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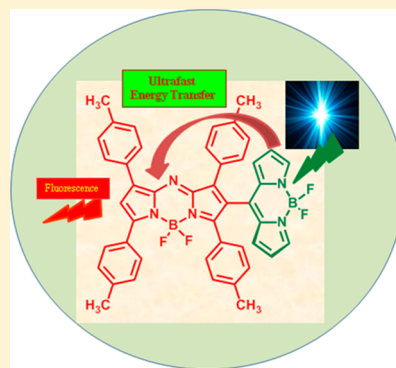
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S Supporting Information

ABSTRACT: Directly connected, strongly interacting sensitizer donor–acceptor dyads mimic light-induced photochemical events of photosynthesis. Here, we devised a dyad composed of BF₂-chelated dipyrromethene (BODIPY) directly linked to BF₂-chelated tetraarylazadipyrromethene (azaBODIPY) through the β -pyrrole position of azaBODIPY. Structural integrity of the dyad was arrived from two-dimensional NMR spectral studies, while single-crystal X-ray structure of the dyad provided the relative orientation of the two macrocycles to be $\sim 62^\circ$. Because of direct linking of the two entities, ultrafast energy transfer from the ¹BODIPY* to azaBODIPY was witnessed. A good agreement between the theoretically estimated Förster energy transfer rate and experimentally determined rate was observed, and this rate was found to be higher than that reported for BODIPY–azaBODIPY analogues connected with spacer units. In agreement with the free-energy calculations, the product of energy transfer, ¹azaBODIPY* revealed additional photochemical events such as electron transfer leading to the creation of BODIPY^{•+}–azaBODIPY^{•−} radical ion pair, more so in polar benzonitrile than in nonpolar toluene, as evidenced by femtosecond transient spectroscopic studies. Additionally, the spectral, electrochemical, and photochemical studies of the precursor compound azaBODIPY–dipyrromethane also revealed occurrence of excited-state events. In this case, electron transfer from the ¹azaBODIPY* to dipyrromethane (DPM) yielded DPM^{•+}–azaBODIPY^{•−} charge-separated state. The study described here stresses the role of close association of the donor and acceptor entities to promote ultrafast photochemical events, applicable of building fast-response optoelectronic and energy-harvesting devices.



INTRODUCTION

In the recent past, BF₂-chelated dipyrromethenes (BODIPYs)^{1–5} have drawn major attention because of their broad range of applications as laser dyes,^{6–8} fluorescent stains and labels in imaging,^{9–12} indicator dyes in sensors and chemosensors,^{13–15} photodynamic therapy agents,^{16–19} and building light-energy-converting donor–acceptor systems.^{20–28} The tremendous potential applications of BODIPY dyes is attributable to their attractive photophysical properties such as narrow absorption and emission bands, high molar absorption coefficients and quantum yields, high solubility in different organic solvents, and low sensitivity to solvent polarity.^{29,30} Furthermore, the properties of the BODIPY can be altered by simple modifications at the appropriate positions of the BODIPY core. One of the modifications on the BODIPY core is the replacement of meso carbon by imine-type nitrogen atom resulting in a new derivative often known as azaBODIPY.^{31–33} Compared to BODIPYs, the azaBODIPYs exhibited red-shifted absorption and emission spectra with high molar absorption coefficients and fluorescence quantum yields, which has captured the attention of researchers to construct azaBODIPY-based photosynthetic model compounds.^{34–50}

The strongly coupled dual chromophoric systems such as covalently linked BODIPY–azaBODIPY are desired to achieve

fast photoinduced intercomponent electron- and energy-transfer events, leading to valuable functions such as energy migration and/or charge separation. In literature, there are reports available on covalently linked BODIPY–azaBODIPY dyads and triads in which the BODIPY and azaBODIPY moieties are connected through spacers but not directly linked with each other.^{35,42,45–50} Herein, we report the synthesis of such a covalently linked, strongly coupled, BODIPY–azaBODIPY dyad, **1** (Figure 1 for structure) using 2-formyl azaBODIPY, **2** as a key reactant that was obtained in high yield under simple reaction conditions. The X-ray structure of the newly synthesized BODIPY–azaBODIPY dyad **1** reveals the spatial orientation of the two macrocycles with respect to one another. Systematic spectral and electrochemical studies were performed to construct an energy-level diagram to envision the excited-state energy and electron-transfer events. Finally, excited-state processes were probed by femtosecond pump–probe transient absorption spectroscopy.

Received: July 2, 2015

Revised: July 8, 2015

Published: July 10, 2015



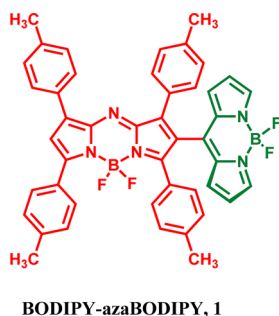


Figure 1. Structure of the directly connected BODIPY-azaBODIPY dyad investigated in the present study.

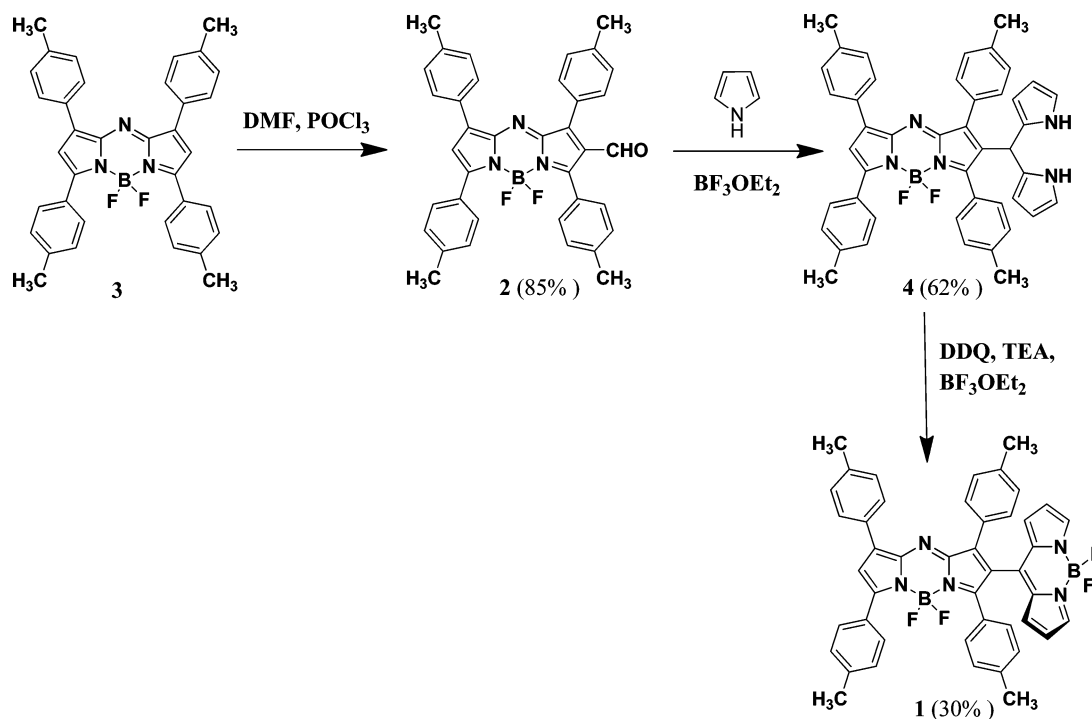
RESULTS AND DISCUSSION

The synthesis of covalently linked BODIPY-azaBODIPY dyad **1** is shown in Scheme 1. In the first step, the 2-formyl azaBODIPY **2** was prepared by reacting 1,3,5,7-tetratolyl azaBODIPY **3** with POCl_3 in dimethylformamide (DMF) under Vilsmeier-Haack reaction conditions that afforded **2** in 85% yield. The formylation was confirmed by a singlet resonance at 9.75 ppm due to $-\text{CHO}$ proton in ^1H NMR and molecular ion peak at 582.2531 in high-resolution mass spectrometry (HRMS). The compound **2** was treated with excess pyrrole under mild acid reaction conditions at room temperature, and the resulting crude reaction mixture was purified by silica gel column chromatography to afford compound **4** in 62% yield. In ^1H NMR of compound **4**, three sets of resonances at 5.86, 6.07, and 6.50 ppm correspond to six protons of dipyrromethanyl moiety; a singlet at 5.59 ppm corresponds to meso-CH proton of dipyrromethanyl moiety; a singlet resonance at 7.00 ppm corresponds to β -pyrrole proton of azaBODIPY; and a broad singlet at 7.55 ppm corresponds to two pyrrole NH protons of dipyrromethene moiety. In the next step, the compound **4** was subjected to oxidation with 2,3-

dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) followed by complexation with $\text{BF}_3 \cdot \text{OEt}_2$ at room temperature. The resulting crude compound was purified by silica gel column chromatography and afforded pure compound **1** as golden red solid in 30% yield.

A detailed one-dimensional (1D) and two-dimensional (2D) NMR analysis was performed for compound **1**. The ^1H NMR, ^1H - ^1H COSY, and NOESY spectra of the BODIPY-azaBODIPY dyad **1** are presented in Figure 2. In compound **1**, first, we identified the most downfield pyrrole proton that appeared at 7.73 ppm as *type a* proton of BODIPY moiety. The *type a* proton at 7.73 ppm showed cross-peak correlation with a resonance at 6.29 ppm, which we assigned to *type b* proton (Figure 2). The resonance at 6.80 ppm was identified as *type c* proton as this resonance showed cross-peak correlation with *type b* resonance in COSY spectrum (Figure 2b). The aryl protons appeared as four sets of resonances, which were identified based on NOE correlations with their corresponding $-\text{CH}_3$ protons. In NOESY spectrum (Figure 2c), we noted four singlets at 2.42, 2.44, 2.34, and 2.27 ppm, which were tentatively assigned to *type I*, *II*, *III*, and *IV* methyl protons. On the basis of NOE correlations between methyl protons and aryl protons, we identified all four sets of aryl protons. The singlet at 7.15 ppm was due to β -pyrrole proton (*type d*) of azaBODIPY. Thus, the NMR spectrum of compound **1** is very clean and identified all resonances by 1D and 2D NMR spectroscopy. In ^{11}B NMR, the compound **1** showed two sets of triplets at 0.17 and 0.89 corresponding to azaBODIPY and BODIPY units, respectively. Similarly, in ^{19}F NMR, the compound **1** also showed one quartet at -131.1 corresponding to azaBODIPY unit and one octet at -146.1 corresponding to BODIPY unit. (see Figures S1 to S14 in the Supporting Information for ^1H , ^{13}C , ^{11}B , and ^{19}F NMR and HRMS spectra).

Scheme 1. Synthesis of Compound **1**



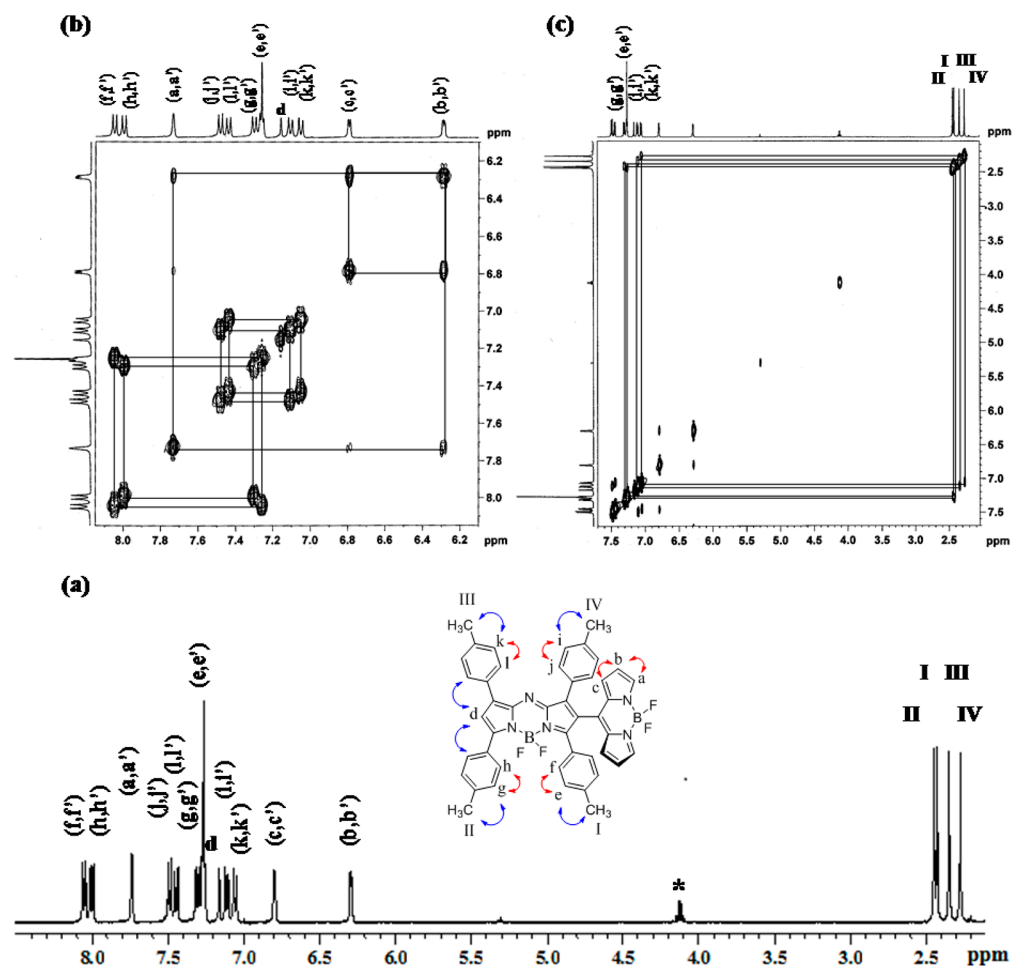


Figure 2. (a) ^1H NMR, (b) ^1H – ^1H COSY, and (c) NOESY spectra of compound **1** recorded in CDCl_3 .

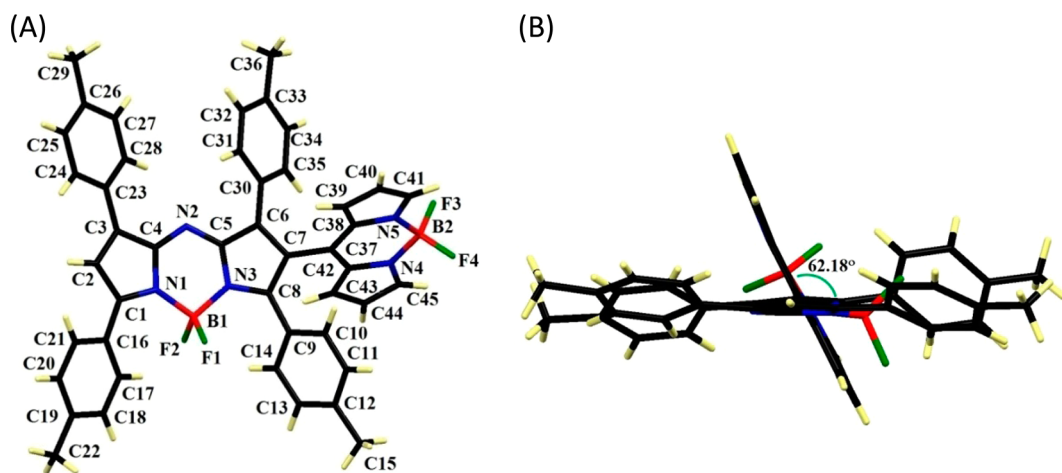


Figure 3. Single-crystal X-ray structure of compound **1** (a) perspective view and (b) side view showing the dihedral angles between the azaBODIPY unit and BODIPY unit.

X-ray Structure of BODIPY–azaBODIPY Dyad **1**.

Suitable diffraction-grade single crystals of compound **1** were grown via slow room-temperature evaporation of *n*-hexane into CHCl_3 solution of **1** over a period of 3 d. The crystal structure of compound **1** is shown in Figure 3; the molecule crystallized in monoclinic space group P_21/n with four molecules in a unit cell. The crystallographic data are given in Table 1, whereas all of the relevant bond distances are tabulated in Table 2. The

crystal structure revealed that the compound **1** is comprised of two units, namely, azaBODIPY and BODIPY units, and one of the β -position (C7) of azaBODIPY unit is linked with the meso carbon of the other BODIPY unit. Both the azaBODIPY and BODIPY units make an angle of $\sim 62^\circ$ between each other indicating that the BODIPY and azaBODIPY units in compound **1** are not in the same plane (Figure 3b), at least in the solid state. The bond distances between bridging

Table 1. Crystal Data and Data Collection Parameters for Compound 1

parameters	compound 1
mol. formula	C ₄₅ H ₃₅ B ₂ F ₄ N ₅
<i>F</i> _w	743.40
cryst. sym.	monoclinic
space group	<i>P</i> ₂ 1/ <i>n</i>
temp [K]	100(2)
<i>a</i> [Å]	16.679(6)
<i>b</i> [Å]	11.552(4)
<i>c</i> [Å]	19.833(7)
α [deg]	90
β [deg]	101.570(5)
γ [deg]	90
<i>V</i> [Å ³]	3744(2)
<i>Z</i>	4
μ [mm ⁻¹]	0.09
ρ_{calcd} [g cm ⁻³]	1.319
<i>F</i> (000)	1544
2 θ range [deg]	3.1–25.0
independent reflection	6569
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.071, 0.143
<i>R</i> 1, <i>wR</i> 2 [all data]	0.082, 0.149
GOF	1.17
largest diff. peak/hole [e Å ⁻³]	0.33, –0.33

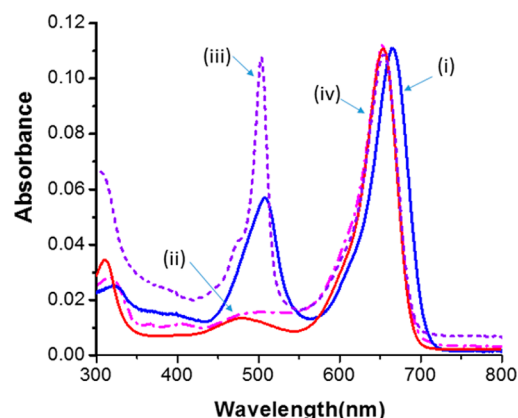
Table 2. Selected Bond Lengths (Å) for Compound 1

parameters	bond length [Å]	parameters	bond length [Å]
N(1)–C(1)	1.370(3)	N(4)–C(42)	1.396(3)
N(1)–C(4)	1.405(3)	N(4)–C(45)	1.345(3)
N(2)–C(4)	1.315(3)	N(5)–C(38)	1.403(3)
N(2)–C(5)	1.329(3)	N(5)–C(41)	1.341(3)
N(3)–C(5)	1.392(3)	N(5)–B(2)	1.549(3)
N(3)–C(8)	1.370(3)	N(4)–B(2)	1.554(3)
N(1)–B(1)	1.576(3)	B(2)–F(3)	1.382(3)
N(3)–B(1)	1.564(3)	B(2)–F(4)	1.385(3)
B(1)–F(1)	1.383(3)		
B(1)–F(2)	1.397(3)		

nitrogen (N2) and the pyrrole carbons (C4–N2 and C5–N2) are 1.314 and 1.329 Å, respectively, supporting the delocalization of π -electrons in azaBODIPY unit of compound 1. All four B–N bond distances in compound 1 are in the range of 1.549–1.576 Å, which indicates the usual delocalization of the positive charge in both of the BODIPY moieties.^{51–53} The average B–F bond distance in both units is 1.383 Å. A close inspection of the structure further reveals that the tolyl groups present at C1 and C3 are almost in plane with the azaBODIPY unit (making dihedral angles of 29° and 26°, respectively), whereas the other two tolyl groups present at C6 and C8 are relatively less planar with respect to the azaBODIPY plane (making a dihedral angle of 35° and 55°, respectively). This is because of the steric hindrance between the tolyl groups present at the C6 and C8 and BODIPY unit present at the C7. To summarize, the crystal structure of 1 showed that the azaBODIPY and BODIPY units are not completely perpendicular but slightly tilted toward plane with each other.

Spectral and Electrochemical Properties. The absorption, steady-state fluorescence, and electrochemical properties of compound 1 along with its reference compounds 2, 3, and 4 were studied in toluene and benzonitrile. In general, the 1,3,5,7-

tetraphenyl azaBODIPY 3 revealed a strong absorption peak at ~653 nm, along with a shoulder peak at ~500 nm, and a weaker band at 318 nm (see Figure 4) in toluene. Upon

**Figure 4.** Absorption spectrum in toluene of (i) BODIPY–azaBODIPY dyad 1, (ii) azaBODIPY–dipyrrromethene 4, (iii) 1:1 mixture of BODIPY and azaBODIPY, and (iv) azaBODIPY.

introduction of formyl group at position-2 of azaBODIPY 2, the absorption band experienced a blue shift of ~10–15 nm and appeared at 649 nm. The DPM–azaBODIPY 4 (DPM = dipyrrromethane) also showed one strong absorption band at ~650 nm. However, the BODIPY–azaBODIPY dyad 1 showed two clear absorption bands at 508 and 665 nm corresponding to BODIPY and azaBODIPY entities, respectively. Thus, the dyad 1 showed the absorption features of both constituent moieties without significant changes indicating that the azaBODIPY and BODIPY moieties retain their individual identity in dyad 1, although the red shift of nearly 15 nm compared to that in either 4 or equimolar mixture of BODIPY and azaBODIPY suggest existence of some intramolecular interactions between these two chromophores. Similar spectra were observed in benzonitrile (Supporting Information Figure S15).

The steady-state fluorescence spectrum of dyad 1 along with appropriate reference compounds were recorded in toluene using excitation wavelength of 505 nm. The 1,3,5,7-tetratolyl azaBODIPY 3 showed a strong fluorescence band at 695 nm with a quantum yield of 0.37. The 2-formyl azaBODIPY 2 was highly fluorescent and showed somewhat bathochromically shifted fluorescence band at 700 nm with a quantum yield of 0.80. The comparison of fluorescence spectra of dyad 1 along with its 1:1 mixture of constituted monomers 3 (azaBODIPY) and BODIPY recorded using excitation wavelength of 488 nm, where the BODIPY unit absorbs strongly, is shown in Figure Sa. The dyad 1, upon excitation at 488 nm, emission was noted at 700 nm corresponding to azaBODIPY, and no emission was observed at ~510 nm corresponding to BODIPY moiety. However, for the 1:1 mixture of monomers azaBODIPY and BODIPY, upon excitation at 488 nm, strong emission at ~510 nm of BODIPY along with weak emission at 700 nm of azaBODIPY were observed. Furthermore, the excitation spectrum of dyad 1 recorded by holding the emission monochromator at 720 nm corresponding to azaBODIPY emission wavelength showed the absorption features of both BODIPY and azaBODIPY units (Supporting Information Figure S16). The above observations support occurrence of

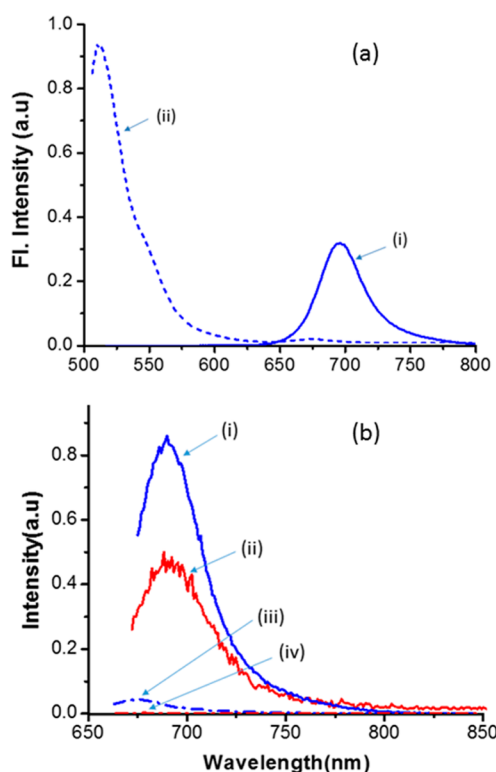


Figure 5. (a) Steady-state fluorescence spectrum of (a) (i) BODIPY-azaBODIPY dyad **1** and (ii) a 1:1 mixture of BODIPY and azaBODIPY in toluene at BODIPY excitation (505 nm). (b) Fluorescence spectrum of BODIPY-azaBODIPY dyad **1** in (i) toluene and (ii) benzonitrile; and (iii) azaBODIPY-DPM, **4** in toluene and (iv) in benzonitrile at azaBODIPY excitation of 665 nm.

efficient singlet-singlet excitation transfer from $^1\text{BODIPY}^*$ to azaBODIPY to yield $^1\text{azaBODIPY}^*$ in the dyad **1**.⁵⁴

The observed energy transfer in the BODIPY-azaBODIPY dyad could be explained either according to Dexter's exchange mechanism⁵⁵ or Förster's dipole-dipole mechanism.⁵⁶ However, considering the near orthogonality of the donor-acceptor entities in the present BODIPY-azaBODIPY dyad, contributions from Dexter's mechanism could be considered minimal.

For Förster mechanism, the rate of excitation transfer, $k_{\text{Förster}}$ is given by the following eq 1.

$$k_{\text{Förster}} = [8.8 \times 10^{-25} \times \kappa^2 \Phi_{\text{D}} J_{\text{Förster}}] / [\eta^4 \tau_{\text{D}} R^6] \quad (1)$$

where η is the solvent refractive index (1.496 in toluene and 1.528 in benzonitrile) and Φ_{D} and τ_{D} are the fluorescence quantum yield and the fluorescence lifetime of the pristine donor BODIPY, which are 0.044 and 3.5 ns in toluene and 0.043 and 2.9 ns in benzonitrile, respectively. R , the donor-acceptor distance, is 1.475 Å, based on the X-ray structure. In eq 1, κ^2 is the orientation factor, which is given in eq 2 and plays a key role in defining the directionality of energy transfer.

$$\kappa^2 = [\cos(\nu) - 3 \times \cos(\alpha)\cos(\beta)]^2 \quad (2)$$

where ν is the angle between the two transition dipoles, and α and β are the angles made by the transition dipoles of the donor and acceptor entities with the line joining the centers of the transitions. The value of κ^2 could range from 0 to 4 depending upon the relative orientation of the donor and acceptor. For parallel transition (head-to-tail) dipoles $\kappa^2 = 4$, for parallel dipoles $\kappa^2 = 1$, and for dipoles orthogonal to one other

$\kappa^2 = 0$, could be calculated. For randomly oriented dipoles a value of $\kappa^2 = 2/3$ is generally used. Considering the flexible nature of the connecting bond in the BODIPY-azaBODIPY dyad, a κ^2 value of two-thirds used for randomly oriented dipoles is employed in the present study.

The spectral overlap integral $J_{\text{Förster}}$ for the emission of the donor and absorption of the acceptor can be evaluated according to eq 3.

$$J_{\text{Förster}} = \int F_{\text{D}}(\lambda) \epsilon_{\text{A}}(\lambda) \lambda^4 d\lambda \quad (3)$$

where $F_{\text{D}}(\lambda)$ is the fluorescence intensity of the donor with total intensity normalized to unity. The $\epsilon_{\text{A}}(\lambda)$ refers to the molar extinction coefficient of the acceptor expressed in units of $\text{M}^{-1} \text{cm}^{-1}$ and λ in nanometers. In the present study, $J_{\text{Förster}}$ was calculated using a software provided by FluoTools.⁵⁷ The calculated $J_{\text{Förster}}$ was found to be $6.37 \times 10^{-14} \text{ M}^{-1} \text{cm}^3$ and $6.29 \times 10^{-14} \text{ M}^{-1} \text{cm}^3$, respectively, in toluene and benzonitrile. Using these $J_{\text{Förster}}$ values, the $k_{\text{Förster}}$ evaluated according to eq 1 was found to be $6.07 \times 10^{12} \text{ s}^{-1}$ in toluene and $6.68 \times 10^{12} \text{ s}^{-1}$ in benzonitrile, respectively. These calculations predict ultrafast singlet-singlet energy transfer in the closely linked BODIPY-azaBODIPY dyad. It may be pointed out here that under the conditions of close proximity of the donor and acceptor, contributions from intramolecular energy transfer via vibrational relaxation could also contribute to the overall excitation transfer process.

To further explore any photo events originated from $^1\text{azaBODIPY}^*$, formed either by direct excitation or by energy transfer in the BODIPY-azaBODIPY and DPM-azaBODIPY dyads, the fluorescence spectra of these compounds were studied in nonpolar toluene and polar benzonitrile, as shown in Figure 5b. The fluorescence intensity of BODIPY-azaBODIPY dyad **1**, excited at azaBODIPY peak maxima in toluene was comparable to that of directly excited pristine azaBODIPY (<10% change). However, the emission intensity of the dyad **1** was found to be quenched over 40% in benzonitrile. Interestingly, for DPM-azaBODIPY **4**, in both solvents azaBODIPY emission was found to be quenched (90% in toluene and 96% in benzonitrile). These results indicate excited-state events occurring from $^1\text{azaBODIPY}^*$ in the dyad **1** in benzonitrile, to a much lesser extent in toluene, and in DPM-azaBODIPY **4** in both solvents.

Further, electrochemical studies using differential pulse voltammetry (DPV) technique of the dyad **1** and DPM-azaBODIPY **4** along with the control compounds in benzonitrile containing 0.10 M ($n\text{Bu}_4\text{N}$)ClO₄ were performed to assess the redox potentials necessary to establish energy-level diagrams. The control compounds, BODIPY and azaBODIPY, revealed their first reversible oxidation and first reversible reduction processes at 0.73 and -1.63 V and at 0.76 and -0.79 V versus Fc/Fc⁺, respectively. The DPVs of azaBODIPY-aldehyde **2** was similar to that of pristine azaBODIPY, however, with easier oxidation and reduction processes (see Figure 6). Two oxidations at 0.56 and 0.86 and two reductions at -0.70 and -1.46 V vs Fc/Fc⁺ for **2** were observed. Interestingly, for azaBODIPY-DPM **4**, the reductions were found to be cathodically shifted compared to that in **2** and appeared at -0.89 and -1.70 V, while the oxidations were at 0.58 and 0.96 V vs Fc/Fc⁺. The harder reduction of azaBODIPY entity in **4** could be ascribed to the electronic effects induced by electron-rich DPM entity directly linked to the pyrrole ring of azaBODIPY unit. Finally, the DPVs of the dyad **1** revealed

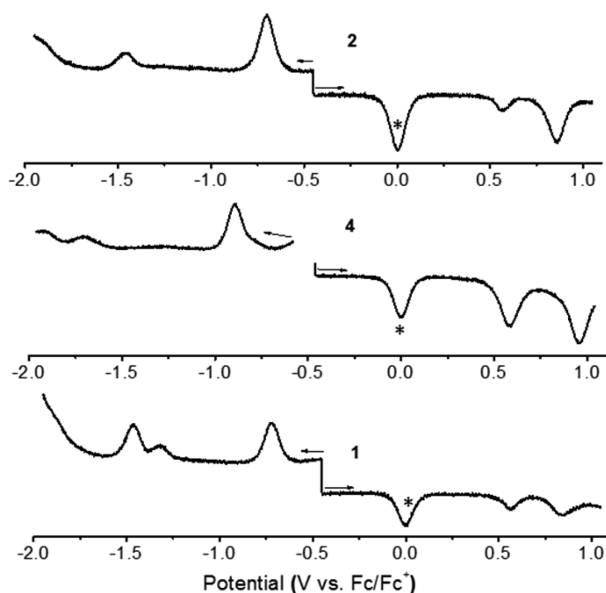


Figure 6. Differential pulse voltammograms of the designated compounds in benzonitrile containing 0.10 M $(^n\text{Bu}_4\text{N})\text{ClO}_4$. Scan rate = 5 mV/s, pulse width = 0.25 s, pulse height = 0.025 V. The asterisk (*) represents oxidation process of ferrocene used as internal standard.

oxidations at 0.56 and 0.84 and reductions at -0.71 , -1.31 , and -1.46 V versus Fc/Fc^+ . By comparison with pristine BODIPY and azaBODIPY DPVs, the first and second reductions are ascribed to azaBODIPY, while the third reduction is for the BODIPY entity. It is also worthwhile to note that the first oxidation processes of 1, 2, and 4 occur almost at the same potential.

The thermodynamic driving forces for the charge recombination ($-\Delta G_{\text{CR}}$) and charge separation ($-\Delta G_{\text{CS}}$) were estimated using eqs 2 and 3:^{58,59}

$$-\Delta G_{\text{CR}} = E_{1/2}(\text{D}^{\bullet+}/\text{D}) - E_{1/2}(\text{A}/\text{A}^{\bullet-}) + \Delta G_{\text{s}} \quad (2)$$

$$-\Delta G_{\text{CS}} = \Delta E_{0-0} - (-\Delta G_{\text{CR}}) \quad (3)$$

where $E_{1/2}(\text{D}^{\bullet+}/\text{D})$ is the potential for the first oxidation process of the donor, $E_{1/2}(\text{A}/\text{A}^{\bullet-})$ is the potential for the first reduction process of the acceptor, ΔE_{0-0} is the energy of the 0–0 transition (gap between the lowest excited state and the ground state of the sensitizers), and ΔG_{s} refers to the static Coulombic energy, calculated by using the “dielectric continuum model” according to eq 4:

$$\Delta G_{\text{s}} = \Delta G_{\text{s}} = e^2/4\pi\epsilon_0 \left[(1/2R_+ + 1/2R_-)\Delta(1/\epsilon_{\text{R}}) - \frac{1}{R_{\text{CC}}\epsilon_{\text{R}}} \right] \quad (4)$$

The symbols ϵ_0 and ϵ_{R} represent vacuum permittivity and dielectric constant of the solvent used for photochemical and electrochemical studies, respectively. R_{CC} is the center-to-center distance between donor and acceptor entities of the dyad. Together with the energy of $^1\text{BODIPY}^*$ (2.40 eV) and $^1\text{azaBODIPY}^*$ (1.85 eV), the free energy for the charge-separation processes ($-\Delta G_{\text{CS}}$) were calculated. Such calculations yielded a ΔG_{CS} value of -0.45 V for charge separation from BODIPY to the $^1\text{azaBODIPY}^*$ in benzonitrile. Similarly, a ΔG_{CS} value of -0.24 V for charge separation from DPM to the $^1\text{azaBODIPY}^*$ in benzonitrile was obtained. These ΔG_{CS} values would be higher by 0.14–0.15 eV in nonpolar toluene. Collectively, possibility of electron transfer in BODIPY– $^1\text{azaBODIPY}^*$ and DPM– $^1\text{azaBODIPY}^*$ is borne out from such calculations.

To probe the excited-state energy and electron-transfer events in the BODIPY–azaBODIPY and DPM–azaBODIPY dyads 1 and 4, respectively, femtosecond transient absorption studies were performed and the discussed below.

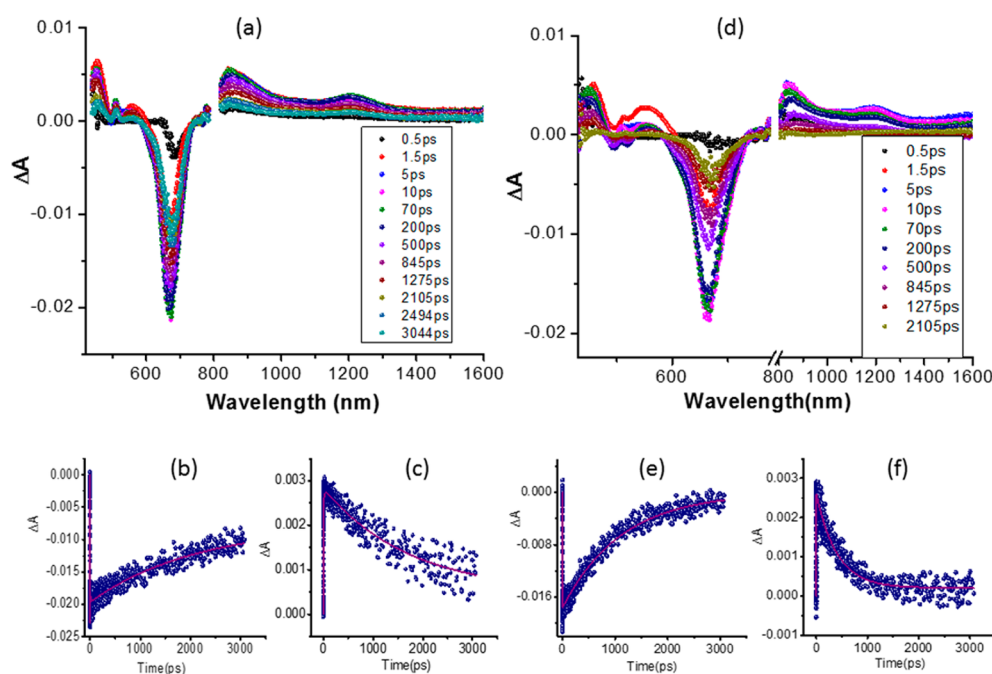


Figure 7. Femtosecond transient absorption spectra (400 nm of 100 fs pulse width) of BODIPY–azaBODIPY dyad at the indicated delay times in (a) toluene and (d) benzonitrile. Time profile of the 670 and 1150 nm peaks in toluene (b, c) and benzonitrile (e, f) are also shown.

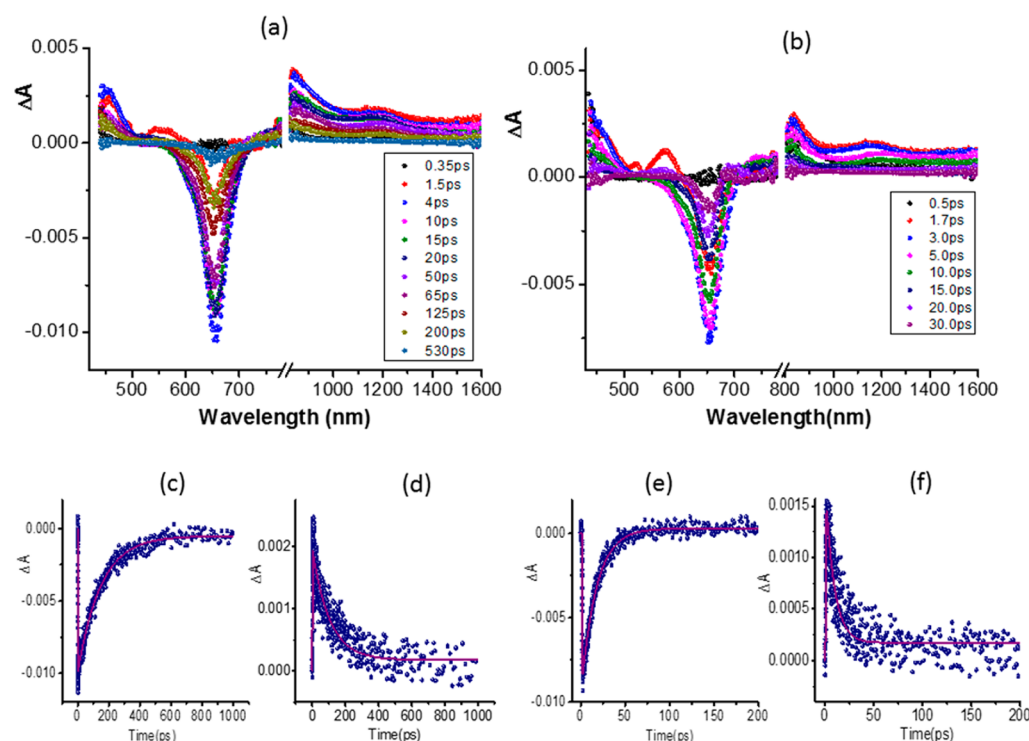


Figure 8. Transient absorption spectra of DPM–azaBODIPY dyad at the indicated delay times in (a) toluene and (d) benzonitrile. Time profile of the 670 and 1150 nm peaks in toluene (b, c) and benzonitrile (e, f) are also shown.

Femtosecond Transient Absorption Studies. The transient spectral features of pristine azaBODIPY and BODIPY are shown in Supporting Information Figure S17 and have been discussed earlier.^{41–43,60} Briefly, both sensitizers upon 400 nm excitation revealed almost instantaneous development of the singlet excited state features. In case of BODIPY, the spectra were dominated by noticeable bleaching in the 500 nm range due to depletion of the ground state and stimulated emission of the probe. Features of the BODIPY singlet excited state were relatively long-lived. The time constants for the recovery of the 505 nm band in toluene was 2500 ps, while for the 508 nm band in benzonitrile it was 1896 ps suggesting a slow intersystem crossing leading to the triplet excited state. Similarly, transient absorption spectra of azaBODIPY in toluene and benzonitrile revealed an almost instantaneously formed singlet excited state with peak maxima in the 515–845 nm range and a minima at 658 nm in toluene and maxima at 544–845 nm range and minima at 664 nm in benzonitrile. The time constant for the recovery of the ~660 nm peak was 3204 ps in toluene and 1825 ps benzonitrile. Extending the monitoring spectral window into the near-infrared region also revealed a new band at 1260 nm region, corresponding to the singlet–singlet transition. The decay time constant for this peak was 2138 ps in toluene and 1778 ps in benzonitrile, which are close to the lifetime determined using time-correlated singlet photon counting (TCSPC) method (1.88 ns in toluene and 1.69 ns in benzonitrile).

Figure 7a,d shows the transient difference spectra of BODIPY–azaBODIPY dyad **1** in toluene and benzonitrile, respectively. In both solvents, the transient bands corresponding to BODIPY were completely absent, and only that of azaBODIPY was observed. These results indicate occurrence of ultrafast singlet–singlet energy transfer that is difficult to resolve using our femtosecond transient setup with laser pulse

width of ~100 fs. Under these conditions, the estimated rate of energy transfer k_{ENT} would be greater than $1 \times 10^{12} \text{ s}^{-1}$, close to the value estimated from theoretical calculations according to Förster mechanism (vide supra). This is anticipated due to closeness of the donor and acceptor entities unlike previous studies on BODIPY–azaBODIPY dyads where the donor and acceptor entities were separated by spacers.^{35,42,45–50} As discussed earlier, formation of BODIPY^{•+}–azaBODIPY^{•-} charge-separated state from ¹azaBODIPY*, formed either by energy transfer or by direct excitation, is an exergonic process. The spectra shown in Figure 7 are supportive of this especially in polar benzonitrile solvent. That is, a broad peak ~800 nm corresponding to azaBODIPY^{•-}³⁴ and a peak at ~450 nm likely due to BODIPY^{•+}, absent in pristine azaBODIPY and BODIPY (see Supporting Information Figure S17), were observed. Faster ground-state recovery of the 660 nm peak and faster decay of the singlet–singlet transition peak of azaBODIPY located at 1150 nm (slightly blue-shifted due to ring substitution) than that observed for pristine azaBODIPY were seen. The decay time constant for the latter peak was found to be 1730 ps in toluene and 539 ps in benzonitrile, respectively, smaller than that observed for pristine azaBODIPY. The rate of charge separation k_{CS} , obtained by monitoring the decay of this peak using the standard procedure,⁶¹ was found to be $1.18 \times 10^8 \text{ s}^{-1}$ in toluene and $1.30 \times 10^9 \text{ s}^{-1}$ in benzonitrile, respectively.

Author: Please verify that the changes made to improve the English still retain your original meaning. The possibility of electron transfer in DPM–azaBODIPY was also investigated. As shown in Figure 8a,d, transient spectral features of the DPM^{•+}–azaBODIPY^{•-} charge-separated state was evident in the investigated solvents. That is, azaBODIPY^{•-} peaks in the 800 nm region and broad spectral features in the 450 nm range likely due to the formation of DPM^{•+} were observed.

Importantly, the recovery of the 670 nm peak and decay of the 1150 nm singlet peak of azaBODIPY were faster than that observed for pristine azaBODIPY or BODIPY–azaBODIPY dyad **1**. The decay time constants for the near-IR peak was found to be 215 and 50 ps in toluene and benzonitrile, respectively, yielding k_{CS} values of $4.24 \times 10^9 \text{ s}^{-1}$ in toluene and $1.90 \times 10^{10} \text{ s}^{-1}$ in benzonitrile, respectively. Faster charge separation in DPM–azaBODIPY dyad **4** than that in BODIPY–azaBODIPY dyad **1** was evident from this study. In case of both BODIPY–azaBODIPY **1** and DPM–azaBODIPY **4**, the charge recombination process provided no proof of $^3\text{BODIPY}^*$ (in case of **1**) or $^3\text{azaBODIPY}^*$ formation suggesting direct relaxation of the charge-separated state to the ground state of the molecules.

Figure 9 summarizes the photochemical/photophysical processes in the form of an energy diagram for the directly

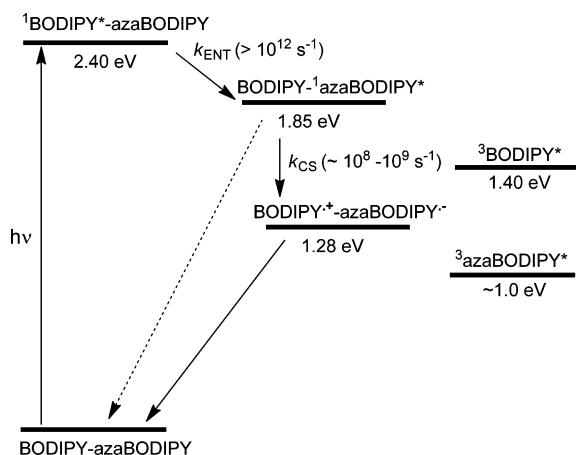


Figure 9. Energy-level diagram depicting photoinduced energy-transfer and electron-transfer processes in the directly linked BODIPY–azaBODIPY dyad in benzonitrile and toluene (solid arrow—dominant process; dashed arrow—less likely process).

linked BODIPY–azaBODIPY dyad **1**. Excitation of the BODIPY entity selectively within the dyad **1** instantaneously creates $^1\text{BODIPY}^*$. Energy transfer from this state to the directly attached azaBODIPY occurs at a rate higher than $1 \times 10^{12} \text{ s}^{-1}$. In both solvents, charge separation from BODIPY to $^1\text{azaBODIPY}^*$ occurs yielding $\text{BODIPY}^{\bullet+}\text{--azaBODIPY}^{\bullet-}$ radical ion pair. The measured kinetic values suggest such a reaction is more facile in polar benzonitrile than that in nonpolar toluene. The charge separation product, $\text{BODIPY}^{\bullet+}\text{--azaBODIPY}^{\bullet-}$ relaxes directly to the ground state without the intermediate creation of the triplet states of either BODIPY or azaBODIPY.

In the case of DPM–azaBODIPY dyad **4**, due to the facile oxidation of DPM entity, electron transfer from $^1\text{azaBODIPY}^*$ leading to the formation of $\text{DPM}^{\bullet+}\text{--azaBODIPY}^{\bullet-}$ charge-separated state is observed. The measured rates in both toluene and benzonitrile are found to be nearly an order of magnitude higher compared to that observed for the BODIPY–azaBODIPY dyad **1**. One possible reason for this behavior could be the flexibility of DPM entity, which would bring the free-to-rotate pyrrole entities of DPM even closer to the azaBODIPY, thus accelerating electron transfer.

SUMMARY

Intramolecular interactions in a newly synthesized, directly linked via β -pyrrole ring carbon, BODIPY–azaBODIPY dyad has been established from spectral and electrochemical studies. The relative orientation of the two macrocycles and the structural integrity was established from X-ray structural, HRMS, and ^1H – ^1H COSY and NOESY NMR studies. As predicted by theoretical calculations, occurrence of ultrafast energy transfer from the $^1\text{BODIPY}^*$ to azaBODIPY within the dyad was witnessed. Further, occurrence of additional electron transfers from $^1\text{azaBODIPY}^*$ to BODIPY in the BODIPY–azaBODIPY dyad leading $\text{BODIPY}^{\bullet+}\text{--azaBODIPY}^{\bullet-}$ charge-separated state and from $^1\text{azaBODIPY}^*$ to DPM in the DPM–azaBODIPY dyad leading to $\text{DPM}^{\bullet+}\text{--azaBODIPY}^{\bullet-}$ charge-separated state were spectroscopically established by femto-second pump–probe spectral studies. The relaxation of the charge-separated species in both cases yielded ground-state molecules without intermediate population of $^3\text{BODIPY}^*$ or $^3\text{azaBODIPY}^*$. Further studies in building fast-responding donor–acceptor systems via energy or electron transfer are in progress in our laboratories.

EXPERIMENTAL SECTION

Parts of the experimental section, including supplier information on chemicals and reagents, methods, and instrumental details, are given in the Supporting Information.

General Procedure for the Preparation of azaBODIPY Precursor Compounds **1, **2**, and **4**. 2-Formyl azaBODIPY **2**.** In an ice bath, a mixture of DMF (5 mL) and POCl_3 (5 mL) was stirred for 5 min under N_2 atmosphere. The mixture was brought to room temperature and stirred for additional 10 min. The sample of 1,3,5,7-tetratolyl azaBODIPY **3** (200 mg, 0.3 mmol) in dichloroethane (50 mL) was added to the reaction mixture. The reaction temperature was slowly raised to 80°C and stirred for 3 h. After it cooled, the reaction mixture was poured into ice-cold saturated aqueous NaHCO_3 (200 mL) solution and stirred for additional 30 min. The organic layer was collected and dried over anhydrous NaSO_4 . The solvent was removed on rotary evaporator under vacuum, and the resulting crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (80:20, v/v) and afforded pure 2-formyl azaBODIPY **2** as a reddish-brown solid. Yield, 85% (180 mg), ^1H NMR (400 MHz, CDCl_3 , δ in ppm): 2.34 (s, 3H; CH_3), 2.36 (s, 3H; CH_3), 2.37 (s, 3H; CH_3), 2.41 (s, 3H; CH_3), 7.10 (s, 1H; py), 7.16 (d, 3J (H, H) = 8.1 Hz, 2H; Ar), 7.21–7.25 (m, 6H; Ar), 7.54 (d, 3J (H, H) = 8.0 Hz, 2H; Ar), 7.70 (d, 3J (H, H) = 8.1 Hz, 2H; Ar), 7.90–7.93 (m, 4H; Ar), 9.75 (s, 1H; CHO). ^{11}B NMR (128.3 MHz, CDCl_3 , δ in ppm): 1.01 (t, 1J (B–F) = 30.1 Hz, 1B). ^{19}F NMR (376.4 MHz, CDCl_3 , δ in ppm): –131.55 (q, 1J (F–B) = 31.0 Hz, 2F). ^{13}C NMR (100 MHz, CDCl_3 , δ in ppm): 21.6, 21.7, 21.8, 126.9, 127.5, 128.1, 128.3, 128.5, 128.7, 129.5, 129.6, 129.7, 130.3, 130.4, 131.9, 140.0, 140.4, 141.3, 143.8, 186.4. HRMS. Calcd for $\text{C}_{37}\text{H}_{31}\text{BF}_2\text{N}_3\text{O}$ [(M + H) $^+$]: m/z 582.2529. Found: m/z 582.2531.

2-Dipyrromethanyl azaBODIPY **4.** To a solution of 2-formyl azaBODIPY **2** (1.75 mmol, 200 mg) and pyrrole (70 mmol) in dichloromethane (100 mL), catalytic amount of $\text{BF}_3\cdot\text{OEt}_2$ (0.175 mmol) was added, and the reaction mixture was stirred at room temperature for 15 min under inert conditions. After standard work up, the crude dark red oil was purified by silica gel column chromatography using petroleum ether/ethyl

acetate (85:15) to afford pure 2-dipyrromethanyl azaBODIPY 4 as a blue-green solid. Yield, 62% (150 mg). ^1H NMR (400 MHz, CDCl_3 , δ in ppm): 2.27 (s, 3H; CH_3), 2.34 (s, 3H; CH_3), 2.42 (s, 3H; CH_3), 2.44 (s, 3H; CH_3), 5.59 (s, 1H; CH), 5.86 (s, 2H; py), 6.06–6.08 (m, 2H; py), 6.49–6.51 (m, 1H; py), 6.96 (s, 1H; CH), 7.17 (d, 3J (H, H) = 8.2 Hz, 4H; Ar), 7.19–7.29 (m, 12H; Ar), 7.55 (s, 1H; NH), 7.87 (d, 3J (H, H) = 8.3 Hz, 2H; Ar), 7.86 (d, 3J (H, H) = 8.2 Hz, 2H; Ar). ^{11}B NMR (128.3 MHz, CDCl_3 , δ in ppm): 0.60 (t, 1J (B–F) = 30.4 Hz, 1B). ^{19}F NMR (376.4 MHz, CDCl_3 , δ in ppm): –132.9 (q, 1J (F–B) = 30 Hz, 2F). ^{13}C NMR (100 MHz, CDCl_3 , δ in ppm): 21.6, 21.6, 21.7, 21.8, 29.9, 35.1, 107.6, 108.6, 117.0, 118.6, 128.6, 128.7, 128.8, 129.0, 129.2, 129.4, 129.5, 129.6, 129.7, 131.2, 131.5, 138.8, 139.7, 140.2, 142.0. HRMS. Calcd for $\text{C}_{45}\text{H}_{39}\text{BF}_2\text{N}_5$ [(M + H) $^+$]: m/z 698.3269. Found: m/z 698.3267.

BODIPY–azaBODIPY Dyad 1. A sample of 2-dipyrromethanyl azaBODIPY 4 (0.14 mmol, 100 mg) was dissolved in dichloromethane (70 mL) and oxidized with DDQ (0.17 mmol) at room temperature for 30 min under stirring. After addition of triethylamine (68 mmol) and $\text{BF}_3\cdot\text{Et}_2\text{O}$ (85 mmol), the reaction mixture was stirred at room temperature for an additional 30 min. The solvent was removed under vacuum, and the resulting crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (80:20) to obtain pure azaBODIPY–BODIPY dyad 1 as golden red solid. Yield 30% (35 mg). ^1H NMR (400 MHz, CDCl_3 , δ in ppm): 2.27 (s, 3H; CH_3), 2.34 (s, 3H; CH_3), 2.42 (s, 3H; CH_3), 2.44 (s, 3H; CH_3), 6.29 (dd, 3J (H, H) = 4.2 Hz, 2H; py), 6.80 (d, 3J (H, H) = 3.9 Hz, 2H; py), 7.05 (d, 3J (H, H) = 8.0 Hz, 2H; Ar), 7.10 (d, 3J (H, H) = 8.0 Hz, 2H; Ar), 7.15 (s, 1H; py), 7.25–7.31 (m, 4H; Ar), 7.43–7.51 (m, 4H; Ar), 7.73 (s, 2H; py), 7.85 (d, 3J (H, H) = 8.0 Hz, 2H; Ar), 8.0 (d, 3J (H, H) = 8.3 Hz, 2H; Ar). ^{11}B NMR (128.3 MHz, CDCl_3 , δ in ppm): 0.17 (t, 1J (B–F) = 160.0 MHz, 1B), 0.89 (t, 1J (B–F) = 30 Hz, 1B). ^{19}F NMR (376.4 MHz, CDCl_3 , δ in ppm): –131.1 (q, 1J (F–B) = 35 Hz, 2F), –146.1 (m, 2F). ^{13}C NMR (100 MHz, CDCl_3 , δ in ppm): 2.16, 21.7, 21.8, 22.0, 118.6, 120.0, 127.6, 128.2, 128.7, 129.0, 129.2, 129.4, 129.6, 129.8, 129.9, 130.3, 130.6, 131.2, 135.9, 139.3, 140.4, 141.1, 142.0, 143.4, 143.9, 146.6, 148.0, 155.4. HRMS. Calcd for $\text{C}_{45}\text{H}_{36}\text{B}_2\text{F}_4\text{N}_5$ [(M + H) $^+$]: m/z 744.3102. Found: m/z 744.3101.

■ ASSOCIATED CONTENT

■ Supporting Information

^1H , ^{13}C , ^{11}B , and ^{19}F NMR and HRMS of the newly synthesized compounds, absorption and emission data in benzonitrile, excitation spectra of 1 in toluene, femtosecond transient spectra of BODIPY and azaBODIPY in toluene and benzonitrile, illustration of dyad ground- and excited-state interactions, and crystallographic information in CIF file. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b06328.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Authors are thankful to the National Science Foundation (Grant No. 1401188 to F.D.) and Department of Science and Technology, Government of India (File No. SR/S1/IC-12/2011 to M.R.) for support of this work.

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