

Interfacing High-Energy Charge Transfer States to a Near-IR Sensitizer for Efficient Electron Transfer upon Near-IR Irradiation

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Abstract: Novel push-pull systems comprised of triphenylamine-tetracyanobutadiene, a high-energy CT species is linked to a near-IR sensitizer, azaBODIPY, for promoting excited state CS. These new systems revealed panchromatic absorption due to combined effect of intramolecular CT, and near-IR absorbing azaBODIPY. Using electrochemical and computational studies, energy levels were established to visualize excited state events. Fs-TA studies were performed to monitor excited state CT events. From target analysis, the effect of solvent polarity, number of linked CT entities, and excitation wavelength dependence in governing the lifetime of CS states was established. Electron exchange between two TPA-TCBD entities in **3** seem to prolong lifetime of the CS state. Importantly, we have been successful in demonstrating efficient CS upon both high-energy CT and low-energy near-IR excitations, signifying importance of these push-pull systems for optoelectronic applications operating in the wide optical window.

Near-IR absorbing molecular systems have been widely used in light energy harvesting, sensing and biosensing, and biomedical applications.^[1] In the area of light energy harvesting, the near-IR sensitizers offer maximum utilization of the useful sunlight in energy harvesting schemes,^[2] while in the area of sensors and biosensors, due to its spectral isolation, near-IR excitation provides excitation selectivity from absorption interference of molecular/biomolecular species present in the sensing environment.^[3] In biomedical applications, near-IR probes are known for their deep tissue penetration properties in imaging applications.^[4]

Push-pull chromophores, derived from closely linked, highly interacting, electron rich and electron deficient entities have been studied for variety of technological applications including multi-photon absorption and organic photovoltaics, and optoelectronics in general.^[5] Under the conditions of strong intramolecular interactions, the push-pull systems are known to result in new type of optical transition called intramolecular charge transfer (ICT) that is different from the regular $\pi-\pi^*$ type transitions of individual chromophores (also called locally excited, LE transitions).^[6] Due to their different origin, spectral properties of ICT and LE transitions differ making this class of compounds as one of the widely studied ones for various light induced applications.^[7]

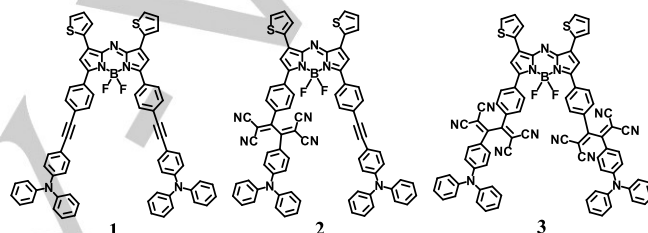


Figure 1. Structure of the high-energy charge transfer, TPA⁶⁺-TCBD⁶⁻, connected to near-IR, azaBODIPY sensitizer, push-pull systems investigated in the present study.

An elegant approach of building ICT molecular systems, developed by Diederich, involves incorporation of a strong electron acceptor such as tetracyanoethylene (TCNE) in a highly facile, catalyst-free [2+2] cycloaddition-retroelectrocyclization reaction with ethynyl functionalized strong electron donor molecules.^[8] Based on this concept, few groups have been successful in building push-pull conjugates.^[9-11] Research teams of Bottari, Torres, and Guldi have also reported phthalocyanine-TCBD and subphthalocyanine-TCBD D-A systems.^[10] Our groups have reported a few TCBD functionalized chromophores, and established excited state charge separation useful for optoelectronic applications.^[11]

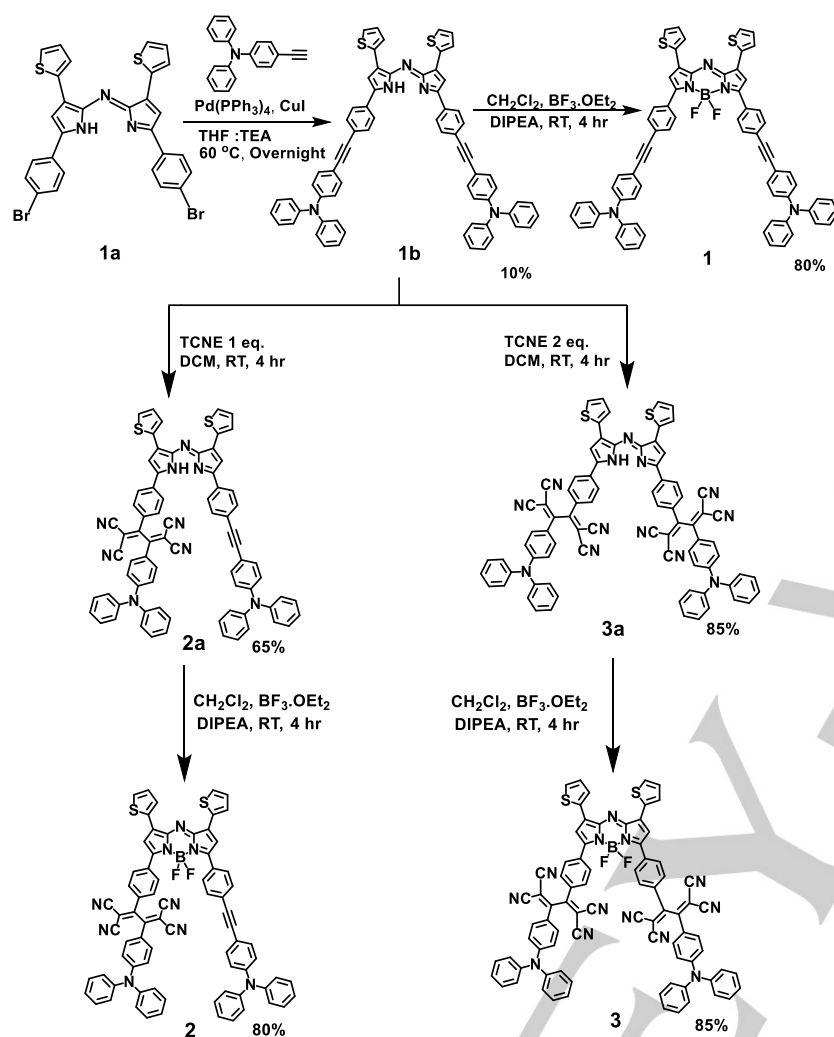
In general, in polar solvents, ICT transitions of push-pull systems occur at the low-energy side of the spectrum while that of LE transitions occur at the high-energy side of the spectrum.^[6] This trend could be reversed if a high-energy ICT exhibiting species can be connected to a near-IR sensitizer.^[10a] If this condition is met, due to different spectral origin, one could observe a reverse trend in optical transitions, viz., low-energy LE and high-energy ICT transitions while extending their spectral coverage. Such compounds due to varying optical properties can offer new class of push-pull systems for light-induced applications. In the present study, an electron deficient near-IR probe, azaBODIPY^[12] has been covalently linked to one or two TPA⁶⁺-TCBD⁶⁻, charge transfer (CT) entities^[8], as shown in Figure 1. The azaBODIPY used here absorbs in the near-IR region of 740 nm region and emits in the 770 nm region, and is highly electron deficient.^[12d] This is unlike the electron rich zinc phthalocyanine near-IR probe employed in a previous study.^[10a] Importantly, due

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Supporting information for this article, experimental and synthetic details, ¹H and ¹³C NMR and MALDI-mass of synthesized compounds. Additional cyclic voltammetric, spectroelectrochemical, computational coordinates, and transient absorption spectral spectra.



Scheme 1. Synthetic methodology for TPA-TCBD connected to azaBODIPY push-pull systems.

to structural arrangement of placing the electron acceptor, TCBD between the electron donor TPA and azaBODIPY, CT is mainly confined to the TPA-TCBD segment and not so much on the TCBD-azaBODIPY segment as both TCBD and azaBODIPY are good electron acceptors (Figure 1). Consequently, the original ICT from TPA-TCBD occurring in the high-energy side of the spectrum is largely unperturbed while the low-energy LE transitions of the near-IR probe, azaBODIPY minimally affected. Further, to seek potential of this class of compounds for light energy harvesting applications, excited state electron transfer upon near-IR and ICT excitations has been investigated in both polar and nonpolar solvents using transient spectroscopy, and meaningful structure-property relationships have been derived.

Synthesis of azaBODIPY derived push-pull systems is shown in Scheme 1 while details are given in the supporting information. Briefly, the di-bromo-aza-dipyrrromethene **1a** was synthesized as per reported procedure.^[13a] The TPA based aza-dipyrrromethene **1b** was synthesized by the Sonogashira cross-coupling reaction of di-bromo aza-dipyrrromethene **1a** (1.0 eq.) with 4-ethynyl-*N,N*-diphenylaniline (2.2 eq.) in a THF/TEA mixture (v/v, 1:1) at 60 °C for overnight under argon atmosphere in 10%

yield. Further the triphenylamine based azaBODIPY **1** was synthesized by chelating BF₂ with aza-dipyrrromethene **1b** in presence of diisopropylethylamine at room temperature (Scheme 1). The [2+2] cycloaddition-retroelectrocyclization reactions of TPA based aza-dipyrrromethene **1b** with one and two equivalents of TCNE in dichloromethane at room temperature for 4 hours resulted in mono-TCBD substituted aza-dipyrrromethene **2a** and di-TCBD substituted aza-dipyrrromethene **3a** in 65% and 85% yield respectively. The TPA based azaBODIPYs, **2** and **3** were obtained by the complexation reaction of aza-dipyrrromethenes **2a** and **3a** with boron trifluoride etherate (BF₃·OEt₂) in dichloromethane solvent and diisopropylethylamine for 4 hours in 80% and 85% yield respectively. The newly synthesized compounds **1-3** were purified by column chromatography using neutral activated alumina. These compounds are readily soluble in common organic solvents such as chloroform, toluene, dichloromethane, and were fully characterized by ¹H NMR, ¹³C NMR and HRMS techniques (see Figures S1-S18 in SI).

Figure 2a shows the absorption spectrum of the investigated compounds in benzonitrile. Compound **1** lacking TCBD entities between the TPA and azaBODIPY revealed two major peaks at 370 and 744 nm. The 744 nm peak was due to the Q-band transition of azaBODIPY while the 370 nm peak had contributions from both TPA and Soret band of azaBODIPY. Introducing TCBD between TPA and azaBODIPY in **2**, resulted in diminished intensity with a small red-shift of 6 nm of the 370 nm peak with the appearance of a new peak at 491 nm. The origin of the new peak stems from CT interactions between TPA-TCBD (TPA^{δ+}-TCBD^{δ-}) from our earlier study,^[11a] and a control experiment involving structurally similar *N,N*-dimethylaminophenyl-TCBD compound whose CT peak was located at 478 nm (see Figure S19 in SI). Introducing a second TCBD into the second arm resulted in compound **3** exhibiting peaks at 380, 484 and 748 nm. The diminished intensity of 380 nm Soret band of azaBODIPY (without TPA contributions) and doubling the intensity of 484 nm peak due to the presence of two TPA^{δ+}-TCBD^{δ-} CT entities was witnessed. Importantly, no significant changes either in azaBODIPY Q-band position in the near-IR region or CT band position from TPA-TCBD interactions in the visible region was observed suggesting that azaBODIPY and TPA-TCBD entities are minimally involved in ground state charge transfer type interactions in **2** and **3**. Since ICT is solvent polarity sensitive, the optical studies were also performed in nonpolar toluene. The absorption spectral trends were almost similar to that observed in benzonitrile (see Figure S20a for absorption spectra). Contrary to the expectations, due to their positioning, location of the TPA^{δ+}-TCBD^{δ-} charge transfer peak in **2** and **3** revealed only a small red-shift (<3 nm) in toluene. Generally, a large red-shift is expected in polar solvents for CT absorption bands.^[6]

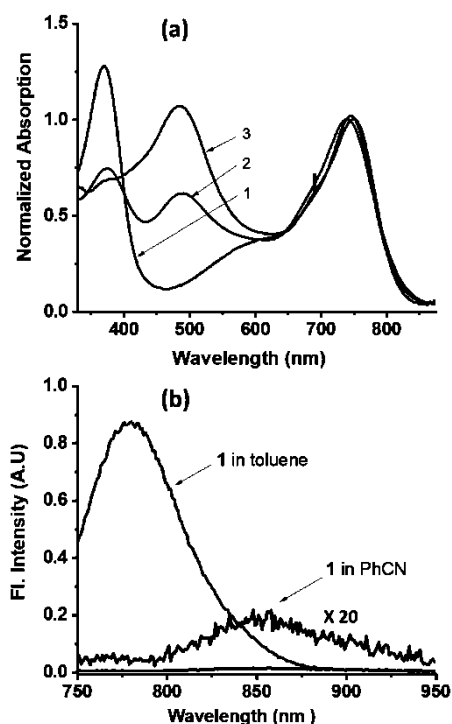


Figure 2. Optical absorption in benzonitrile, and fluorescence in benzonitrile and toluene of indicated compounds. Samples were excited at near-IR peak maxima.

Fluorescence of these compounds was also investigated. In benzonitrile, only compound **1** was found to be weakly fluorescent with peak maxima around 856 nm. However, in toluene a relatively more intense peak with a peak maxima at 780 nm was observed (see Figure 2a). Measured fluorescence quantum yields, Φ_f , were found to be 0.04 in toluene and <0.003 in benzonitrile with respect to pristine azaBODIPY ($\Phi_f = 0.23^{[13b]}$). Red-shift of fluorescence in polar media but not in absorption suggests stabilization of excited state dipoles and not the ground state dipoles of **1**. An optical gap of 1.55 eV in benzonitrile and 1.63 eV in toluene for **1** was possible to arrive from these data (HOMO-LUMO gap, midpoint energy of 0,0 transitions of absorption and fluorescence peaks). Lifetime of **1** in toluene measured using time correlated single photon counting method (629 nm pulsed nanoLED excitation) was found to be 1.56 ns (see Figure S20b for decay profile). The lack of emission in **2** and **3** indicate occurrence of excited state events, such as electron or energy transfer in **2** and **3** in both polar and nonpolar solvents.^[14] For compound **1**, having electron rich TPA and electron

deficient azaBODIPY, excited state CT appears to be occurring, more so, in polar benzonitrile.

Systematic electrochemical studies using differential pulse voltammetry (DPV), cyclic voltammetry (CV), and spectroelectrochemical studies in an optically transparent thin-layer cell-assembly were carried out. The electrochemical redox potentials of multi-modular systems is key in accessing energetics of electron and energy transfer between the components while spectroelectrochemical data is vital in securing spectral evidence of electron transfer products. DPVs of the investigated compounds is shown in Figure 3a-b in benzonitrile containing 0.1 M (TBA)ClO₄. Reversibility of each redox wave was assessed with the help of CV (see Figure S21 for CVs). The first reversible reduction of **1** was located at -0.23 V vs. Ag/AgCl and was attributed to reduction of azaBODIPY as TPA had no reduction in this potential range. The first quasi-reversible oxidation was located at 1.10 V, and from earlier studies,^[11a] this was assigned to the TPA oxidation while the subsequent oxidation located at 1.28 V was due to azaBODIPY oxidation. The determined electrochemical HOMO-LUMO gap (potential difference between azaBODIPY centered oxidation and reduction) was 1.51 eV that agreed well with the optical bandgap value of 1.55 eV discussed

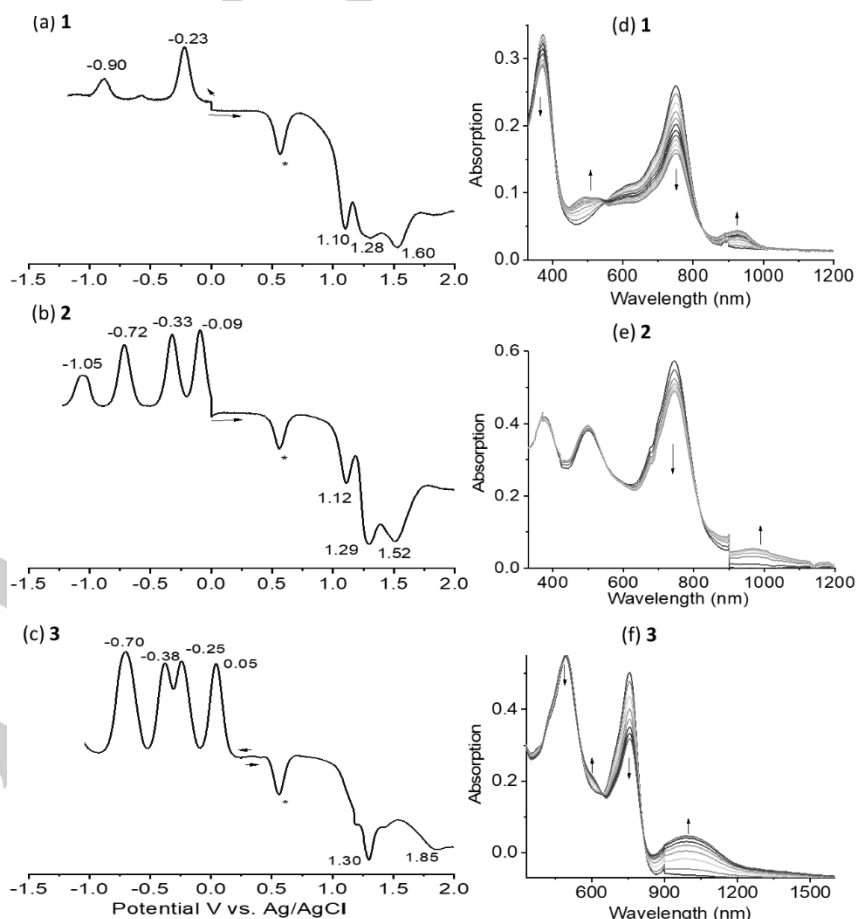


Figure 3. (a-c) DPVs of **1-3** in benzonitrile containing 0.1 M (TBA)ClO₄. The “*” indicates oxidation of ferrocene used as internal reference ($E_{ox} = 0.55$ V). (d-f) Spectral change observed during first reduction of **1-3** in benzonitrile, 0.2 M (TBA)ClO₄. Potentials past 80 mV of the first reduction potential was applied in each case and spectra were recorded until no additional spectral changes were observed. The spike in the spectra at 900 nm is due to change of visible to near-IR detectors.

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earlier. The TCBD entity in compound **2** revealed reversible reductions at -0.33 and -0.72 V while reduction of azaBODIPY was slightly facile and appeared at -0.09 V due to the electronic influence of neighbouring TCBD. Assignment of TCBD reductions was based on a control compound carrying a TCBD entity without the azaBODIPY (see Figure S22 for the structure, CV and DPV curves). The TPA and azaBODIPY oxidations revealed a slight 10–20 mV positive shift. In the case of compound **3**, where two TPA-TCBD entities are positioned on azaBODIPY arms, the first reversible reduction of TCBD was found to be split and appeared at -0.25 and -0.38 V, that is, about 130 mV separation suggesting the TCBD entities interact through the azaBODIPY π -system or could be due to different structural arrangement of the appended TCBD-TPA entities as shown in Figure 4a(iii) and b(iii). The second TCBD reduction was located at -0.70 and had the expected current of two one-electron reductions (from integrating the area under the curve). Interestingly, the reversible azaBODIPY reduction appeared at +0.05 V, more positive than that in **1** or **2** owing to the presence of two neighbouring TCBD entities. A slight anodic shift of oxidation potentials was also witnessed, however, the TPA and azaBODIPY oxidations were overlapped. Importantly, both CT excitation at 490 nm (2.52 eV) or LE excitation (1.63 eV in toluene and 1.55 eV in benzonitrile) are higher in energy compared to the energy gap (HOMO-LUMO gap) between the donor-acceptor (TPA-azaBODIPY) confirming possibility of excited state electron transfer in these systems.

Next, spectroelectrochemical studies were performed to spectrally characterize the one-electron oxidation and one-electron reduction products of compounds **1–3**. For all three investigated compounds no drastic spectral changes involving generation of new peaks during first oxidation were witnessed (see Figure S23 in SI), as this process was TPA centered. Only a small reduction of peak intensities was observed, especially for the TPA absorption bands. Interestingly, during first reduction which is azaBODIPY centered, decreased intensity of the azaBODIPY centered peaks was accompanied by new peaks (see Figure 3d–f). Peaks of **1** were located at 495 and 930 nm while for **2**, a single peak at 972 nm and for **3**, signature peaks at 605 (shoulder type) and 992 nm was observed. One or more isosbestic points were observed in all three cases. The systematic bathochromic shift of the azaBODIPY near-IR peak on increasing the number of TCBD entities suggests greater delocalization of the radical anion across the TCBD moieties. Further, the final spectrum of the radical anion and radical cation of a given compound was averaged and subtracted from the neutral compound, as shown in (see Figure S24). This spectrum would resemble the differential absorption spectrum of charge separation product from transient absorption studies. Main observations involved two negative peaks in the visible and far-red region due to loss of original intensity of the neutral compound, and a broad positive peak in the near-IR region covering 850–1200 nm region, corresponding to the radical anion absorption in this region.

The electronic structures were computationally investigated to gain additional support on the extent of orbital delocalization among different entities of a given push-pull system and orbitals involved in charge transfer process. For this, the geometries were fully optimized on a Born-Oppenheimer potential energy surface using B3LYP/6-31G(d, p) model chemistry (see SI for coordinates

of optimized geometries),^[15] and the frontier orbitals, generated both in gas phase and polar benzonitrile, as shown in Figure 4. In the case of gas phase **1**, the HOMO was delocalized over the TPA-azaBODIPY while the LUMO was solely on the azaBODIPY. From the location of these orbitals a CT state, $\text{TPA}^{\delta+}\text{-azaBODIPY}^{\delta-}$, could be arrived in the gas phase. In polar benzonitrile, however, the CT state could undergo complete charge separation to yield $\text{TPA}^+\text{-azaBODIPY}^-$ charge separated state upon photo-excitation. This is supported by the frontier HOMO and LUMO where majority of the HOMO on TPA arm (donor) and LUMO solely on azaBODIPY (acceptor) of **1** was observed (see Figure 4b(i)).

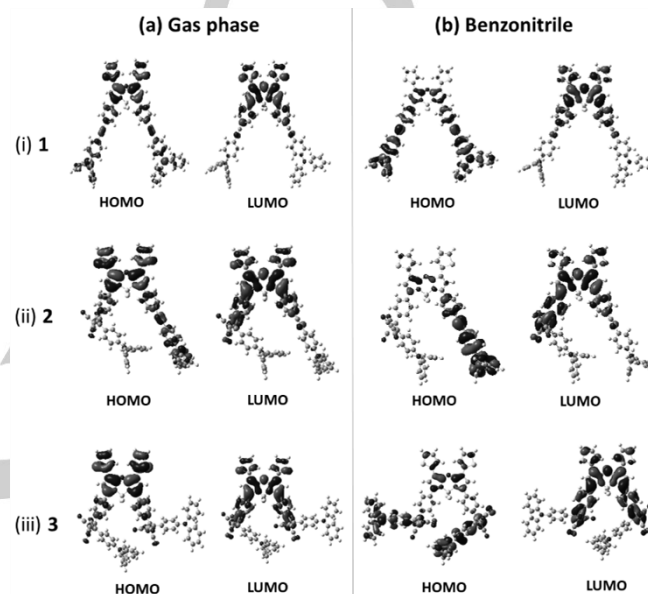


Figure 4. Frontier orbitals of compounds **1–3** generated on B3LYP/6-31G(d, p) optimized geometries in (a) gas phase and (b) polar benzonitrile.

In the case of gas phase **2**, HOMO on the TPA-azaBODIPY arm and LUMO on TCBD-azaBODIPY and LUMO+1 on the TCBD (see Figure S25 for HOMO-1 and LUMO+1 in gas phase) was observed. From the orbital location, a $\text{TPA}^{\delta+}\text{-(azaBODIPY-TCBD)}^{\delta-}\text{-TPA}$ CT state could be envisioned. Interestingly, in benzonitrile, HOMO mainly on the free TPA arm without TCBD, and LUMO on TCBD-azaBODIPY was observed. This suggests formation of $\text{TPA}^+\text{-(azaBODIPY-TCBD)}^-$ TPA electron transfer product in polar solvent. In the case of gas phase **3**, HOMO-1 on TCBD-TPA (Figure S25), HOMO on azaBODIPY, LUMO on azaBODIPY-TCBD, and LUMO+1 on TCBD-TPA was observed. Symmetric distribution of LUMO on TCBD-azaBODIPY-TCBD suggests formation of initial $\text{TPA}^{\delta+}\text{-(TCBD-azaBODIPY-TCBD)}^{\delta-}\text{-TPA}$ CT state. Interestingly, in benzonitrile, majority HOMO on TPA-TCBD (more on TPA) and LUMO on TCBD-azaBODIPY was observed. This suggests the CT state could undergo complete charge separation to yield $\text{TPA}^+\text{-(TCBD-azaBODIPY-TCBD)}^-$ TPA in polar media. These results suggest formation of CT states in nonpolar solvent toluene, and charge separated state in polar solvent, benzonitrile in compounds **1–3**. The gas phase HOMO-LUMO were found to be 1.04, 1.06 eV and 1.08 eV that compared with the electrochemical gap of 1.33, 1.21 and 1.25 eV, respectively, for **1**, **2** and **3**.

Having envisioned the different possibilities of CT and CS in these high-energy CT-near-IR sensitizer conjugates, energy level diagrams were built to verify thermodynamic feasibilities of the envisioned photo-events. Here, $E_{0,0}$ stands for excitation energy of $^1\text{azaBODIPY}^*$ ($= 1.67$ eV) and E_{CT} stands for excitation energy of the CT state, $\text{TPA}^{\delta+}\text{-TCBD}^{\delta-}$ state ($= 2.52$ eV for **2** and 2.56 eV for **3**) were calculated from the optical data. Please note that the E_{CT} is higher by nearly 0.89 eV compared to $E_{0,0}$. The free-energy for charge separation, $-\Delta G_{\text{CS}}$ and charge recombination, $-\Delta G_{\text{CR}}$ were estimated according to Rehm-Weller approach^[16] using equations i-iii.

$$\Delta G_{\text{S}} = e^2/4 \pi \epsilon_0 [-1/R_{\text{CC}} \epsilon_{\text{R}}] \quad (\text{iii})$$

The symbols ϵ_0 and ϵ_{R} represent vacuum permittivity and dielectric constant of benzonitrile used for photochemical and electrochemical studies ($= 26.0$). R_{CC} are the center-to-center distance between donor and acceptor entities from the computed structures.

Figure 5a shows the energy diagram for compound **1** having donor TPA and acceptor azaBODIPY entities. In polar benzonitrile, CS from $^1\text{azaBODIPY}^*$ to yield $\text{TPA}^+\text{-azaBODIPY}^-$ is thermodynamically possible with an energy of charge separated state of 1.31 eV ($=\Delta G_{\text{CR}}$). Formation of charge separation could also involve an intermediate CT state, as shown in Figure 5a. The energy of the CS state in this case is about 0.3 eV higher than that of $^3\text{azaBODIPY}^*$ ($E_{\text{T}} \sim 1.0$ eV),^[17] and under such conditions, the CS state could undergo charge recombination (CR) to populate the low-lying $^3\text{azaBODIPY}^*$ state. The $^3\text{azaBODIPY}^*$ could relax back to the ground state slowly via the spin-forbidden triplet (phosphorescence) emission.

In the case of compound **2** ($\text{TPA-azaBODIPY-TCBD}^{\delta-}\text{-TPA}^{\delta+}$), exciting the sample at 490 nm corresponding to the CT state would produce excited $\text{TPA-azaBODIPY-}^1[(\text{TCBD}^{\delta-}\text{-TPA}^{\delta+})]^*$ state (Figure 5b). Being higher in energy, this state could readily populate the $^1\text{azaBODIPY}^*$ state that could also be produced by direct excitation of **2** at 700 nm (LE excitation). Supported by the earlier discussed spectral and computational studies, $^1\text{azaBODIPY}^*$ could yield $\text{TPA}^+\text{-(azaBODIPY-TCBD)}^{\delta-}\text{-TPA}$ CT state, and in polar solvent would yield $\text{TPA}^+\text{-(azaBODIPY-TCBD)}^{\delta-}\text{-TPA}$ CS product. Alternatively, the CT and CS states could be formed directly from the excited $\text{TPA-azaBODIPY-}^1[(\text{TCBD}^{\delta-}\text{-TPA}^{\delta+})]^*$ in competition with populating the $^1\text{azaBODIPY}^*$ (see Figure 5b). In nonpolar solvent, where the energy of CS state is higher than the CT state (lack of solvent stabilization), the CT state could relax directly to the low-lying $^3\text{azaBODIPY}^*$ and then return to the ground state (see Figure S26 in SI for energy diagram in toluene).

Likewise, in the case of compound **3**, ($\text{TPA}^{\delta+}\text{-TCBD}^{\delta-}\text{-azaBODIPY-TCBD}^{\delta-}\text{-TPA}^{\delta+}$), excitation of CT peak at 490 nm would produce the $(\text{TPA}^{\delta+}\text{-TCBD}^{\delta-})\text{-azaBODIPY-}^1[(\text{TCBD}^{\delta-}\text{-TPA}^{\delta+})]^*$ state that would populate the low-lying $^1\text{azaBODIPY}^*$ state or directly involve in producing the $\text{TPA}^+\text{-(TCBD-azaBODIPY-TCBD)}^{\delta-}\text{-TPA}$ CT state, supported by earlier discussions (see Figure 5c). In polar benzonitrile, the CT state could produce the $\text{TPA}^+\text{-(TCBD-azaBODIPY-TCBD)}^{\delta-}\text{-TPA}$ CS state. This state, being higher in energy would populate the $^3\text{azaBODIPY}^*$ state prior returning to the ground state. Similar to that anticipated for **2**, in toluene, the $\text{TPA}^+\text{-(TCBD-azaBODIPY-TCBD)}^{\delta-}\text{-TPA}$ CT state could directly relax to the $^3\text{azaBODIPY}^*$ without yielding a charge separated state (see Figure S26 in SI for energy diagram in toluene). In summary, these energy level diagrams have helped to unravel different photo-events, and successfully figure out structure-photofunctionality of these high-energy charge transfer-near-IR sensitizer systems.

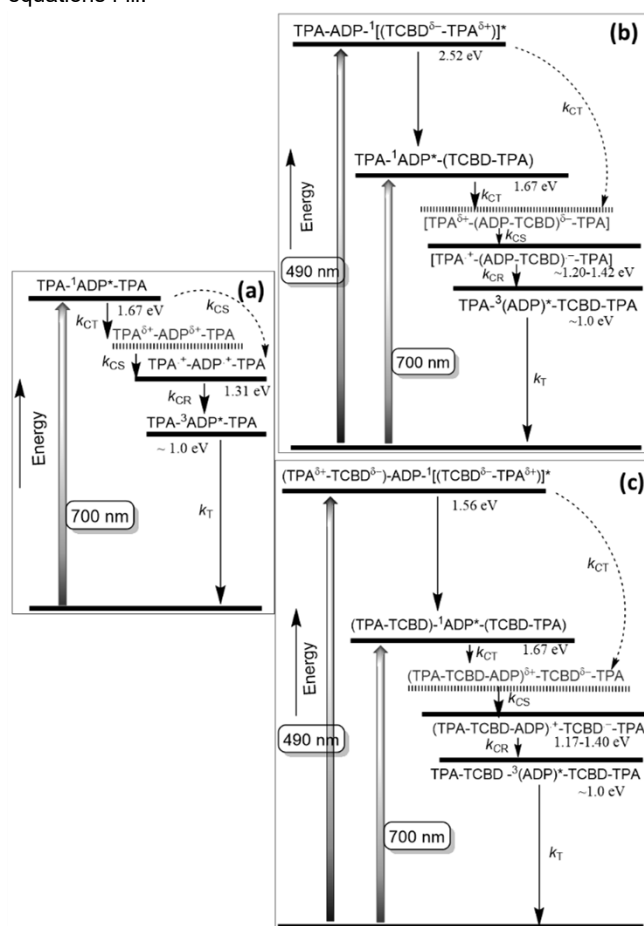


Figure 5. (a-c) Energy level diagram depicting different CT and CS processes in compounds **1-3**, respectively, upon photoexcitation of either the CT or LE states in benzonitrile. Abbreviations: ADP = azaBODIPY and T = triplet emission. Solid arrow: most likely process, dashed arrow: less likely process.

$$-\Delta G_{\text{CR}} = E_{\text{ox}} - E_{\text{red}} + \Delta G_{\text{S}} \quad (\text{i})$$

$$-\Delta G_{\text{CS}} = \Delta E - (-\Delta G_{\text{CR}}) \quad (\text{ii})$$

where $\Delta E_{0,0}$ corresponds to the excited energy $E_{0,0}$ of $^1\text{azaBODIPY}^*$ and E_{CT} is that of $\text{TPA}^{\delta+}\text{-TCBD}^{\delta-}$ state (calculated from CT peak maxima). The term ΔG_{S} refers to electrostatic energy calculated according to dielectric continuum model (see equation iii). The E_{ox} and E_{red} represent the first oxidation potential and the first reduction potential, respectively, of the donor (TPA) and acceptor (azaBODIPY or TCBD) moieties of the conjugates.

Finally, in order to verify whether near-IR excitation of azaBODIPY and direct excitation of the CT band of TPA^{δ+}-TCBD^{δ-} in these push-pull systems would promote charge transfer and charge separation, femtosecond transient absorption (fs-TA) spectral studies were performed. Figure 6a-c show fs-TA spectra at the indicated delay times of **1-3** in benzonitrile at the excitation wavelength of 700 nm exciting mainly the azaBODIPY entity.

The corresponding spectra in toluene are shown in Figure S27 in SI. From earlier discussed spectral data, a charge separation process was anticipated in the case of **1** in polar benzonitrile and may not be in nonpolar toluene. Figure 5a shows fs-TA spectra at the indicated delay times of **1** in benzonitrile upon azaBODIPY excitation. The ¹azaBODIPY* revealed positive peaks at 466 and 1206 nm due to excited state absorption (ESA) and a negative peak at 750 nm due to ground state bleach (GSB) (see Figure S28 for fs-TA of pristine azaBODIPY revealing ~1100 nm near-IR singlet-singlet transition). Within the next 2-3 ps, peaks expected for the charge separated state were evolved, especially 1⁻ peak expected in the 935 nm range. The near-IR peak in the 1300 nm range is due to excited TPA (perhaps due to simultaneous excitation, see Figure S29 for fs-TA of a TPA control compound revealing ~1350 nm ¹TPA* transition). However, as shown in Figure S27a, spectra recorded for **1** in toluene revealed no strong spectral features characteristic of the charge separated state from the initial CT state. Instead weak features of ³azaBODIPY* started emerging (see Figure S30 for nanosecond transient spectra of ³azaBODIPY*),^[17] suggesting CT state directly relaxing to the ³azaBODIPY* instead of generating charge separated species.

The fs-TA transient spectra of **2** and **3** in benzonitrile proved formation of charge separation upon near-IR excitation of azaBODIPY, as shown in Figures 6b and c. For both compounds, faster recovery of the GSB/ESA peaks resulted in the expected 2⁻ peak in the 970 nm range and that of 3⁻ in the 990 nm range appeared as a shoulder peak to main peak at 1100 nm, providing spectral evidence of charge separation. Changing the solvent to

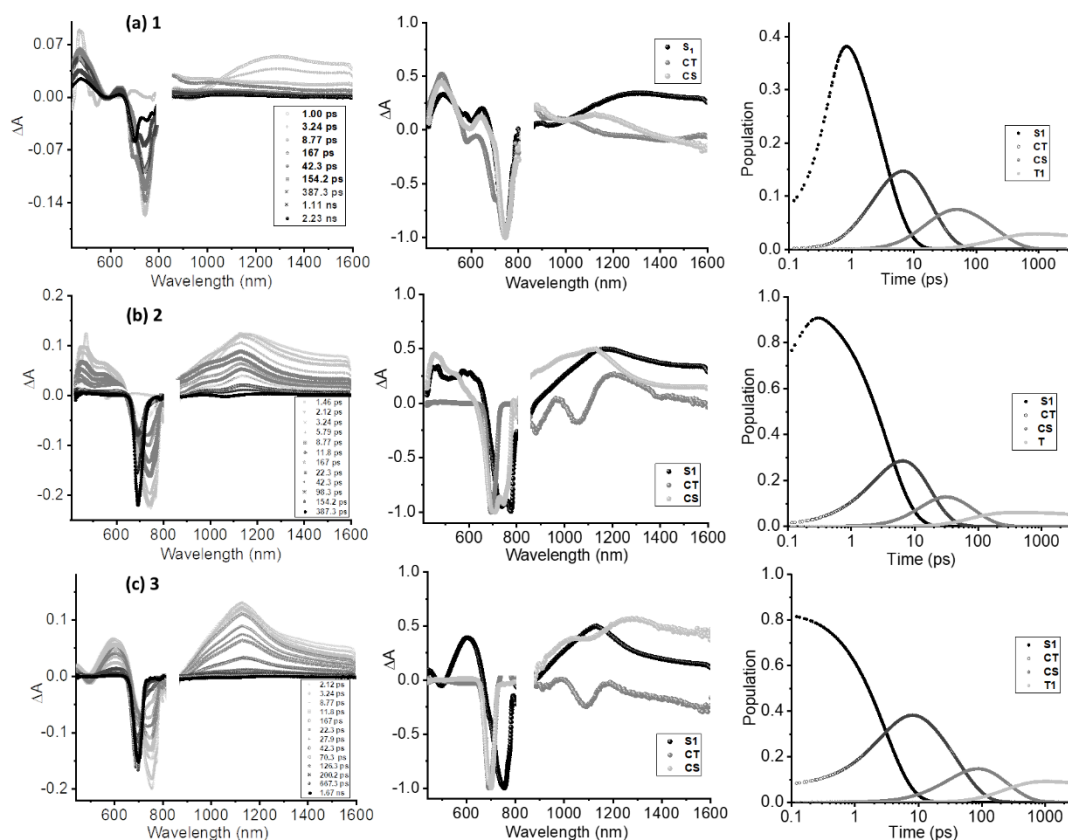


Figure 6. (a-c) Fs-TA spectra of indicated compounds in benzonitrile at the excitation wavelength of 700 nm corresponding to azaBODIPY excitation. The species associated spectra and population kinetics from global target analysis are shown on the middle and right hand side panels for the corresponding compound. SAS of T₁ state is not shown for simplicity, only the major species are shown. The sharp peak at 700 nm both in fs-TA and SAS is due to excitation pulses. The spectra are blocked in the 800 nm region from the noises generated at the extreme end of the detectors (detector change was at 800 nm).

toluene provided very weak spectral evidence for charge separation (Figure S27).

Table 1. Time constants for various photo-events from global target analysis of transient data of compounds **1-3** in benzonitrile

Compound	Solvent	λ_{ex} , nm	$\tau_{(\text{CT})\text{int}}$, ps	τ_{S1} , ps	τ_{CT} , ps	τ_{CS} , ps	τ_{T1} , ns
1	PhCN	700		4.03	11.4	63.3	> 3
2				3.68	12.9	72.5	> 3
3				3.06	41.4	218.7	> 3
2		490	1.02	7.25	28.4	295.5	> 3
3			0.58	8.69	34.4	283.4	> 3
1	Tol	700		4.94	33.3	--	> 3
2				4.68	20.1	--	> 3
3				4.32	53.9	--	> 3
2		490	2.22	12.67	34.8	--	> 3
3			1.33	18.18	49.7	--	> 3

and toluene.

The transient data was subjected to global target analysis,^[17] and species associated spectra (SAS) and population kinetics of different species were generated for the best fit. These results are shown in Figure 6 middle and right hand side columns for the corresponding system. In all the studied systems, the data

could be satisfactorily fitted to four components. The first SAS appearing in 3–5 ps had peaks characteristic of $^1\text{azaBODIPY}^*$ and the second SAS with features that could be attributed to the anticipated charge transfer state while the third SAS had features expected for the charge separated state from earlier discussed spectroelectrochemical results, thus confirming occurrence of charge separation upon near-IR excitation in these conjugates. Finally, the last SAS lasting over 3 ns had features of developing $^3\text{azaBODIPY}^*$ suggesting that the CS state relaxes to the triplet state prior returning to the ground state (SAS not shown, see spectrum at latter delay times in fs-TA spectra). Time constants evaluated from population kinetics plots (right hand panel) are listed in Table 1.

Having established successful excited state charge separation upon near-IR irradiation, next, compounds **2** and **3** having strong CT absorption in the visible region were excited at 490 nm corresponding to the high-energy CT state. Characteristic peaks of $^1\text{azaBODIPY}^*$ started developing from the initial excited CT state within the first 1–2 ps, as predicted from the energy diagram in Figure 5b and c (denoted as $\tau_{(\text{CT})\text{int}}$ in Table 1). Following this, photo-events from $^1\text{azaBODIPY}^*$ tracked largely that observed when azaBODIPY was directly excited, leading to the process of charge transfer, charge separation and population of $^3\text{azaBODIPY}^*$, as shown in Figure 7. Changing the solvent to nonpolar toluene revealed CT formation without much evidence for CS (see Figure S31).

Global analysis of these transient data needed up to five component fits resulting in five SASs, as shown in the middle panel of Figure 7. The first SAS with a time constant of 0.5–2.2 ps was attributed to excited charge transfer state (denoted as $\tau_{(\text{CT})\text{int}}$ in Table 1), that relaxes to populate the $^1\text{azaBODIPY}^*$ in about 8–20 ps (see Figure 7 right hand panel for population kinetics). The time constant for this process was slightly longer than that observed for direct excitation of azaBODIPY at 700 nm where a time constant of 3–5 ps was observed. The third SAS attributed to excited CT state (see Figure 5b and c, marked in red) had also had slightly large time constants in the order of 28–50 ps as against 11–54 ps when the sample was excited at 700 nm. The fourth SAS (blue) resembled to that expected for the charge separated state with higher time constants. Finally the slowly developing fifth SAS was attributable to $^3\text{azaBODIPY}^*$.

Transient spectral results discussed above and the kinetic data secured from global target analysis as summarized in Table 1 revealed several unprecedented observations. First and

foremost, the observation of near-IR excitation leading to charge separation in these novel ‘high-energy CT coupled near-IR push-pull systems’ opens up new design strategies for wide-band capturing, multi-modular push-pull systems for ultrafast charge separation. Second, presence of a second TCBD in **2**, made both τ_{CT} and τ_{CS} last longer. It is likely that the electron exchange between the two TCBD entities upon electro-reduction as shown in Figure 3b prolongs lifetime of charge separated state, along with any structure variations, a property that was never been reported to-date. Third, as a consequence of closely positioned, strongly interacting push-pull nature of the present systems, changing the solvent from polar to nonpolar did not hinder the process of charge transfer, although no clear evidence for charge separated state could be established in toluene. Finally, exciting the samples corresponding to their high-energy CT states, almost instantaneously populated the low-lying $^1\text{azaBODIPY}^*$ state (~ 2 ps) which in turn promoted the subsequent CT and CS processes in sequence in polar benzonitrile.

It may be pointed out here that in benzonitrile at the excitation wavelength of 700 nm corresponding to azaBODIPY, both τ_{CT} and τ_{CS} of **1** are shorter than those observed for **2** and **3** (Table 1). This suggests existence of strong excited state interactions between electron rich TPA and electron deficient azaBODIPY entities in **1**.

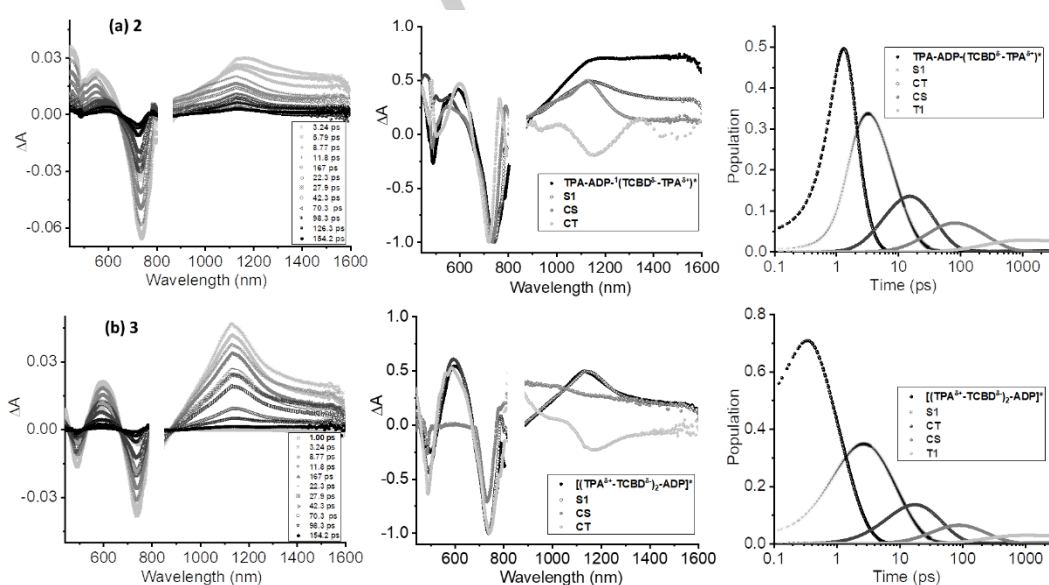


Figure 7. (a-b) Fs-TA spectra of indicated compounds in benzonitrile at the excitation wavelength of 490 nm corresponding to CT excitation. The species associated spectra and population kinetics from global target analysis are shown on the middle and right hand side panels for the corresponding compound. SAS of T1 state is not shown for simplicity, only the major species are shown. The sharp peak at 490 nm both in fs-TA and SAS is due to excitation pulses. The spectra are blocked in the 800 nm region from the noises generated at the extreme end of the detectors.

In conclusion, this work reports on interfacing high-energy charge transfer states to near-IR sensitizer for wide-band capture and ultrafast charge separation. Interfacing the high-energy absorbing, one or two $\text{TPA}^{\delta+}\text{-TCBD}^{\delta-}$ charge transfer entities onto near-IR absorbing azaBODIPY caused marginal perturbation of their ground state optical properties, however, their combination made them panchromatic light absorbing multi-modular systems. In compound **3**, having two symmetrically attached TPA-TCBD entities, electron exchange between the TCBD entities

upon electroreduction was observed, that is, electron exchange through the central azaBODIPY was possible to witness. Presence of TPA-TCBD entities caused quantitative quenching of azaBODIPY fluorescence indicating occurrence of excited state events. Electrochemical results coupled with computational studies, revealed presence of different charge transfer and charge separation states in **2** and **3**. Further, spectroelectrochemical studies provided spectral proof in the form of new near-IR bands upon one-electron reduction, and from further analysis of such data, it was possible to deduce spectrum of the charge separated species. Finally, although fairly complex, it has been possible to dissect different photo-events and successfully figure out structure-photofunctionality in these high-energy charge transfer-near-IR sensitizer systems. That is, systematic studies performed using fs-TA coupled with global target analysis successfully demonstrated charge separation upon photoexcitation corresponding to either near-IR or CT excitation in benzonitrile. The CS states lasted longer in **3** likely due to an electron exchange mechanism, a result new to this class of compounds. The present strategy of building, broad-band capturing, push-pull systems for excited state charge separation is expected to open up a new direction in building novel modular systems for different energy and optoelectronic applications. Further studies along this line are in progress in our laboratories.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgements

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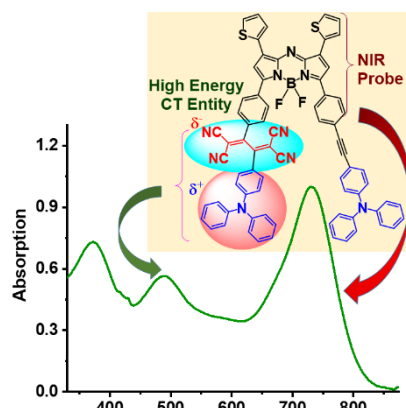
Keywords: High energy charge transfer, near-infrared sensitizer, excited state charge separation, panchromatic absorbance, ultrafast spectroscopy.

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Entry for the Table of Contents

Panchromatic push-pull systems comprised of one or two entities of high-energy absorbing TPA δ^+ -TCBD δ^- charge transfer complexes covalently linked to a near-IR sensitizer, azaBODIPY, have been newly synthesized and excited state electron transfer upon CT or near-IR excitation is demonstrated.



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Interfacing High-Energy Charge Transfer States to a Near-IR Sensitizer for Ultrafast Electron Transfer upon Near-IR Irradiation