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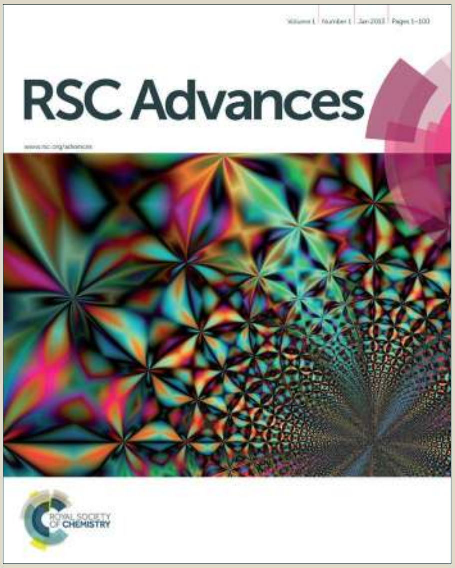

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COMMUNICATION

Regioisomeric Donor-Acceptor-Donor Triads based on Benzodithiophene and BODIPY with Distinct Optical Properties and Mobilities†

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Two regioisomeric triads D-A1-D and D-A2-D composed of benzodithiophene donors and BODIPY acceptors were synthesized which exhibit spectral coverage upto 700 nm due to efficient intramolecular charge transfer. Structural differences and planarity of these triads lead to distinct photoinduced electron transfer characteristics and charge carrier mobilities of upto ~ 10^{-4} cm^2/Vs.

Covalently connected small molecule donor-acceptor (D-A) light harvesting (LH) systems have found widespread applications in organic photovoltaics (OPV).[1–4] D-A systems usually possess complementary absorption properties, resulting in narrow optical bandgaps and broader absorption.[1,2] Low lying charge transfer states in D-A systems lead to red-shifted absorption bands[2] and high intrinsic charge carrier mobilities.[5] Recently, record power conversion efficiencies have been achieved with D-A type small molecular systems[6–8] as well as polymers having benzo[1,2-b: 4,5-b′]dithiophene (BDT) unit as donor.[9–11] Interestingly, planar structure, deep lying HOMO levels of ~ -5.4 to -5.6 eV render BDT a suitable ambient stable donor.[12] Furthermore, their optical properties can be easily tuned by tuning their chemical structures making them a useful class of synthons for the design of D-A type systems.[12,13] BDT polymers are also known to exhibit high charge carrier mobilities.[13-15] Although there are numerous reports on D-A polymers composed of BDT units as efficient LH materials for OPV, monofunctionalized BDT donor based dyads and triads are unprecedented.

A proper selection of acceptors to design D-A dyads and triads for efficient light harvesting is crucial. In this context, 4,4′-Difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) dyes are an interesting class of LH materials possessing high molar extinction coefficients and near unity fluorescence quantum yields.[16–20] Their chemical structure provides synthetic versatility and their optical and redox properties are readily tunable.[19] Furthermore, BODIPY polymers have been shown promising optoelectronic properties.[21-23] A preliminary assessment of the optical and redox properties of BDT and BODIPY indicate that their absorption profiles are complementary and their frontier molecular orbital (FMO) levels provide suitable band edge matching for design of D-A systems. Therefore their dyads or triads might have appealing (opto)electronic properties.

BODIPY based multichromophoric systems are well known to exhibit photoinduced electron transfer (PET) and förster resonance energy transfer (FRET).[17–20] BODIPYs have been reported as active layer material in organic photovoltaic with efficiencies upto 4.7 %[24,25] in bulk heterojunction (BHJ) solar cells and 6.4% in dye sensitized solar cells.[26] For OPV's based on D-A type materials, PET has enormous significance because, partial charges on donor and acceptor moieties facilitate efficient charge separation and lead to photo induced conductivities.[5,6,8] Donors such as carbazole which is well known for hole conduction have also been reported with BODIPY acceptor based D-A materials with enhanced absorption in near infra red region for OPV apllications.[27,28] Additionally combination of BDT and BODIPY based D-A systems have been reported based on easily accessible disubstituted BDT.[29,30] However, D-A-D type triad systems based on monofunctionalized BDT as donor and BODIPY as acceptor have not been reported.

Herein, we report the design, synthesis and characterization of two new regioisomeric D-A-D triads **D-A1-D** and **D-A2-D** (Fig. 1) based on dibrominated BODIPY as acceptors and monostannylated BDT as donor. Based on their structural and geometrical differences, notable dissimilarities were observed in optical properties such as absorption, fluorescence, solvatochromism and charge carrier mobilities.

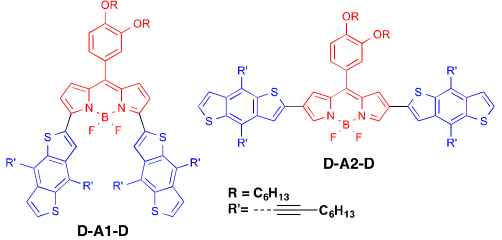

Fig. 1 Chemical structures of triads **D-A1-D** and **D-A2-D** synthesized and investigated in this work.

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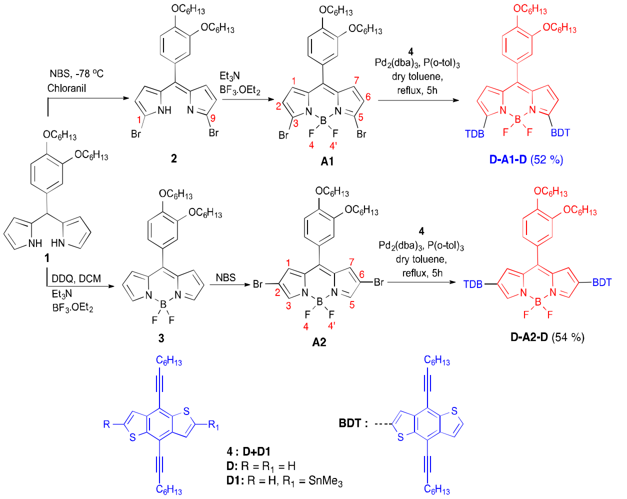
For the design and synthesis of covalently connected BODIPY-BDT triads, BDT units[31] with monofunctionalization will be suitable donor synthons and brominated BODIPYs will be useful acceptor synthons.[32-38] Covalently connected BODIPY oligomers have been synthesized using palladium (Pd) catalyzed cross coupling reactions such as Suzuki and Sonogashira reactions.[32,34,35] Different geometries of oligomers of BODIPY are accessible from □ and □ substitutions at the BODIPY core (i. e., 2,6- or 3,5-positions) (see A1 and A2 in Scheme 1).[35] Owing to the fact that 1,9-positions possess least positive charge in dipyrromethane (DPM) whereas for BODIPY, 2,6-positions possess least positive charge, electrophilic substitution reactions are facilitated at 1,9-positions for DPM and at 2,6-positions for BODIPY.[16] Bromination of BODIPY preferentially takes place at 2,6-positions by using N-Bromosuccinimide (NBS)[32] or bromine[37] while bromination of DPM is preferred at 1,9-positions by using NBS.[38] Accordingly, regioisomeric brominated BODIPYs A1 and A2 were synthesized as depicted in Scheme 1. DPM 1 functionalized with meso phenyl substituent containing solubility inducing hexyloxy chains was brominated by addition of 2 equiv. of NBS followed by oxidization by tetrachloro-1,4-benzoquinone (chloranil) to obtain 2. Subsequently, triethylamine (Et3N) and boron trifluoride diethyletherate (BF3.OEt2) were added to obtain the corresponding 3,5-dibromo BODIPY, acceptor A1. A slightly different synthetic route was adopted for the synthesis of acceptor A2, where, DPM 1 was first oxidized by the addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), followed by addition of Et_3N and $BF_3.OEt_2$ to obtain BODIPY **3**. In the next step, **3** was brominated selectively at 2,6-positions using 2.4 equiv. of NBS[37] to obtain acceptor **A2**.

For the synthesis of D-A-D compounds by Pd-catalyzed Stille coupling, monofunctionalized BDT such as monostannylated BDTs are required. In this regard, BDT donor precursor **D** (Scheme 1) was synthesized[31] followed by its conversion to the corresponding mono-stannylated derivative **D1** using ~ 1.5 equiv. butyllithium (BuLi) solution and trimethyltin chloride ($SnMe_3Cl$) (see ESI).



Scheme 1. Synthetic scheme for BODIPY acceptors **A1**, **A2** and triads **D-A1-D** and **D-A2-D**.

The product obtained using ~ 1.5 equiv. of BuLi and $SnMe_3Cl$ consisted of BDT and monostannylated derivative, **4** which was directly used for Stille coupling. Syntheses of triads **D-A1-D** and **D-A2-D** were accomplished by Stille coupling of **A1** and **A2** respectively, and using ~ 2.1 equiv. of **D1** with catalytic amounts of tris(dibenzylidene-acetone)dipalladium(0) ($Pd_2(dba)_3$) and tri(otolyl)phosphine (P(o-tol)$_3$) in refluxing toluene. The significant differences in retention factors (R_f) of BDT **D**, which elutes in petroleum ether, and the coupled D-A-D products that elute in petroleum ether/ethyl acetate mixtures facilitated their convenient separation by column chromatography. Triads **D-A1-D** and **D-A2-D** were purified using column chromatography with petroleum ether/ethyl acetate (97/3, v/v) and (95/5, v/v) as eluents respectively. **D-A1-D** and **D-A2-D** were obtained in yields of 52 % and 54 % respectively and ^1H, ^{13}C NMR and mass spectrometry confirmed their identity and purity (see ESI).

Optical properties of synthesized triads were characterized by UV/Vis studies in dichloromethane (DCM) solutions in which they are molecularly dissolved. Fig. 2 shows the absorption spectra of triads **D-A1-D** and **D-A2-D**. Interestingly, the absorption bands of triads **D-A1-D** and **D-A2-D** were extended upto 700 nm and the bands appearing in the 600-700 nm range are attributed to intramolecular charge transfer (ICT) from the two terminal BDT donors to the central BODIPY acceptor. For **D-A1-D**, BDT absorption maximum occurred at 384 nm, BODIPY maximum at 526 nm and the CT band occurred at 690 nm (Fig. 2a). For **D-A2-D**, BDT absorption maximum occured at 366 nm while the BODIPY absorption maximum was at 530 nm and the new CT band appeared at 625 nm (Fig. 2a). The optical band gaps of triads **D-A1-D** and **D-A2-D** were estimated as 1.67 eV and 1.69 eV in solution and 1.53 and 1.44 eV in films from the onset of their respective absorption spectra. In addition to significant spectral coverage in solution, their absorption spectra were broadened in thin films, with absorption maxima shifted to 705 nm for **D-A1-D** and 665 nm for **D-A2-D** (ESI). The difference in optical bandgaps obtained from UV/Vis measurements in solutions and in thin films could be attributed to the fact that spectral shift and broadening of **D-A2-D** is higher than in **D-A1-D** as the former is more planar and thus aggregates better in films.

Cyclic voltammetry (CV) measurements were performed to assess the electrochemical properties of triads **D-A1-D** and **D-A2-D** (Fig. 2b). CV studies of **D-A1-D** and **D-A2-D** revealed their oxidation potential onsets at +0.42 V and +0.40 V respectively. Accordingly, the HOMO levels were calculated using the empirical formula, HOMO = - (E_{ox}^{onset} + 4.76) eV,[39] while the LUMO levels were calculated using the HOMO values and the optical band gaps. The optical and redox properties of **D-A1-D** and **D-A2-D** are summarized in Table 1.

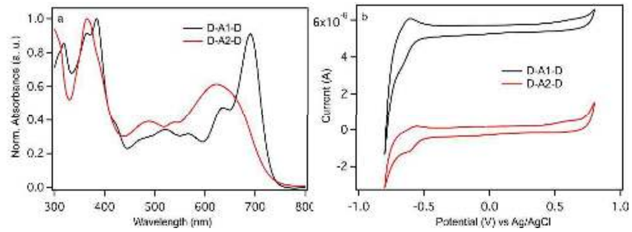


Fig. 2 a) UV/Vis absorption spectra of **D-A1-D** and **D-A2-D** in DCM ($c = 1 \times 10^{-5}$ M) b) Cyclic voltammogramms of **D-A1-D**, and **D-A2-D** in DCM and 0.1 M tetrabutylammonium hexafluorophosphate (TBAHPF) as supporting electrolyte.

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Density functional theory (DFT) calculations performed on these triads using B3LYP functional and 6-31G (d,p) basis set show that highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are localized on BDT and BODIPY units respectively (Fig. 3). The calculated HOMO/LUMO values as well as the FMO distribution for HOMO-1 and LUMO+1 are provided in the ESI. Furthermore, geometry optimization by B3LYP/6-31G(d,p) provided the torsion angles of **D-A1-D** and **D-A2-D** showing that **D-A2-D** is more planar (torsion angles of Φ_1 = 2.5° and Φ_2 = 11.1°) compared to **D-A1-D** (torsion angles of Φ_1 = 14.4° and Φ_2 = 27.2°, see ESI).

Table 1 Optical and redox properties of triads **D-A1-D** and **D-A2-D**.

Triads	λ_{max} (nm)	ε□ ($M^{-1}cm^{-1}$)	E_g^{opt} (eV)	E_{ox}^{onset}(V)/ HOMO (eV)	E_{red}^{onset}(V)/ LUMO (eV)
D-A1-D	384, 690	65239, 58774	1.53^a $(1.67)^b$	+0.42/ -5.18	-0.58/-4.18
D-A2-D	366, 625	64752, 37214	1.44^a $(1.69)^b$	+0.40/ -5.16	-0.57/-4.19

[a]Obtained from absorption onset of thin films, [b]from absorption onset of solution, [c]from CV measurement.

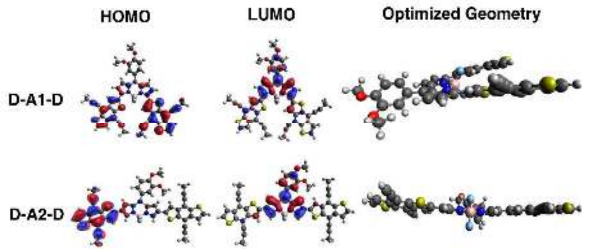

Fig. 3 Frontier molecular orbitals (FMOs) and optimized geometry (side view) of **D-A1-D** and **D-A2-D** obtained by B3LYP/6-31G(d,p) method.

Since these triads show pronounced charge transfer bands, the thermodynamic feasibility for PET in these triads was estimated using optical properties and HOMO, LUMO values. Gibbs free energy change for charge separation (ΔG_{CS}) was calculated for these triads using Rehm-Weller equation,[40] given by:

$$\Delta G_{CS} = e[E(D^+/D) - E(A/A^-)] - E_{00} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_s R_{CC}}$$

where, $E(D^+/D)$ is the first oxidation potential of D, $E(A/A^-)$ is the first reduction potential of A in the D-A system, E_{00} is the energy of first singlet excited state and R_{CC} is the centre-to-centre distance of D and A in D-A system. Accordingly, ΔG_{CS} of -0.62 eV and -0.69 eV were obtained for **D-A1-D** and **D-A2-D** respectively. Table 2 summarizes the calculation of ΔG_{CS} for **D-A1-D** and **D-A2-D**. Higher negative value of ΔG_{CS} for **D-A2-D** over **D-A1-D** indicates that **D-A2-D** has higher driving force for PET than **D-A1-D**. In order to corroborate the distinct CT behavior of these triads, fluorescence measurements were performed for these triads. Emission spectra for triads **D-A1-D** and **D-A2-D** were measured in DCM at different excitation wavelengths and their emission maxima appeared at 726 nm and 729 nm respectively (Fig. 4).

Table 2 Thermodynamic feasibility of PET in **D-A1-D** and **D-A2-D** in DCM.

Triads	E (D^+/D) (V)	E (A/A^-) (V)	R_{cc} (Å)	ΔG_{CS} (eV)
D-A1-D	+0.61	-0.65	7.58	-0.62
D-A2-D	+0.58	-0.61	8.90	-0.69

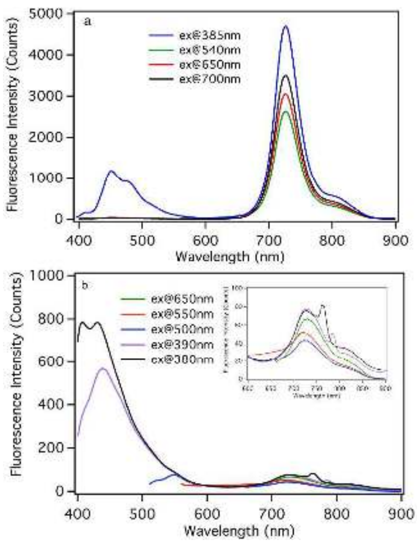

Fig. 4 Fluorescence emission spectra of a) **D-A1-D** and b) **D-A2-D** in DCM at different excitation wavelengths.

A significant quenching was observed in the fluorescence which validates stronger PET in **D-A2-D** than **D-A1-D**. Fluorescence quantum yields of 0.107±0.022 and 0.039±0.013 were obtained for **D-A1-D** and **D-A2-D** by absolute fluorescence quantum yield measurement by an integrating sphere set-up (see ESI). It is worth to mention that competing förster resonance energy transfer processes are unlikely to occur in these triads because the donor emission and the acceptor absorption profiles do not overlap significantly (see ESI). Fluorescence studies were performed for the triads in solvents of different polarities such as acetonitrile (ACN), ethanol (EtOH), DCM, chloroform, chlorobenzene and toluene (Tol) in order to investigate solvatochromic effect. **D-A1-D** showed a hypsochromic shift of the emission maximum in solvents of increasing polarity from DCM (726 nm) to ACN (714 nm). This negative solvatochromism of fluorescence as usually observed for BODIPY dyes.[41,42] Solvents of increasing polarity energetically stabilize the polar ground state preferably over the first excited state, thereby increasing the optical band gap leading to hypsochromic shift of the emission band.[43] Additionally, **D-A1-D** has a conformationally restricted structure and as a result internal rotation of the BDT units needed for relaxation is hindered, reducing the non-radiative relaxation of excited states. Notably, **D-A2-D** has a negligible fluorescence owing to more efficient charge transfer and shows no solvatochromic effect. Additionally, its quenched fluorescence is attributed to the more planar structure of **D-A2-D** that facilitates easy rotation of the BDT and consequently relaxation.

The difference in chemical structures and consequently planarity of these regioisomers is further revealed by their charge carrier mobilities. Planarity is a vital criterion for efficient charge carrier transport in π-conjugated systems.[44] In order to assess their inherent charge transport properties, hole mobilities of these triads were measured using space charge limited current (SCLC) method[8,45] in hole only device architecture ITO/PEDOT:PSS/Active Layer/Au (see ESI). Hole mobilities of triads were extracted from the SCLC region of the curve as shown in Fig. 5. Hole mobilities of 7.01 × 10^{-5} cm^2/V.s

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and 3.63 $\times$ 10^{-4} cm^2/V.s were obtained for triads **D-A1-D** and **D-A2-D** respectively. Higher mobility of **D-A2-D** can be attributed to its improved planarity over **D-A1-D**, which facilitates better π-π stacking in thin films leading to improved charge transport and higher mobility value.

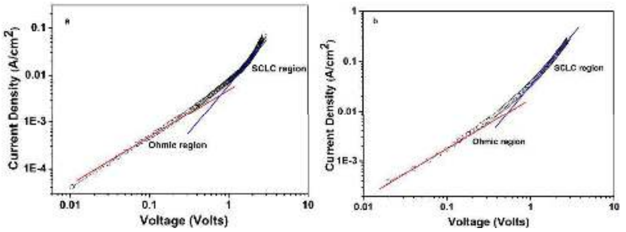

Fig. 5 Space charge limited current (SCLC) mobility plots for a) **D-A1-D** and b) **D-A2-D**.

In summary, two narrow optical bandgap regioisomeric D-A-D triads based on BDT donors and BODIPY acceptors were synthesized by Pd catalyzed Stille coupling reaction. Triads **D-A1-D** and **D-A2-D** were soluble in common organic solvents and showed appreciable spectral coverage in the visible spectral region with pronounced ICT bands at 690 nm and 625 nm. Moreover, they possess optical bandgaps of 1.53 eV and 1.44 eV respectively in thin films which make them suitable for OPV applications. Gibbs free energy estimation and fluorescence emission studies of these triads revealed that PET was more efficient in **D-A2-D** than in **D-A1-D**. Additionally, owing to the structural planarity and enhanced π-π stacking, triad **D-A2-D** showed higher charge carrier mobility than that of **D-A1-D**. The findings of this work suggest the suitability of BDT-BODIPY as light harvesters for OPV applications in D-A-D configuration. Currently, the photovoltaic properties and performances of these triads are being investigated.

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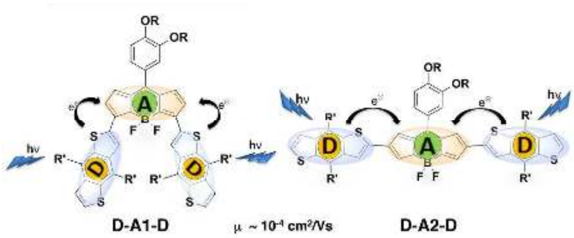

Two regioisomeric donor-acceptor-donor triads composed of benzodithiophene and BODIPY exhibit distinct optical, charge transfer properties and mobilities of ~10^{-4} cm^2/Vs