-Alkynylation thus allows for flexible molecular orbital engineering of BODIPY derivatives, which leads to a tactical molecular design for applications such as dye-sensitized solar cells (DSSCs), organic light-emitting diodes (OLEDs), and artificial photosynthesis.

Acknowledgements

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Keywords: alkynylation · BODIPY · conjugation · electrochemistry · fluorescence

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COMMUNICATION

Fluorescent Dyes

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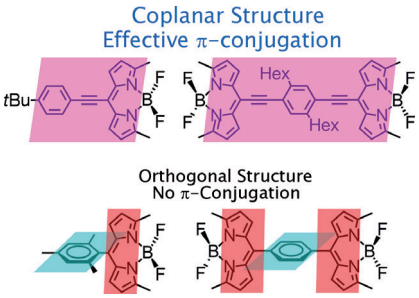
meso-Alkynyl BODIPYs: Structure, Photoproperties, π-Extension, and Manipulation of Frontier Orbitals



Bodipy building: *meso*-Alkynyl BODIPY monomers and dimers were synthesized and their crystal structures, photochemical properties, and electronic structures disclosed. The *meso*-arylethynyl group is coplanar with the BODIPY core. The resulting efficient π-conjugation red-shifts the intense absorption and bright fluorescence by about 40–70 nm. Cyclic voltammetry and DFT calculations revealed that the LUMO level is stabilized by *meso*-alkynylation, while the HOMO level remains constant.