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Synthesis of Diazo-Bridged BODIPY Dimer and Tetramer by Oxidative Coupling of β-Amino-Substituted BODIPYs

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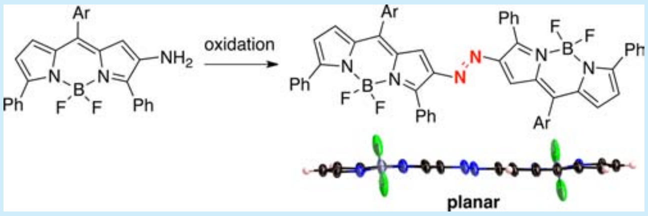
Ⓢ *Supporting Information*

ABSTRACT: A diazo-bridged BODIPY dimer and tetramer were prepared by the oxidative coupling reaction of β-amino-substituted BODIPYs. The structure of the dimer was elucidated by X-ray diffraction analysis, showing its coplanar orientation of two BODIPY units. Effective extension of π-conjugation was confirmed by optical and electrochemical investigations.



BODIPY, 4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene, has been one of the most important functional dyes in a wide area of material science due to its high thermal and photochemical stability as well as strong absorption and emission in the visible region.[1] A number of BODIPY-based molecules have been extensively explored for bioimaging probes,[2] photodynamic therapy,[3] and light emitting devices.[4] Recently, BODIPY oligomers with covalent linkages have attracted much interest for their near-IR light absorbing property.[5] Although a number of BODIPY oligomers have been reported, there is no example of diazo-bridged ones.

Diazo-bridged π-conjugated materials represented by azobenzene are photoactive materials, exhibiting photochromic behavior through *cis*–*trans* isomerization.[6] The diazo linkage also enables effective π-conjugation due to its less sterically demanding nature in comparison to ethylene and imino linkages.[7] In addition, the electron-withdrawing feature of diazo groups effectively stabilizes π-conjugated systems to prevent decomposition by air oxidation. Here, we describe the synthesis of a diazo-bridged BODIPY dimer and tetramer as novel covalently linked BODIPYs through oxidative dimerization of amino-substituted BODIPYs.

We prepared 3,5-diphenyl-2-amino BODIPY **4** as a starting substrate from 3,5-diphenyl BODIPY **1** in three steps (Scheme 1). 2-Bromo BODIPY **2** was obtained in 94% yield by treatment of **1** with 1.1 equiv of NBS. The palladium-catalyzed cross-coupling reaction of **2** with benzophenone imine followed by acidic hydrolysis furnished **4** in good yield. Compound **4** was stable enough for handling under air and concentrated conditions. This is in sharp contrast to 2-amino BODIPYs without α-substituents, which decomposed during concentration by rotary evaporator.[5j] We next attempted oxidative coupling of **4** with several oxidizing reagents.[8] A copper-mediated oxidative coupling resulted in the formation of a complex mixture. On the other hand, oxidation of **4** with DDQ in chloroform provided a diazo-linked BODIPY dimer **5** in 8% yield (Table 1). In this reaction, we also observed the formation of DDQ adducts as side products. Accordingly, we further optimized the reaction conditions with other oxidants. Oxidation of **4** with p-chloranil improved the yield to 12%. However, a large amount of the starting material remained unreacted. The use of MnO_2 as the oxidant furnished **5** in 17% yield. ^{t}BuOI, recently reported by Minakata et al.,[9a] worked well

Scheme 1. Synthesis of 2-Amino Substituted BODIPY 4

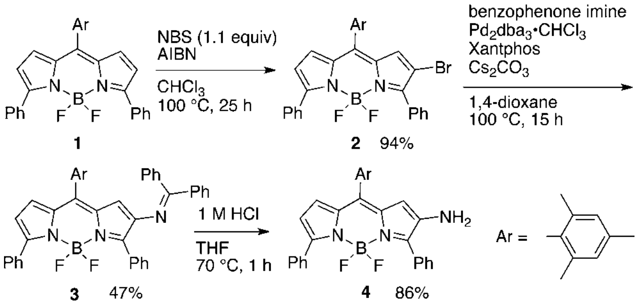
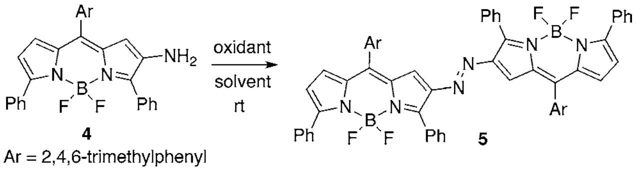


Table 1. Oxidative Dimerization of 4



entry	oxidant (equiv)	time (h)	solvent	yield (%)
1	DDQ (2.1)	1	$CHCl_3$	8
2	p-chloranil (2.1)	23[a]	$CHCl_3$	12
3	MnO_2 (26)	24	$CHCl_3$	17
4	^{t}BuOCl (2.0) + NaI (2.0)	13	DME	33
5	$PhI(OCOCF_3)_2$ (2.1)	2	$CHCl_3$	34

[a] The reaction was conducted at rt for 17 h and at 60 °C for an additional 6 h.

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to provide **5** in 33%, but inseparable chlorinated byproducts were formed. Oxidation with bis(trifluoroacetoxy)iodobenzene (PIFA) afforded the desired product **5** in 34% yield without formation of chlorinated byproducts.[9b,c] In this case, the starting material **4** was completely consumed. Recently, we have reported the formation of pyrazine-fused BODIPY trimers through oxidation of 2-amino BODIPYs without α-substituents.[5j] However, none of the pyrazine-fused products were detected in the oxidation of **4**.

The product **5** was assigned by spectroscopic methods. The parent mass ion peak observed at m/z = 951.4119 (calcd for $(C_{60}H_{49}B_2F_4N_6)^+$ = 951.4154 [$(M + H)^+$]) indicated its dimeric structure. In its ^{1}H NMR spectrum, peaks for pyrrole protons of **5** were shifted in the lower field as compared to **4** and the broad NH_2 signal of **4** disappeared after oxidation. This spectral change indicates conversion of the electron-donating NH_2 group to the electron-withdrawing diazo linkage. Finally, the structure of **5** was unambiguously elucidated by X-ray diffraction analysis.[9] Figure 1 displays the X-ray crystal structure of **5**, revealing its highly planar structure including the diazo linkage. The deviation from the mean plane which consisted of the two BODIPY cores and the diazo moiety is 0.088 Å, and the dihedral angle between the BODIPY unit and the diazo linkage is only 1.1°. The length of the C(2)−N(3) bond is 1.40 Å, which is shorter than the standard C_{sp^2}−N_{sp^2} single bond length. These structural features indicate the presence of effective conjugation between two BODIPY cores through the diazo linkage.

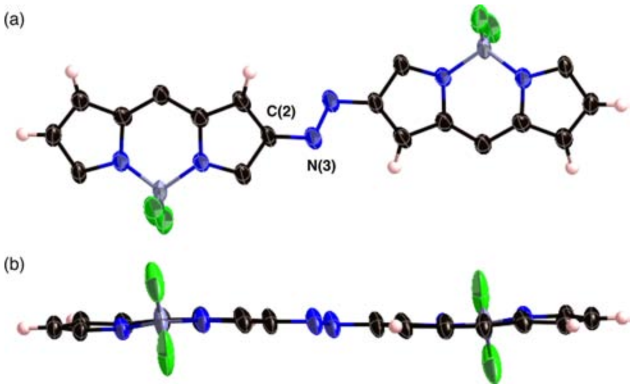

Figure 1. X-ray crystal structure of **5**. (a) Top view and (b) side view. The thermal ellipsoids are scaled at 50% probability level. The mesityl and phenyl groups in (b) are omitted for clarity.

We then attempted to obtain higher oligomers. Bromination of **5** with NBS proceeded regioselectively. Amino-substituted BODIPY dimer **6** was prepared in a similar manner as **4**. Oxidation of **6** with MnO_2 furnished tetramer **7** in 4% yield. The yield was improved to 24% with PIFA as an oxidant (Scheme 2). The formation of **7** was confirmed by mass and NMR spectroscopic analyses. The high-resolution mass spectrum of **7** exhibits the parent mass ion peak at m/z = 1927.8142, indicating its tetrameric structure. The ^{1}H NMR spectrum of **7** showed a C_2 symmetric feature. Singlet signals for pyrrole protons of **6** at 6.51, 6.36, and 5.87 ppm were shifted further downfield to 6.58, 6.57, and 6.52 ppm in **7**, suggesting the formation of a new diazo group. Although the yield of the oxidative coupling reaction was not high, tetramer **7** was stable under the aerobic conditions, demonstrating the prospective utility of the diazo linkage to obtain stable and highly conjugated BODIPY oligomers.

Scheme 2. Synthesis of 2-Amino Substituted BODIPY

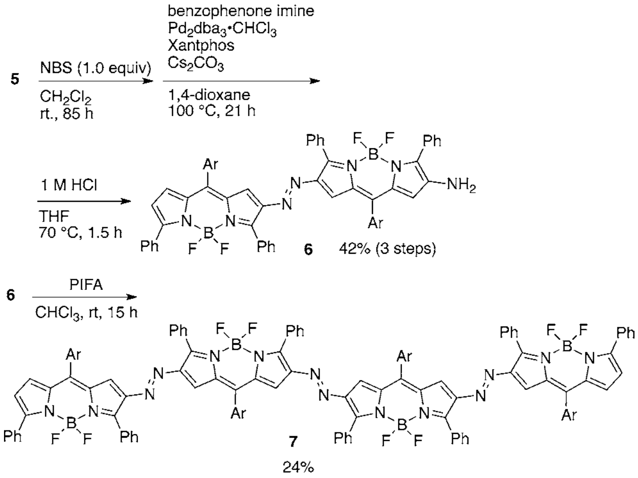

Figure 2a shows the UV/vis absorption spectra of **1**, **5**, and **7** in dichloromethane. The lowest energy bands were substantially shifted to the low energy region in the order of **7** > **5** > **1**, indicating effective expansion of π-conjugation upon oligomerization. The splitting absorption band at 690 nm for **5** also indicates strong π-conjugation, showing an anisotropic transition over the BODIPY plane.[11] Tetramer **7** exhibited an intense absorption band in the near-infrared region at 802 nm. The intense emission was observed for **1** with a fluorescence

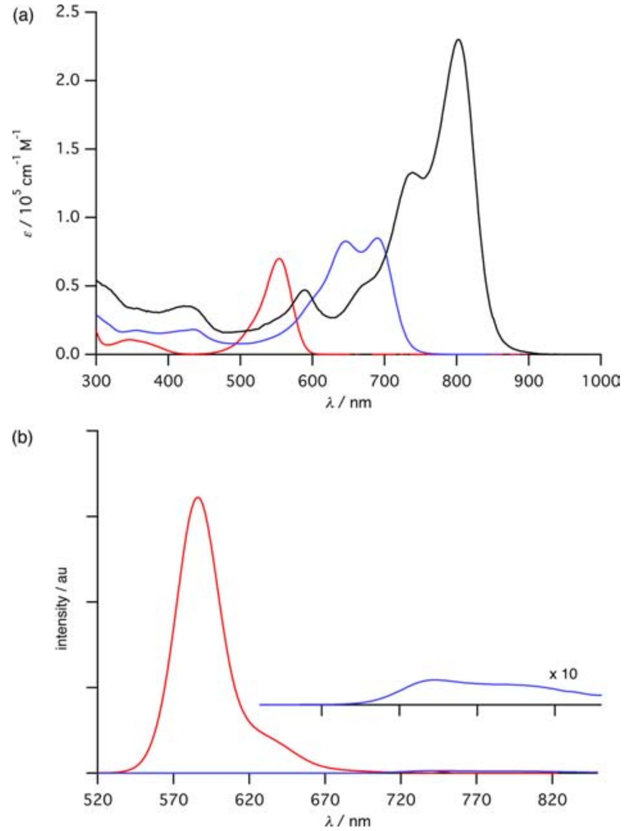

Figure 2. (a) UV/vis absorption and (b) emission spectra of **1** (red), **5** (blue), and **7** (black) in dichloromethane.

quantum yield of 0.88, while dimer **5** exhibited weak and red-shifted emission ($\Phi_f = 0.02$) at 743 nm (Figure 2b). The quenching of fluorescence might be due to *cis*−*trans* isomerization dynamics at the excited state.[12] However, no isomerization product was detected upon irradiation.

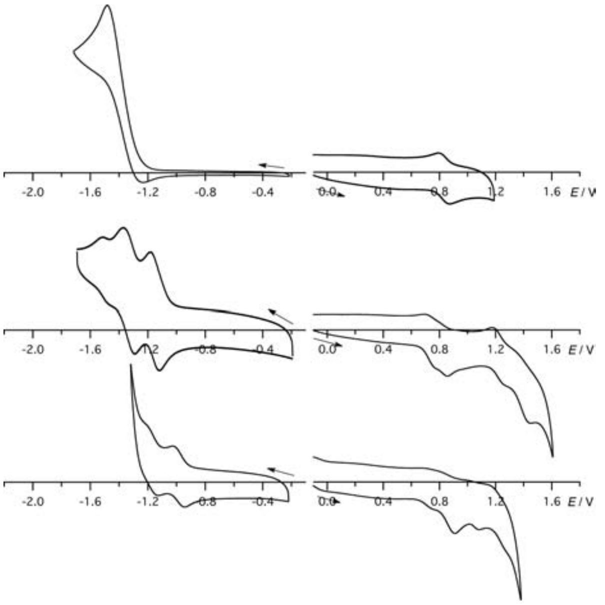

Figure 3. Cyclic voltammograms of **1** (top), **5** (middle), and **7** (bottom).

To investigate the electronic structure of oligomers **5** and **7**, electrochemical analysis was performed by cyclic voltammetry (Figures 3, S19). Dimer **5** exhibited three reversible oxidation waves at 0.708, 0.818, and 1.19 V and two reversible reduction waves at −1.15 and −1.33 V. In the case of tetramer **7**, two reversible reduction waves at −0.985 and −1.19 V and irreversible oxidation waves were observed. The gaps between the first oxidation and first reduction potentials decrease in the order **1** > **5** > **7**. This tendency is consistent with the result by optical analysis. Furthermore, both oxidation and reduction potentials in **5** and **7** are split, indicating the effective electronic communication between two BODIPY units. Interestingly, significant changes were observed for reduction potentials of **1**, **5**, and **7**, while their first oxidation potentials remained almost unchanged. This is probably caused by the electron-withdrawing feature of the diazo groups, which only affect the energy level of LUMOs. These results demonstrate that the connection of the BODIPY units with the diazo linkage is beneficial to obtain air-stable BODIPY-based oligomers and polymers.[13]

In conclusion, we have synthesized diazo-bridged BODIPY dimer **5** and tetramer **7** by oxidative coupling of 2-amino-substituted BODIPYs. The structure of **5** was unveiled by X-ray diffraction analysis, showing its highly planar conformation. Optical and electrochemical studies indicate the presence of effective enlongation of π-conjugation through the diazo bridge. These diazo-linked BODIPY oligomers have potential as a novel near-IR light absorbing dye.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and spectral data for all new compounds. Crystallographic data (CIF file) for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) Crystallographic data for **5**: $C_{63}H_{54}B_2Cl_3F_4N_6$, Mw = 1099.09, triclinic, $P\bar{1}$, a = 12.4210(6) Å, b = 14.0537(5) Å, c = 17.9628(6) Å, α = 66.48(2)°, β = 79.82(3)°, γ = 80.77(2)°, Z = 2, R = 0.0812 ($I > 2.0\ \sigma(I)$), Rw = 0.2603 (all data), GOF = 1.079.

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