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Directly Attached Bisdonor-BF₂ Chelated Azadipyrromethene-Fullerene Tetrads for Promoting Ground and Excited State Charge Transfer

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Abstract: The efficiency and mechanism of electron- and energy transfer events occurring in both in natural and synthetic donor-acceptor systems depend on their distance, relative orientation, and the nature of the surrounding media. Fundamental knowledge gained from model studies is key in building efficient energy harvesting and optoelectronic devices. Faster charge separation and slower charge recombination in donor-acceptor systems is often sought out. In our continued effort to build donoracceptor systems using near-IR sensitizers, in the present study, we report ground and excited state charge transfer in newly synthesized, directly linked, tetrads featuring bisdonor (donor = phenothiazine ferrocene), **BF₂-chelated** and azadipyrromethane (azaBODIPY) and C₆₀ The tetrads synthesized using entities. multi-step synthetic procedure revealed strong charge transfer interactions in the ground state involving the donor and azaBODIPY entities. The near-IR emitting azaBODIPY acted as a photosensitizing electron acceptor along with fullerene while the phenothiazine and ferrocene entities acted as electron donors. The triads (bisdonor-azaBODIPY) and tetrads revealed ultrafast photoinduced charge separation leading to D⁺⁺-azaBODIPY⁻⁻-C₆₀ and D⁺⁺ azaBODIPY-C₆₀⁻⁻ (D = phenothiazine c ferrocene) charge separated states from th femtosecond transient absorption spectra studies in both polar and nonpolar solver media. The charge separated state populated the triplet excited state c azaBODIPY prior returning to the groun state.

Keywords: charge separation . BF_2 chelated azadipyrromethene . C_{60} . ferrocene, phenothiazine

Introduction

Development of functional materials capable of light capture and conversion are key in building devices capable of efficient conversion of solar energy either into electricity or fuel.^[1] This would offer environmentally clean energy for human needs.^[2] By mimicking the natural photosynthesis^[3] using electron donor-acceptor based molecular/supramolecular assemblies, photocatalysis for the production of clean fuels and materials for optoelectronics are often targeted.^[4-10] In the construction of such assemblies, development of electron donor and electron acceptor molecules capable of wide-band capture covering the visible and near-infrared region of the electromagnetic spectrum and well-tuned redox states are realized to be important. Engineered molecules with matched spectral and redox states are expected to result in fast and efficient charge transfer events.

BF₂-chelated azadipyrromethene (azaBODIPY),^[11] a structural analogue of BF₂-chelated dipyrromethene (BODIPY[®]),^[12] has recently gained much attention for its novel photophysical/photochemical properties. AzaBODIPY absorbs in the 300-700 nm region with very high molar absorptivities, and desirable emission in the red region (660-750 nm) with quantum yields exceeding 40%.^[11] Additional peripheral modifications of

azaBODIPY allows the excitation and emission well into the near IR region.^[13] Consequently, azaBODIPYs are one of the highl sought out fluorophores for energy harvesting,^[8] sensing,^[14] an imaging^[15] applications. Interestingly, the facile reduction c azaBODIPYs makes it a rarely encountered electron acceptor photosensitizer molecule.^[16] They differ from other electro acceptor-photosensitizer molecules due to their ability to emit in th near-IR region with high fluorescence quantum yields.



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Supporting information for this article, additional spectral and femtosecond spectra, ¹H and ¹³C NMR and MALDI-mass of triads and tetrads.

Figure 1. Structures of the newly synthesized, directly linked bisdonor-azaBODOPY- C_{60} tetrads, 1 and 2, and bisdonor-azaBODOPY triads, 1d and 2d.

Photosynthetic model compounds developed using azaBODIPY have revealed several interesting features. For example, when azaBODIPY was connected to ferrocene, efficient

photoinduced electron transfer from ferrocene to singlet excited azaBODIPY was observed.^[16] Alternatively, when C₆₀ was covalently linked azaBODIPY, electron transfer leading to the formation of azaBODIPY⁺⁺-C₆₀⁻⁻ was observed.^[17] Excitation transfer was observed when either chlorophyll derivatives or BODIPY was covalently linked to azaBODIPY.^[18] Interestingly, when a bisporphyrin was covalently linked to azaBODIPY, the resulting 'molecular clip' supramolecularly assembled to C60 via metal-ligand coordination. In this supramolecular assembly, control over energy and electron transfer events was possible to accomplish.^[19a] Furthermore, by a combination of zinc porphyrin, BODIPY and azaBODIPY, a broad-band capturing the emitting supramolecular triad useful for energy harvesting and building optoelectronic devices was recently reported.^[19b] This strategy was used to develop and demonstrate excited state charge separation in bisferrocene-azaBODIPY-C₆₀ tetrads.^[20] However, this was not the case when ferrocene entities were replaced by phenothiazine entities due to harder oxidation of the latter.^[21] Using V-configuration of triads, through-space and through-bond electron transfer events was also demonstrated.^[22] Competitive electron transfer in a supramolecular triad featuring subphthalocyanine/BODIPY, azaBODIPY and fullerene was recently reported.^[23] Self-assembly approach involving metal-ligand axial coordination was utilized for azaBODIPY-phthalocyanine and azaBODIPYbuild naphthalocyanine conjugates and occurrence of excited state energy and electron transfer were reported.^[24] More recently, by performing peripheral functionalization of azaBODIPY to extend the absorption and emission into the near-IR region, the dyads formed by using C₆₀ as electron acceptor were shown to undergo charge separation upon photoexcitation.^[25]

Inspired by the above findings and our continued effort to unravel the donor and acceptor behavior of azaBODPY derived higher supramolecular analogs, in the present study, we report syntheses, physico-chemical characterization, and excited state charge transfer in directly linked bisdonor-azaBODIPY-C₆₀ tetrads and bisdonor-azaBODIPY triads^[26] whose structures are shown in Figure 1. As a result of direct covalent connectivity between the donor (phenothiazine or ferrocene) entities and azaBODIPY, strong electronic coupling have been observed. Cross-communication between the two donor entities via the azaBODIPY macrocycle both in the triads and tetrads have been witnessed from electrochemical studies. This was unlike the previous studies^[20] where the donor and acceptor entities were spatially well-separated thus avoiding strong intramolecular interactions. Excited state events in these triads and tetrads are probed by using femtosecond transient absorption spectroscopy.

Results and Discussion

Synthesis of the triads and tetrads: Scheme 1 summarizes the syntheses of triads and tetrads while details are given in the experimental section. Briefly, compound 1 was synthesized using intermediates **1a-1e**. To synthesize the chalcone, phenothiazine was used to obtain the needed aldehyde derivative according to Scheme 2, first, using N-alkylation to synthesize N-ethylphenothiazine. Then, by formylation using the phosphoryl chloride method. Chalcone, **1a** was then obtained by combining N-ethylphenothiazine aldehyde and acetophenone in the presence of KOH. The chalcone was combined with nitromethane in the presence of diethylamine and then allowed to run under reflux conditions for 24 hours. This yielded the nitro derivative, **1b**. Compound **1b** was reacted with ammonium acetate and reaction proceeded as described above. Chelation of compound **1c** was achieved using the boron trifluoride diethyl etherate to obtain **1d**. Following chelation, an aldehyde

derivative was obtained by reacting **1d** with aluminum chloride and dihydroxybenzaldehyde to yield **1e**. Finally, **1e** was dissolved in toluene and combined with fullerene and sarcosine to yield compound **1**.

For the synthesis of 2, the desired chalcone was obtained by grinding ferrocene carboxaldehyde and acetophenone in the NaOH.^[26d] Following presence of purification and characterization, chalcone was combined with nitromethane in the presence KOH and then allowed to run under reflux for 24 h. This yielded the nitro derivative which was reacted with ammonium acetate in ethanol under reflux conditions. Chelation of compound 2c was achieved by combining 2c with diisopropylethylamine and boron trifluoride diethyl etherate to obtain 2d. Following chelation, an aldehyde derivative, 2e wa obtained by combining starting material with aluminum chlorid followed by reacting it with 3,4-dihydroxybenzaldehyde Finally, 2e was dissolved in toluene and combined with C₆₀ an sarcosine to yield compound 2. All of the new compounds wer fully characterized by ¹H and ¹³C NMR, Maldi-TOF-Mass absorption/emission, and electrochemical methods. Th compounds were stored in dark prior doing photochemica studies.



Scheme 1. Synthetic methodology developed for triads, 1d and 2d, and tetrads, 1 and 2.

Absorption and emission studies: Significant intramolecula interactions leading to new charge tranfer band in the longe wavelength region was observed for the studied triads an Figure 2a shows the absorption spectra of th tetrads. investigated compounds along with the reference pristin azaBODIPY (the peripheral phenothiazine or ferrocene entitie were replaced by phenyl entities). The absorption bands c pristine azaBODIPY were located at 484 and and 658 nm. Scanning the wavelength beyond 700 nm revealed no absorbance bands. In contrast, a new broad absorbance peak at higher wavelengths was observed for the triads and tetrads. For 1d and 1, the new broad peak was located at 709 and 690 nm, respectively, while the visible band of azaBODIPY core was blue-shifted compared to pristine azaBODIPY and appeared at 602 and 610 nm. The characteristic peak of fulleropyrrolidine at 432 nm was also observed for the tetrad, 1. From a solvent polarity study, the new broad near-IR peak was assigned to charge transfer band (red-shif with increased solvent polarity).

Similar observations were also made for compounds 2d and 2. For triad 2d, the absorption bands were located at 464, 632 and 864 nm while for tetrad, 2 these peaks were located at 462, 620, and 882 nm. The fulleropyrrolidine peak at 432 nm was also observed for 2. These spectral trends were similar to that observed for 1d and 1. In summary, strong charge transfer type interactions leading to a new absorption band in the near-IR region in the directly connected donor-acceptor systems is witnessed. This is in contrast to the earlier reported donor-acceptor systems with azaBODIPY^[20] where due to distal separation, no such such charge transfer was witnessed.



Figure 2. (a) Normalized absorption and (b) fluorescence spectra of the indicated compounds in benzonitrile (see Figure 1 for structures). The samples were excited at the most intense visible peak maxima.

As shown in Figure 2b, the fluorescence spectrum of azaBODIPY revealed a peak at 682 nm. However, for the triads and tetrads, no detectable fluoresence was observed (>98% quenching). Such quenching behavior was also observed in nonpolar toluene.

Electrochemical, spectroelectrochemical and computational studies: First, electrochemical studies using cyclic and differential pulse voltammetry were performed in benzonitrile. As reported earlier, the first reversible oxidation and reduction processes of azaBODIPY were located at 1.26 and -0.32 V vs. Ag/AgCl. For 1d with two phenothiazine entities directly attached onto the azaBODIPY π -system, the first oxidation involving the phenothiazine entities revealed split peaks located at 0.75 and 0.79 V (a 40 mV separation) instead of the anticipated a single twoelectron process involving the two phenothiazine entities (Figure 3a). Such split suggests communication between the two redox active phenothiazine entities via azaBODIPY π -system.²⁶ Larger the magnitude of peak separation, higher is the interaction between them. A third oxidation at 1.27 V vs. Ag/AgCl corresponding to azaBODIPY oxidation was also observed. The two reductions of azaBODIPY were located at -0.34 and -1.13 V vs. Ag/AgCl. Appending C₆₀ at the boron center of azaBODIPY did not perturb

the electronic communication between the two phenothiazine entities as shown in Figure 3b. That is, split oxidation corresponding to phenothiazine located at 0.77 and 0.82 V were observed. The splitting between these two peaks was around 50 mV. The fullerene reductions in 1 appeared at -0.52 and -0.94, that is, after the first reduction of azaBODIPY reduction located at -0.32 V vs. Ag/AgCl. A similar trend in the redox chemistry of 2 and 2d where two ferrocene entities were directly attached to the azaBODIPY core was also observed. In the case of 2d, the split ferrocene oxidations were located at 0.56 and 0.64 V, that is, an 80 mV potential separation was witnessed. The azaBODIPY oxidation and reductions were located at 1.34 and -0.46 V, respectively (Figure 3c). Covalent attachment of C₆₀ at the boron center retained the overall behavior in 2 (Figure 3d). That is, split oxidation wit peak positions located at 0.55 and 0.66 V and a third oxidation a 1.39 V corresponding to azaBODIPY were observed. On th reduction side, azaBODIPY reduction at -0.46 and C60 reductions a -0.54 and -0.96 V vs. Ag/AgCl were observed. Higher splitting i 2d/2 compared to 1d/1 indicated better ferrocene-ferrocen interaction over phenothiazine-phenothiazine interaction via th azaBODIPY π -system in the investigated multi-modular systems Also, harder azaBODIPY reduction in 2 over 1 were noteworth observations. The electrochemical data is summarized in Table below.



Figure 3. Differential pulse voltammograms of the indicated compounds i benzonitrile containing 0.1 M (TBA)ClO₄. The potentials are referenced t Ag/AgCl. Scan rate = 5 mV/s, pulse width = 0.25 s, pulse height = 0.025 V The peak shown in asterisk corresponding to ferrocene used as interna reference.

Table 1. Redox Potentials (V vs. Ag/AgCl) of the investigated compounds i deaerated PhCN containing 0.1 M (TBA)ClO₄ (ADP = azaBODIPY; D phenothiazine or ferrocene))

Compound	C ₆₀ -/C ₆₀	ADP -/ADP	D*+/D	ADP ·+/ADP
ADP		-0.32		1.26
1d		-0.34	0.75, 0.79	1.27
1	-0.52	-0.32	0.77, 0.83	1.28
2d		-0.46	0.56, 0.64	1.34
2	-0.54	-0.46	0.55, 0.66	1.39

Next, spectroelectrochemical studies were performed to spectrally characterize the first oxidized and reduced species of compounds 1 and 2. Figure 4a and b, respectively, show the spectral changes during the first oxidation and reduction of 1 in benzonitrile containing 0.1 M (TBA)CIO₄. During the first oxidation, the peaks of neutral 1 located at 612 and 688 nm revealed

diminished intensity with the appearance of new peaks at 493, 598, and 780 nm. The shift of the charge transfer band from 688 nm to 780 nm is noteworthy. During the reduction, diminished intensity of the peaks of neutral 1 was accompanied by new peaks at 473 and 850 nm, corresponding mainly to the azaBODIPY ring reduction was observed. An isosbestic point at 530 nm was also observed. For 2 with directly attached ferrocene units, the peaks of the neutral compound located at 462, 620 and 878 nm revealed diminished intensity with the appearance of new peaks at 642 and 906 nm (Figure 4c). Isosbestic points at 482, 552, and 725 nm were observed. During the first reduction of 2, disappearance of the peaks corresponding to the neutral compound was accompanied by a broad peak in the 420 and 800-1000 nm range (Figure 4d). An isosbestic point at 516 nm was also observed. These spectral data help interpretation of the transient absorption spectral data discussed in the next section.



Figure 4. Spectral changes observed during first (a) oxidation of **1**, (b) reduction of **1**, (c) oxidation of **2**, and (d) reduction of **2** in benzonitrile, 0.1 M (TBA)ClO₄.



Figure 5. APFD/6-311G** (H, B, C, N, O, F) APFD/6-311G(df) (S, Fe) optimized geometry (a and b) and molecular electrostatic potential map (c and d) of 1 and 2.

Geometry optimizations using the APFD method and a mixed basis of $6-311G^{**}$ for H, B, C, N, O, and F atoms and 6-311G(df) for S and Fe atoms^[27] on both the tetrads were performed. As shown in Figure 5a and b, no steric constraints either at the directly

linked donor (phenothiazine or ferrocene) or acceptor C_{60} sites was observed. The dihydroxyphenyl spacer group between the boron center and fulleropyrrolidine assumed a perpendicular orientation with respect to the plane of the azaBODIPY ring. The two donor entities were facing away due to the nature of substitution on the azaBODIPY ring causing no intramolecular type interactions between them. As discussed earlier, intramolecular interactions between the two donor entities was observed through the azaBODIPY π -system. The molecular electrostatic potential map (MEP map) for the tetrads is shown in Figures 5c and d revealed the expected electron rich (donor location) and deficient (azaBODIPY and C₆₀ locations) sites. In summary, a very good agreement between the optical, electrochemical and computed electronic structures of the tetrads were observed.

Energy calculations: The energy of the charge-separated states (free-energy of charge recombination, ΔG_{CR}) were calculated usin the redox, geometric and optical data, according to Rehm-Welle approach^[28] and dielectric continuum model to account for th solvation energy (see Table 2 footnote for pertinent equations). B comparing these energy levels of the charge-separated states wit the energy levels of the excited singlet states of azaBODIPY or C_{6} the driving forces of charge separation (- ΔG_{CS}) were also evaluated The data thus generated for the triads and tetrads is given are Tabl 2 below. The generation of PTZ⁺⁺-ADP⁻⁻-C₆₀ and PTZ⁺⁺-ADP-C₆₀ in 1, and Fc⁺-ADP⁻-C₆₀ and Fc⁺-ADP-C₆₀⁻ in 2 is found to b exergonic either from the singlet excited state of azaBODIP' $(^{1}azaBOPDY^{*})$ or the singlet excited state of C_{60} $(^{1}C_{60}^{*})$. However the processes originating from the ¹azaBODIPY* state were foun to be energetically much more favorable than the processe originating from ${}^{1}C_{60}*$.

Table 2. Free-energy for charge recombination (ΔG_{CR}) and charg separation (ΔG_{CS}) from ¹azaBOPDY* and ¹C₆₀* in the investigate compounds (D = PTZ or ferrocene; ADP = azaBODIPY) i benzonitrile.

Compound	$\Delta G_{ m CR}{}^{ m a}$		$\Delta G_{\rm CS}{}^{ m b}$		
	D*+-ADP*-	D++-C ₆₀	D++-ADP	D•+C ₆₀ •-	
1d	-1.13		-0.72°		
1	-1.13	-1.33	-0.72°	-0.52°	
			-0.62 ^d	-0.41 ^d	
2d	1.05		-0.80°		
2	1.06	1.10	-0.80°	-0.72°	
			-0.70 ^d	-0.62 ^d	
a –/	$-\Delta G_{\rm CR} = E_{\rm ox} - E_{\rm red} + \Delta G_{\rm S}$			(i)	
b/	$\Lambda G_{aa} = \Lambda F_{aa} = (-$	$\Lambda G_{\rm cm}$	(ii)		

where ΔE_{00} corresponds to the energy of ¹azaBODIPY* (= 1.85 eV) an ${}^{1}C_{60}*$ (1.75 eV). The term ΔG_{S} refers to electrostatic energy calculate according to dielectric continuum model (see equation iii). The E_{ox} and E_{r} represent the oxidation potential of the electron donor (PTZ or ferrocene) and the reduction potential of the electron acceptor (azaBODIPY or C_{60}), respectively.

$$\Delta G_{\rm S} = \Delta G_{\rm S} = e^2 / 4\pi\varepsilon_0 \left[\left(\frac{1}{2R_+} + \frac{1}{2R_-} \right) \Delta \left(\frac{1}{\varepsilon_R} \right) - \frac{1}{R_{\rm CC}\varepsilon_R} \right]$$
(iii)

The symbols ε_0 , and ε_R represent vacuum permittivity and dielectric constant of the solvent used for photochemical and electrochemical studies, respectively. R_+ and R_- represent radii of the cation and anion, respectively. R_{CC} is the center-to-center distance between donor and acceptor entities of the dyad from the computed structures in Figure 5. ^efrom ¹azaBODIPY*

dfrom 1C60*

Energy level diagrams were established to secure a complete picture of the possible photophysical events in the studied compounds. Figures S1a and S1b in the supporting information (SI) illustrate energy level diagrams for 1d and 2d, respectively. Formation of charge separated states, PTZ^{+} -azaBODIPY⁻ in 1d and Fc⁺-azaBODIPY⁻ in 2d is thermodynamically possible upon selective excitation of the azaBODIPY to its singlet excited state. The energy of the charge separated state in both cases is slightly above that of ³azaBODIPY^{*}. Under these conditions, the charge separated state could populate the ³azaBODIPY^{*} instead of direct charge recombination to the ground state. Additionally, in the case of 2d, the ³azaBODIPY^{*} could undergo further triplet-triplet energy transfer to the low-lying ³Fc^{*.[29]} from which the molecule could return to the ground state via nonradiative decay path.



Figure 6. Energy level diagram showing the different photochemical events occurring in (a) **1** and (b) **2** in benzonitrile. Energies of different states were evaluated from spectral and electrochemical studies. Solid arrows indicate major photo-processes, dashed arrow indicates minor photo-process. EnT – energy transfer, CS = charge separation, CR = charge recombination, and T = emission from triplet excited state.

For the tetrads **1** and **2**, a slightly more complicated energy level diagrams were arrived, as shown in Figure 6a and b. Formation of two types of charge separated states, viz., PTZ⁺⁺azaBODIPY⁻-C₆₀ and PTZ⁺⁺-azaBODIPY-C₆₀⁻⁻ in the case of **1**, and Fc⁺-azaBODIPY⁻-C₆₀ and Fc⁺-azaBODIPY-C₆₀⁻⁻ in the case of **2** from the ¹azaBODIPY^{*} were energetically feasible. Additionally, singlet-singlet energy transfer from ¹azaBODIPY^{*} to C₆₀ within the tetrad is also possible as the energy level of ¹C₆₀^{*} is slightly below that of ¹azaBODIPY^{*}. However, the spectral overlap between azaBODIPY fluorescence and C₆₀ absorption was poor. Energetically, both charge separated states were slightly above that of ³azaBODIPY^{*} but not that of ³C₆₀^{*} ($E_T = 1.50 \text{ eV}$). Under such conditions, the charge separated state could populate the ³azaBODIPY^{*} prior returning to the ground state. Additionally, in the case of **2** (see Figure 6b), the ³azaBODIPY* could undergo triplet-triplet energy transfer to populate the ³Fc* prior returning to the ground state. Systematic studies were performed in polar benzonitrile and nonpolar toluene to unravel the mechanistic details of these photochemical events.

Photodynamics probed by femtosecond transient absorption spectroscopy: The photodynamics of the triads and tetrads were examined in polar and nonpolar solvents by femtosecond transient spectral measurements using 400 nm excitation wavelength where azaBODIPY to a large extent and C₆₀ to a lesser extent were excited. The transient spectra of pristine azaBODIPY in benzonitrile and toluene are shown in Figure S2. The instantaneously formed ¹azaBODIPY* revealed positive peaks at 542 and 1260 nm due to transitions originating fror ¹azaBODIPY*. A negative peak observed at 662 nm ha contributions from both the ground state bleaching and stimulate emission. Similar observations were also made for azaBODIPY i toluene. The recovery of negative peaks was relatively slow (se Figure S2 right hand panel for time profiles) consistent with th relatively longer lifetime of ¹azaBODIPY* being 1.64 ns i benzonitrile and 1.78 ns in toluene.

First, femtosecond transient spectral studies of the triads, 1 and 2d were performed. As shown in Figures 7a and b, immediatel after excitation, the instantaneously formed ¹azaBODIPY* reveale the following spectral features. In benzonitrile, positive peaks wit maxima at 490 (sh) and 532 nm, and a broad negative peak centere around 680 nm were observed. In toluene, the positive peak wa located at 523 nm, in addition, a broad peak at 1180 nm wa observed (see spectrum at delay time 1 ps). In addition, broa negative peaks with minima at 640 and 720(sh) were observed. Th near-IR peak has been assigned to singlet-singlet transitio involving ¹azaBODIPY* while the negative peak was attribute mainly to the ground state bleaching of the visible and charg transfer bands of 1d. Decay of the positive peaks and recovery c the negative peaks resulted into the formation of new peak centere 985 nm in benzonitrile (see spectrum at 10 ps delay time), and 91 nm in toluene (see spectrum at 25 ps delay time). Supported by th previously discussed spectroelectrochemical results, the spectrum a these delay times have been attributed to the PTZ*+-azaBODIPY charge separated state. With higher delay times, intensity of th near-IR band started diminishing in intensity with new peaks at 58 and 613 nm in benzonitrile (see spectrum at 30 ps delay time), an 600 and 660 nm toluene (see spectrum at 200 ps delay time). Thes spectra have been attributed to ³azaBODIPY* formed during th process of charge recombination (see Figure S1a in SI for energ Nanosecond transient spectra were also recordec diagram). however, no detectable signal was observed. This suggests that th decay of ³azaBODIPY* is faster than the detection limit of ou nanosecond setup being about 20 ns or signal being too weak.

The transient spectra of **2d** is shown in Figures 7c and c respectively, in benzonitrile and toluene. The instantaneousl, formed ¹azaBODIPY* revealed a positive peak at 522 and a broad peak at 1230 nm, and negative peak at 630 nm in benzonitrile (see spectrum at 20 ps delay time). In toluene, these positive peaks were located at 523 nm and 1232 nm and the negative peak at 628 nm. In addition to these spectral features, a broad negative signal in the 800-900 nm range where the charge transfer absorption of **2d** was observed (see Figure 2a). The positive peaks to transitions originating from the singlet excited state and negative peak to ground state bleaching of **2d** were assigned. Decay of the positive peaks and recovery of the negative peak revealed a weak, broad peak at 1040 nm within 20 ps that has been attributed to the Fc⁺- azaBODIPY⁻ charge separated state. At higher delay times, a broad peak in the 585 nm range in benzonitrile (see spectrum at 400 ps delay time) and in the 600 nm range in toluene started to emerge, attributable to the formation of ³azaBODIPY*. In summary, both **1d** and **2d** revealed transient spectral features corresponding to rapid formation of D⁺-azaBODIPY⁻ (D = phenothiazine or ferrocene) charge separated state that subsequently relaxed to the ground state via populating ³azaBODIPY*, as predicted by the energy diagram in Figure S1a and b.



Figure 7. Femtosecond transient spectra at the indicated delay times of 1d (a and c) and 2d (b and d) in benzonitrile (a and b) and toluene (c and d).



Figure 8. Femtosecond transient spectra at the indicated delay times of 1 (a and c) and 2 (b and d) in benzonitrile (a and b) and toluene (c and d).

Femtosecond transient spectral features of tetrads 1 and 2 in the investigated solvents is shown in Figure 8. For 1 in benzonitrile, decay of the instantaneously formed ¹azaBODIPY* revealed positive peaks at 545 and 1330 nm and negative peaks at 610 and 694 nm (Figure 8a). Signature peaks representing the charge separated state were observed as early as 2 ps in this solvent with peaks at 515, 920 and 1000 nm. While the 920 nm peak represented that of azaBODIPY⁺ (see Figure 4a and b), the 1000 nm peak that was absent in 1d was due to C₆₀⁻. These results unambiguously

proved the formation of PTZ⁺-azaBODIPY⁻- C_{60} and PTZ⁺-azaBODIPY- C_{60}^{-} charge separated states in the case of **1**. This was also the case in toluene, however, clear formation of the charge separated state we seen at a delay time of 3 ps. With time th signature peaks of the charge separated stat started disappearing with the appearance c new peak in the 600-650 nm rang attributable to ³azaBODIPY* (see spectrur at 10 ps in Figure 8a and 40 ps in Figure 8c)

For 2, peaks corresponding to th charge separated state, Fc^+ -azaBODIPY⁻ C_{60} and Fc^+ -azaBODIPY- C_{60}^- were visibl as early as 1 ps in benzonitrile and 4 ps i toluene (Figures 8b and d). Subsequer decay of the radical peaks populated th ³azaBODIPY* at higher delay times in bot solvents as witnessed by new peak in the 60 nm range, however, peak intensity c ³azaBODIPY* was relatively less compare to that observed in 2d. This implies that th ³azaBODIPY* could undergo triplet-tripl¢ energy transfer to populated ³Fc* in th

tetrad. The ${}^{3}Fc^{*}$ thus formed is expected to nonradiatively decay t the ground state, as shown in the energy level diagram in Figure 6t

It may also be pointed out here that th absence of transient peak in the 700 nr range corresponding to ${}^{3}C_{60}*$ suggests lac of population of this state as predicted from the energy diagram.

The time constants for charg separation observed here for the triads an tetrads (few ps) are much lower than thos reported earlier for triad and tetrad featurin some of these entities but having larg spacer groups connecting them.^[20] Th close association of the donor and acceptc entities in these multi-modular donor acceptor systems promoted excited stat charge separation. However, the charg recombination was also found to efficier even in the case of the tetrads featuring the charge stabilizing fullerene entity(10-20 ps), in part due to their close association and populating the low-lying ³azaBODIPY* which would promote faster charge recombination process.

Conclusions

In summary, the new series of multi-modular donor-acceptor systems designed and synthesized in the present study revealed

several interesting results. These include: (i) Charge transfer interactions between the directly attached donor entities to the electron deficient azaBODIPY resulting in the formation of new charge transfer bands spanning the visible and near-IR spectral regions. (ii) The electronic communication between the two donor via the azaBODIPY π -system as witnessed by electrochemical studies where splitting of the peak corresponding to the oxidation of donor entity in both the triads and tetrads was observed. (iii) Computational studies revealed no steric constraints in the polyads even though the entities were spatially close. (iv) The reversible oxidation and reduction was further supported by spectroelectrochemical studies where new peaks for the oxidized and reduced species were witnessed. (v) The established energy level diagrams revealed the feasibility of excited state charge transfer from the singlet excited azaBODIPY in the triads and tetrads. (vi) Occurrence of excited state charge transfer was proved by studies involving femtosecond transient spectroscopy. Owing to the close association of the donor and acceptor entities, the time constants for charge separation were few ps thus establishing ultrafast charge transfer process. (vii) Finally, the charge separated state relaxed to ground state by populating the triplet excited states of ³azaBODIPY* (and ³Fc* in the case of 2d and 2 via triplet-triplet energy transfer). The present study brings out the importance strongly coupled donor-acceptor systems in governing ultrafast photophysical events applicable towards building new generation of optoelectronic devices.

Experimental Section

Chemicals. Buckminsterfullerene, C_{60} (+99.95%) was from SES Research, (Houston, TX). All the reagents were from Aldrich Chemicals (Milwaukee, WI) while the bulk solvents utilized in the syntheses were from Fischer Chemicals. The tetra-*n*-butylammonium perchlorate (TBA)ClO₄ used in electrochemical studies was from Fluka Chemicals.

Syntheses of triads and tetrads

Synthesis of **1a.** First, N-ethylphenothiazine was synthesized according to the following method. Phenothiazine (5g, 25 mmol) was dissolved in DMF and cooled to 0 °C. NaH (1.8g, 75 mmol) and bromoethane (8.2 g, 75 mmol) were added and allowed to react at room temperature overnight. Reaction was quenched with ice, extracted with DCM, and purified via silica gel column chromatography at a 2:3 DCM:Hexanes ratio. ¹H NMR; (400 MHz, CDCl₃) δ = 7.12 (4H, d), 6.85 (3H, s), 1.42 (3H, t). UV-Vis (benzonitrile) λ_{max} (nm): 312.8.

Next, formylation of N-ethylphenothiazine was achieved by adding POCl₃ (13.8g, 90 mmol) dropwise to DMF (6.58 g, 90 mmol) at 0 °C until a glassy solid appeared. Solid dissolved in DCM, and stirred for one hour. N-ethylphenothiazine (4.1g, 18 mmol) was then dissolved in DCM and added to mixture which was then allowed to react overnight at 90 °C. Product was purified via silica gel column chromatography in 100% DCM. ¹H-NMR (400 MHz, CDCl₃) δ = 9.79 (1H, s), 7.62 (1H, q), 7.55 (1H, d), 7.14 (1H, m), 7.1 (1H, m), 6.94 (1H, m), 6.9 (2H, m), 4.0 (2H, q), 1.4 (3H, t).

Finally, for the synthesis of **1a**, acetophenone (1.53 g, 12.77 mmol), Nethylphenothiazine aldehyde (3.257g, 12.77 mmol), and KOH (1.21 g, 25.55 mmol) were dissolved in 85/15 v/v ethanol/water mixture. Mixture was allowed to react at room temperature for 48 hours, then cooled on an ice bath and acidified to precipitate product (**1a**). Crude mixture was filtered yielding a yellow solid which was purified via silica gel column chromatography at a 45:5 DCM to Hexanes ratio (57% yield). ¹H-NMR (400 MHz, CDCl₃) δ = 8.0 (2H, d), 7.7 (1H, d), 7.55 (1H, m), 7.50 (2H, m), 7.45 (2H, s), 7.43 (1H, m), 7.1 (2H, m), 6.9 (1H, t), 6.85 (2H, t), 3.9 (3H, q), 1.35 (3H, t). Synthesis of **1b**. **1a** (2.6 g, 7.28 mmol) was dissolved in ethanol and combined with nitromethane (4.44 g, 72.8 mmol) in the presence of diethylamine (2.66g, 36.4 mmol) and then allowed to run under reflux for 24 hours. Reaction mixture was cooled on an ice bath and then acidified to yield the nitro derivative compound **1b**. In high concentration this compound appeared to be a deep red, but investigation using TLC chromatography showed a characteristic yellow color. Crude product was extracted with DCM, washed the organic layer with water and then dried. The compound was purified using silica gel column chromatography with 100% DCM. Product was directly moved forward into ring close reaction.

Synthesis of **1c. 1b** (3.18g, 8.58 mmol) was dissolved in ethanol. Ammonium acetate (22.9g, 297.5 mmol) was then added and allowed to reflux 24 hours. After 1-2 hours a significant color change was observed, reaction was monitored via TLC chromatography and allowed to go until completion. Crude product was extracted with DCM, washed the organ layer with water and dried. The compound was purified using silica g column chromatography at a 45:5 DCM:Hexanes ratio. ¹H NMR; (400 MH CDCl₃) $\delta = 8.18$ (2H, t), 7.85 (2H, d), 7.8 (2H, m), 7.7 (1H, d), 7.5 (5H, m 7.4 (4H, m), 7.0 (4H, m) 6.92 (2H, m), 6.8 (2H, m), 6.75 (2H, m), 3.8 (4H, r 1.3 (6H, m).

Synthesis of **1d.** Chelation was achieved by dissolving **1c** (0.500 g, 0.6t mmol) in dry dichloromethane, followed by purging with nitrogen for 1 minutes. Diisopropylethylamine (1.33 g, 10.3 mmol) and boron trifluorid diethyl etherate (2.553 g, 17.98 mmol) were added and mixture was allowd to react for 24 hours yielding compound **1d**. A color change was observed between compound **1c** and **1d**, and after purification using silica gel colum chromatography at a 45:5 DCM: Hexanes, a metallic red sheen was observed (yield 60%). ¹H NMR (400 MHz, CDCl₃) $\delta = 7.98$ (4H, m), 7.92 (2H, M 7.85 (2H, d), 7.45 (6H, t), 7.15 (2H, m), 7.06 (2H, d), 7.0 (2H, d), 6.9 (4H, r 6.85, (2H, m), 4.0 (4H, m), 1.35 (6H, t). UV-Vis (benzonitrile) λ_{max} (nr 317.6, 624.9. HR-MS (MALDI – no matrix): m/z calc'd for C₄₈H₃₆BF_{2N5S₂} 795.2473 found = 795.5, 767.7 (M - C₂H₄), 738.6 (M - (C₂H₄)₂).

Synthesis of **1e**. Aldehyde was obtained by dissolving **1d** (0.159 g, 0.2 mmc in dry dichloromethane, followed by purging for 10 minutes with nitroge Aluminum chloride (0.134 g, 1.01 mmol) was then added to the flask, at after observing a significant color change 3,4-dihydroxybenzaldehyde (0.15 g, 1.01 mmol) was added. Reaction was monitored using TL chromatography and after thirty minutes was purified directly using first a alumina column (45:5 DCM:Ethyl acetate), followed by silica gel colum chromatography in 100% DCM (68% yield). ¹H NMR; (400 MHz, CDCl₃) = 9.5 (1H, s), 7.96 (1H, d), 7.94 (1H, d) 7.88 (2H, d), 7.20 (3H, m), 7.15 (2I t), 7.04 (4H, m), 6.9 (12H, m), 6.64 (2H, s), 6.5 (1H, d), 6.02 (1H, d).

Synthesis of 1. 1e (0.31 g, 0.35 mmol), C_{60} (0.400 g, 0.7 mmol), at sarcosine(0.155 g, 1.75 mmol) were combined and dissolved in toluen Reaction was allowed to proceed at room temperature overnight. Cruc product was evaporated via rotary evaporation and was directly purified usir silica gel column chromatography, which was first flushed with toluene, the product came with 100% DCM (20% yield). ¹H NMR δ = 7.90 (2H, m), 7.8 (2H, m), 7.62 (1H, m), 7.46 (1H, m), 6.95 (6H, m), 6.8 (6H, t), 6.6 (2H, c 4.9 (2H, d), 4.8 (1H, d), 4.12 (2H, m), 3.9 (4H, q), 2.48 (3H, s), 1.35 (6H, m UV-Vis (benzonitrile) λ_{max} (nm): 325.2, 610.7. ¹³C NMR (500 Mhz, CDCl₃) =167.678, 132.469, 130.868, 129.160, 129.054, 128.811, 128.257, 128.04 127.719, 127.590, 127.461, 127.301, 126.952, 125.328, 124.038, 123.43 122.938, 147.304, 146.317, 146.204, 146.158, 146.037, 145.946, 145.32., 144.565, 144.345, 143.601, 143.138, 143.062, 142.948, 142.675, 142.455, 142.212, 142.121, 141.681, 141.507, 140.118, 140.042, 139.807, 139.769, 139.594, 115.221, 115.198, 68.121, 42.366, 38.785, 32.024, 30.430, 30.331, 30.142, 30.013, 29.808, 29.557, 29.474, 29.186, 29.003, 23.828, 23.100, 23.024, 22.819, 21.514, 14.214, 14.138, 13.114, 11.035. HR-MS (MALDI no matrix): m/z calc'd for C₁₁₇H₄₅BFN₆O₂S₂ = 1640.3138 (M), found 921.5 (M-C₆₀), 893.5 (M - C₆₀+2(CH₂CH₃)].

Synthesis of 2a. Acetophenone (1.39g, 11.6 mmol) and ferrocenecarboxaldehyde (2.5 g, 11.6 mmol) were ground in the presence of NaOH (0.64 g, 16.24 mmol). The mixture was initially a liquid, and began to thicken until solidifying over the course of fifteen minutes. After solidifying

grinding continued for an additional five minutes. The solid was dissolved in DCM and then washed with water. The organic layer was then evaporated using rotary evaporation and resultant dark red solid was purified via silica gel column chromatography using 45:5 DCM:hexanes ratio (66% yield). ¹H NMR (400 MHz, CDCl₃) δ = 7.90 (2H, m), 7.72 (1H, d), 7.50 (1H, m), 7.44 (2H, m), 7.08 (1H, d), 4.54 (2H, m), 4.42 (2H, m), 4.11 (5H, s).

Synthesis of **2b**. **2a** (3.9 g, 12 mmol) was dissolved in ethanol and combined with nitromethane (14g, 240 mmol) in the presence KOH (0.13g, 2.4 mmol) and then allowed to run under reflux for 24 hours. This yielded the nitro derivative compound **2b** (56% yield). In high concentration this compound appeared to be a deep red, but investigation using TLC chromatography showed a characteristic yellow color when developed in 100% DCM. Crude product was extracted with DCM and washed with water and dried, and purified using silica gel column chromatography, dark orange spot came off the column as a yellow color with 100% DCM. Purified product was directly moved forward into ring close reaction.

Synthesis of **2c**. **2b** (2.5g, 6.82 mmol) was dissolved in ethanol. Ammonium acetate (18.5g, 238.6 mmol) was then added and allowed to reflux for 24 hours. After 1-2 hours a significant color change was observed, reaction was monitored via TLC chromatography and allowed to go until completion. Crude product was extracted with DCM, washed with water and dried, purified using silica gel column chromatography, 40:10 DCM: Hexanes ratio. ¹H NMR (400 MHz, CDCl₃) δ = 7.98 (4H, m), 7.89 (2H, s), 7.46 (6H, m), 5.18 (4H, m), 4.48 (4h, m), 4.12 (10H, s).

Synthesis of **2d**. Chelation was achieved by dissolving **1c** (0.500 g, .739 mmol) in dry dichloromethane, followed by purging with nitrogen for 10 minutes. Diisopropylethylamine (1.33 g, 10.3 mmol) and boron trifluoride diethyl etherate (2.553 g, 17.98 mmol) were added and mixture was allowed to react for 24 hours yielding compound **1d**. A color change was observed between compound **1c** and **1d**, and after purification via silica gel column chromatography, 40:10 DCM: Hexanes ratio a metallic red sheen was observed (yield 70%). ¹H NMR (500 MHz, CDCl₃) δ = 8.12 (4H, m), 7.45 (6H, m), 6.79 (2H, s), 5.24 (4H, m), 4.74 (4H, m), 4.22 (10H, s). UV-Vis (benzonitrile) λ_{max} nm: 308.8, 635.2, 892.8. ¹³C NMR (500 MHz, CDCl₃) δ = 157.54, 146.727, 132.112, 130.261, 129.236, 128.455, 116.260, 77.462, 77.303, 77.052, 76.794, 73.698, 72.788, 70.397, 53.475.HR-MS (MALDI – no matrix): m/z calc'd for C₄₀H₃₀BF₂Fe₂N₃ = 713.1120 found 713.3 (M), 508.7 (M-{2(C₆H₅)+BF₂).

Synthesis of **2e**. Aldehyde was obtained by dissolving **2d** (0.369 g, 0.51mmol) in dry dichloromethane, followed by purging for 10 minutes with nitrogen. Aluminum chloride (0.337 g, 2.53 mmol) was then added to the flask, and after observing a significant color change 3,4-dihydroxybenzaldehyde (0.349 g, 2.53 mmol) was added. Reaction was monitored using TLC chromatography and after thirty minutes was purified directly using first a neutral alumina column (45:5 DCM:Ethyl Acetate ratio), followed by silica gel column chromatography (100% DCM). ¹H NMR (68% yield); (500 MHz, CDCl₃) δ = 9.45 (1H, s), 7.16 (4H, m), 6.89 (2H, m), 6.82 (5H, m), 6.44 (1H, d), 6.38 (2H, s), 6.02 (1H, d), 5.2 (4H, d), 4.85 (4H, s), 4.20 (10H, s).

Synthesis of **2**: **2e** (0.31 g, 0.35 mmol), fullerene (0.400 g, 0.7 mmol), and sarcosine (0.155 g, 1.75 mmol) were combined and then dissolved in toluene. Reaction was allowed to proceed at room temperature overnight. Crude product was evaporated via rotary evaporation and was directly purified using silica gel column chromatography, which was first flushed with toluene, then product came with 100% DCM. Yield was 90.1%. ¹H-NMR δ =7.36 (1H, s), 6.425 (1H,s), 6.435 (1H,s), 5.23 (4H, t), 5.21(2H, s) 4.88 (2H, d) 4.73 (4H, t), 4.53 (1H,s), 4.23 (10H, s), 4.11 (2H, d), 2.45 (3H, s); ¹³C-NMR (500 MHz, CDCl₃) δ = 227.427, 223.535, 220.962, 216.356, 211.985, 206.795, 204.450, 200.596, 192.628, 189.122, 184.220, 179.887, 177.558, 174.925, 171.146, 166.737, 162.601, 159.513, 154.495, 150.650, 145.384, 142.789, 140.269, 137.097, 130.693, 127.612, 123.697, 118.233, 115.775, 112.626, 109.575, 106.882, 101.342, 98.276, 93.845, 90.202, 84.739, 81.430, 76.953, 71.604, 67.741, 65.366, 60.601, 56.852, 54.212, 50.971, 48.596, 42.943, 39.217, 30.354, 27.349, 24.466, 18.851, 14.669, 11.528, 5.222, 1.14. HR-MS

 $\label{eq:matrix} \begin{array}{l} (MALDI-no\ matrix):\ m/z\ calc'd\ for\ C_{109}H_{39}BFe_2N_4O_2=1558.1895\ found\\ 1558.6\ (M),\ 839.4\ (M-C_{60}),\ 837.4\ (M-(C_{60}+2H). \end{array}$

Instruments: The UV-visible spectral measurements were carried out with a Shimadzu Model 2550 double monochromator UV-visible spectrophotometer. The fluorescence emission was monitored by using a Horiba Yvon Nanolog coupled with time-correlated single photon counting with nanoLED excitation sources. A right angle detection method was used. The NMR spectra were recorded in CDCl₃ on Bruker 500 MHz instrument. Tetramethylsilane [Si(CH₃)₄] was used as an internal standard. All samples were prepared in CDCl₃ and chemical shifts were referenced to CHCl₃ at 7.26 ppm for ¹H NMR and referenced to the CDCl₃ at 77.0 ppm for ¹³C NMR.

Differential pulse and cyclic voltammograms were recorded on an EG&G PARSTAT electrochemical analyzer using a three electrode system. A platinum button electrode was used as the working electrode. A platinu wire served as the counter electrode and an Ag/AgCl electrode was used the reference electrode. Ferrocene/ferrocenium redox couple was used as a internal standard. All the solutions were purged prior to electrochemical ar spectral measurements using argon gas.

Spectroelectrochemical studies were performed by using a cell assemb (SEC-C) supplied by ALS Co., Ltd (Tokyo, Japan). This assembly comprise of a Pt counter electrode, a 6 mm x 6 mm Pt gauze working electrode, and a Ag/AgCl reference electrode in a 1.0 mm path length quartz cell. The optic transmission was limited to 6 mm X 6 mm covering the Pt gauze workin electrode.

The computational calculations were performed with the use GAUSSIAN 09 software package^[27].

Femtosecond pump-probe transient spectroscopy. Femtosecond transie absorption spectroscopy experiments were performed using an Ultrafa Femtosecond Laser Source (Libra) by Coherent incorporating diode-pumpe mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavi doubled Nd:YLF laser (Evolution) to generate a compressed laser output 1.45 W. For optical detection, a Helios transient absorption spectromet coupled with femtosecond harmonics generator both provided by Ultrafa Systems LLC was used. The source for the pump and probe pulses we derived from the fundamental output of Libra (Compressed output 1.45 V pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundament output of the laser was introduced into harmonic generator, which produce second and third harmonics of 400 and 267 nm besides the fundamental 80 nm for excitation, while the rest of the output was used for generation white light continuum. In the present study, the second harmonic 400 n excitation pump was used in all the experiments. Kinetic traces at appropria wavelengths were assembled from the time-resolved spectral data. Da analysis was performed using Surface Xplorer software supplied by Ultrafa Systems. All measurements were conducted in degassed solutions at 298 K.

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Intramolecular Charge Transfer

Directly Attached Bisdonor-BF₂ Chelated Azadipyrromethene-Fullerene Tetrads for Promoting Ground and Excited State Charge Transfer

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Close encounters of the charge transfer kind: Directly connected supramolecular triads and tetrads featuring bisphenothiazine or bisferrocene, azaBODIPY, and C₆₀ have been newly synthesized to demonstrate ground and excited state intramolecular charge transfer.