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‘Two-Point’ Self-Assembly and Photoinduced Electron Transfer in *meso*-Donor Carrying Bis(Styryl Crown Ether)BODIPY-Bis(Alkyl Ammonium)Fullerene Donor-Acceptor Conjugates

Shuai Shao,[a] Habtom B. Gobeze,[a] Paul A. Karr,[b] and Francis D’Souza*[a]

Abstract: BF$_2$-chelaed dipyrromethene, BODIPY, was functionalized to carry two stryryl crown ether tails and a secondary electron donor at the *meso*-position. Using a ‘two-point’ self-assembly strategy, a bis-alkyl ammonium functionalized fullerene, C$_{60}$ was allowed to self-assemble the crown ether voids of BODIPY to obtain multi-modular donor-acceptor conjugates. As a consequence of the two-point binding, the 1:1 stoichiometric complexes formed yielded complexes of higher stability in which fluorescence of BODIPY was found to be quenched suggesting occurrence of excited state processes. The geometry and electronic structure of the self-assembled complexes were derived from B3LYP/3-21G(*) method where no steric constraints between the entities was observed. An energy level diagram was established using spectral, electrochemical and computational results to help understand the mechanistic details of excited state processes originating from ^{1}bisstyrylBODIPY*. Femtosecond transient absorbance studies were indicative of the formation of an exciplex state prior to the charge separation process to yield bisstyrylBODIPY$^{\bullet+}$-C$_{60}^{\bullet-}$ radical ion-pair. The time constants for charge separation were generally lower compared to charge recombination process. The present studies bring out the importance of multi-mode binding strategy to obtain stable self-assembled donor-acceptor conjugates capable of undergoing photoinduced charge separation needed in artificial photosynthetic applications.

Introduction

The extraordinary ability of crown ethers to form supramolecular complexes with different carbon nanostructures, and the impact of size/composition dependent modulation of π–π, n-π, CH-π, dispersion and charge transfer type of interactions has witnessed steady growth over the years.[1] Often the crown ether-cation self-assembled conjugates are built by utilizing redox- and photo-active molecular entities for various applications including sensing, switching, excited state charge separation, and other pertinent electrochemical and optoelectronic applications. In this regard, development of photo responsive supramolecular donor-acceptor conjugates capable of mimicking early events of photosynthesis, viz., energy and electron transfer, by transforming light energy into chemical potential are highly sought in the pursuit of sustainable energy sources.[1-18] Photosensitizers such as porphyrins, phthalocyanines, BF$_2$-chelated dipyrromethenes (BODIPY) and inorganic luminescent compounds as electron donors combined with nanocarbon electron acceptors such as fullerene, nanocarbon and graphene have been widely used in these constructions.[1-18] In designing donor-acceptor systems, either the donor or the acceptor entity is functionalized with a crown ether host while the other entity is functionalized with a complimentary binding, alkyl ammonium cation. The conjugates are often formed by simple mixing of the two entities in solution.[1]

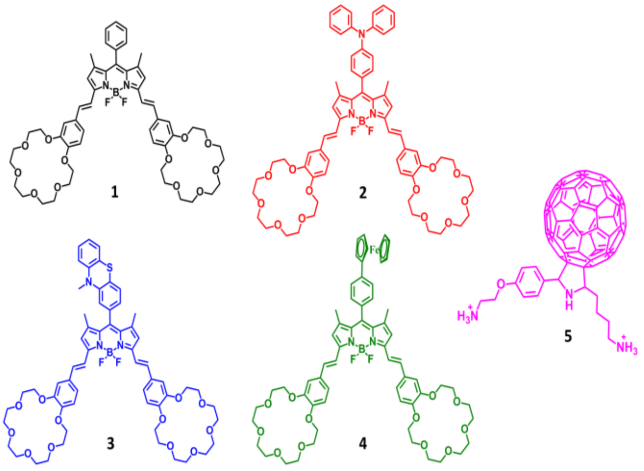

Figure 1. Structures of the *meso*-donor carrying bis(styryl crown ether) functionalized BODIPYs (donor = triphenylamine, phenothiazine or ferrocene) and bis alkyl ammonium functionalized C$_{60}$ used to form ‘two-point’ bound donor-acceptor conjugates.

A literature survey shows that most of the donor-acceptor conjugates assembled using this strategy utilized a single crown ether binding to a single alkyl ammonium cation.[19-20] Although such assembly is relatively stable ($K_{association}$ ~ 10^4 M^{-1}), the structures formed are often flexible resulting in several conformers in solution. One way to

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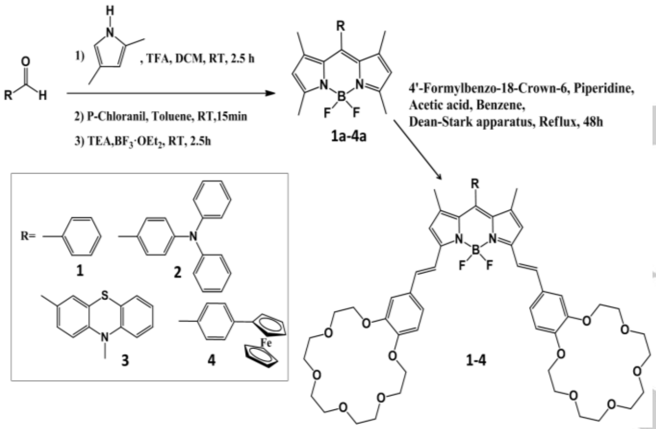
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/caj.xxxx fluorescence decay curves, frontier orbitals of the bisstyryl compounds; additional DPVs, spectral changes during oxidation of compounds **1-4**; MALDI-TOF-mass, ^{1}H and ^{13}C NMR spectra of compounds **1-4**.

combat this situation is by having donor and acceptor entities carrying multiple numbers of appropriately positioned complimentary binding sites promoting cooperative binding with defined geometry. This approach has been explored in the present study where BODIPY has been functionalized with two entities of benzo-18-crown-6 carrying styryl entities while the acceptor C_{60} has been functionalized to carry two entities of alkyl ammonium cations (see Figure 1 for structures).[21] Having two styryl entities on the BODIPY periphery resulted in red-shifting the absorption and emission significantly[22] while the V-type configuration of the crown ether tails were adequate to accommodate the bis-alkyl ammonium functionalized fullerene. Additionally, the BODIPYs were functionalized with a secondary electron donor (triphenylamine, phenothiazine and ferrocene) at the *meso*-position for charge stabilization. The formation, spectral, computational and electrochemical characterization, and excited state charge transfer in these novel donor-acceptor hybrids have been systematically performed and summarized in the following paragraphs.



Scheme 1. Synthetic methodology adopted for *meso*-donor carrying bis(styryl crown ether) functionalized BODIPYs, **1-4**.

Results and Discussion

Synthesis of *meso*-donor carrying bis(styryl crown ether) functionalized BODIPYs

The syntheses of these molecules were carried out according to Scheme 1 and the details are given in the experimental section. Briefly, 2,4-dimethyl pyrrole was reacted with appropriate aldehydes (benzaldehyde for **1a**, 4-formyl triphenylamine for **2a**, 3-formyl-N-methyl phenothiazine for **3a**, and 4-ferrocenyl benzaldehyde for **4a** in trifluoroacetic acid in the presence of p-chloranil followed by treatment with boron trifluoroborane ethrate in triethylamine.[21] The desired compounds **1a-4a** were purified over silica gel column. For syntheses of compounds **1**-**4**, appropriate **1a-4a** were used as the starting material and were treated with 4'-formylbenzo-18-crown-6 in dry benzene using Dean-Stark apparatus to separate water from the reaction mixture for 48 h. The final compounds were purified by column chromatography and purify was check by thin-layer chromatography. The structural integrity was established from ^{1}H and ^{13}C NMR, MALDI-TOF-Mass, spectral and electrochemical studies. Synthesis of bis-alkyl ammonium functionalized C_{60}, **5** was carried out according our published method.[23] The compounds were stored in dark prior to doing spectral and transient absorption measurements.

Absorption and fluorescence studies

Figure 2a shows the normalized absorption spectra of compounds **1-4** in benzonitrile. As expected for the π-extended by means of the two styryl groups, the BODIPY peak was found to be red-shifted and appeared in the 654-658 nm range. It may be noted here that pristine BODIPYs reveal absorption and emission maxima at around 505 and 520 nm, respectively.[24] In addition to this intense peak, additional peaks at 602 and 385 nm range were observed. The *meso*-substituents in compounds **2-4** revealed a broad peak in the 330 nm range, however, caused no drastic spectral shifts of BODIPY transitions.

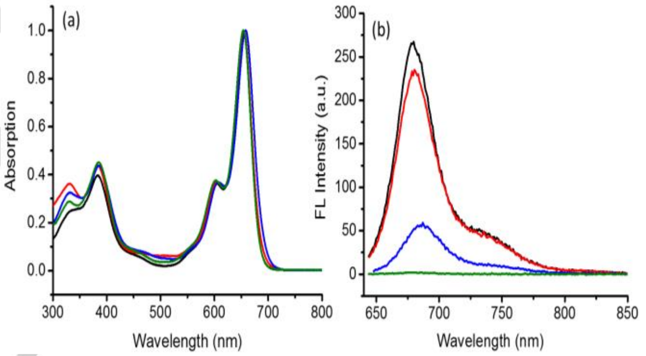


Figure 2. (a) Normalized to the intense visible peak maxima absorption spectra of compounds **1-4** in benzonitrile (**1**-black, **2**-red, **3**-blue and **4**-green). (b) Fluorescence spectra of compounds **1-4** (**1**-black, **2**-red, **3**-blue and **4**-green) in benzonitrile. The samples were excited at the intense absorption peak maxima.

Figure 2b shows the fluorescence spectra of compounds **1-4** in benzonitrile, excited at the most intense peak maxima. In agreement with the absorbance behavior, the fluorescence spectra of compounds **1-4** revealed red-shifted peaks and appeared in the 680 nm range compared to pristine BODIPY emission in the 520 nm range. The peak intensity of compound **2** carrying triphenylamine substituent was about 90% of that of **1** carrying only a toluyl substituent. Additionally, peak intensity of compound **3** having phenothiazine substituent and compound **4** having ferrocene substituent was found to be quenched by 80 and 98%, respectively, suggesting occurrence of intramolecular $D^{\delta+}$-BODIPY$^{\delta-}$ (D = ferrocene, TPA and PTZ).type excited state events. The fluorescence lifetimes of compounds **1** and **2** were also determined using time correlated single photon counting (TCSPC) technique. Both compounds revealed monoexponential decay ($\chi^2 < 1.2$) with lifetimes of 3.73 and 3.39 ns, respectively (see Figure S1 in SI for decay curves).

Formation and characterization of 'two-point' bound self-assembled supramolecular donor-acceptor conjugate

Figure 3a shows the spectral changes observed during binding of bis-alkyl ammonium functionalized fulleropyrrolidine, **5** to compound **1** carrying two crown ether receptor sites in benzonitrile. Increased addition of **5** to a solution of **1** revealed diminished intensity of the peak located at 653 nm with a small blue-shift of 2 nm. In the 310 nm range increased absorption and a sharp peak at 432 nm due to fulleropyrrolidine were also observed. An isosbestic point at 588 nm indicating the presence of only one equilibrium process was observed. The binding constant and stoichiometry were calculated using Benesi-Hildebrand[25] and mole ratio methods as shown in Figures 3b and c, respectively. The calculated binding constant was found to be 5.9 x 10^5 M^{-1}, which is an order of magnitude higher compared to mono-alkyl ammonium cation functionalized fulleropyrrolidine binding to benzo-18-crown-6 functionalized BODIPY from our previous study.[22a] The mole ratio plot revealed a break at 0.5 as expected for the 1:1 stoichiometry. These results assertively prove binding of bis-alkyl ammonium functionalized fulleropyrrolidine, **5** to **1** carrying appropriately positioned crown ether receptor sites in a cooperative fashion.

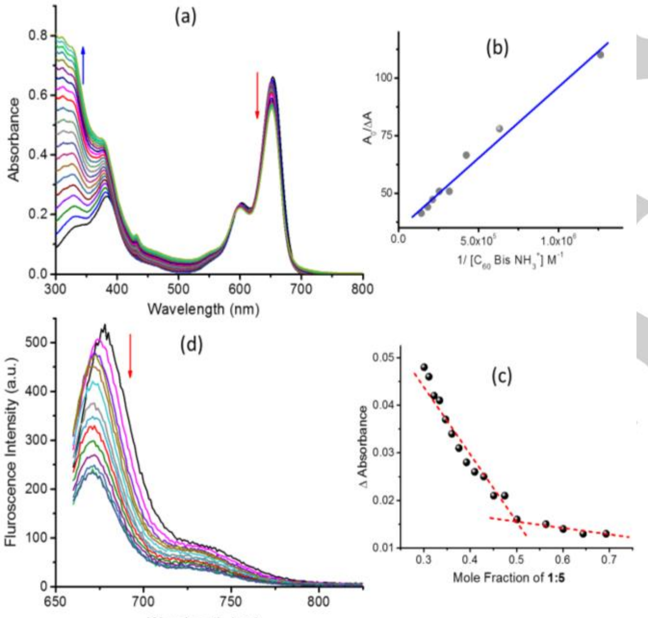


Figure 3. (a) Spectral changes observed for compound **1** during increased addition of compound **5** in benzonitrile. (b) Benesi-Hildebrand plot constructed using absorption data to evaluate the binding constant. (c) Mole-ratio plot constructed using absorption titration data to evaluate the supramolecular stoichiometry. (d) Fluorescence of **1** upon increasing addition of **5** in benzonitrile. The sample was excited at 653 nm.

The fluorescence of **1** during the titration of **5** was also monitored as shown in Figure 3d. Successive addition of **5** diminished the peak intensity of compound **1** suggesting the occurrence of excited state events such as energy or electron transfer in the newly formed donor-acceptor conjugate.[26] In a control experiment, compound **1** was titrated with pristine C_{60}, under these conditions, the quenching of **1** was less than 3%, emphasizing the importance of cation-crown ether binding to form the supramolecular complex and subsequently promote intramolecular excited state events.

Energy optimization of the supramolecular 'two-point' bound bis-styrylBODIPY-C_{60} conjugates

Computational studies were performed to visualize the geometry and electronic structure of the supramolecular 'two-point' bound bis-styrylBODIPY-C_{60} conjugates. In these studies, the gas phase geometry of the starting compounds, **1-5**, and of the supramolecular structures were optimized to a stationary point on the Born-Oppenheimer surface using the B3LYP DFT method and the 3-21G(*) split valence basis set[27] as parametrized in the *Gaussian-09* software suite. The structures and frontier orbitals (HOMO and LUMO) were visualized with the *GaussView* 5.0.9 software. The optimized structures and HOMO and LUMO of the starting compounds is shown in Figure S2. The V-type disposition of the two crown ether entities was apparent. In majority of these structures the HOMO and LUMO were largely delocalized over the BODIPY π-structure involving the styryl tails.

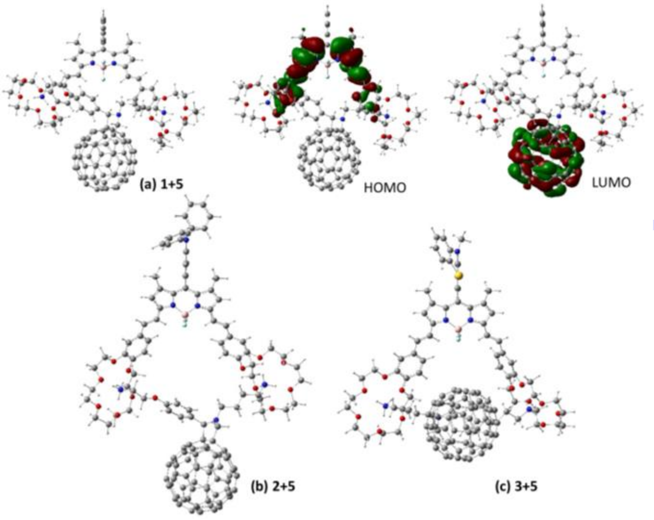


Figure 4. (a) Optimized structures of 1**+5**, **2+5** and **3+5** at the B3LYP/3-21G(*) level. The HOMO and LUMO of **1+5** conjugate is also shown.

Figure 4 shows the optimized structures, and frontier HOMO and LUMO of **1+5**, and optimized structures of **2+5** and **3+5** conjugates. Similar structure was also obtained for **4+5** conjugate. In all these structures, the bis-alkyl ammonium cations binding to the crown ether entities via H-bonding was evident (NH···O distances were around 1.85 Å). The center-to-center distance between fullerene to boron of BODIPY was found to be 11.5 Å while the edge-to-edge distance between fullerene to styryl π-system in these conjugates was 4.1 and 4.5 Å, for an average distance of 4.3 Å, respectively. The center of the fullerene to the center of the styryl phenyl was found to be

8.7 Å and 9.3 Å for an average distance of 9.0 Å. Close distance between the bis styryl BODIPY π-structure and fullerene π-structure in these conjugates was apparent. The gas phase binding energies, estimated from the difference between the energies of the optimized structures and the sum of the energies of the individual entities, was found to range between -740 to -825 kJ/mol. These values compared with an earlier reported gas phase values of ~-250 kJ/mol for 'single-point' binding of benzo-18-crown-6 functionalized BODIPY binding to alkyl ammonium cation functionalized C_{60}.[22a] The higher stability in the present conjugates in the gas phase and also the earlier discussed binding data from optical studies in solution could be attributed to the 'two-point' binding strategy utilized in the present study.

Electrochemistry and energy level diagram

Electrochemical studies using differential pulse voltammetry (DPV) were performed to evaluate the redox potentials of compounds **1-5** and also to calculate the energetics of the charge separation processes. Figure 5 shows the DPV curves for compounds **1-5** in benzonitrile, 0.1 M (n-Bu_4N)ClO_4. Multiple oxidation processes involving BODIPY and *meso*-donor substituents were observed. The redox potentials of the bis-styryl functionalized BODIPY were different from that of pristine BODIPY.[28] That is, smaller electrochemical HOMO-LUMO gap due to facile oxidation and reduction of BODIPY were observed. Appending additional triphenylamine or phenothiazine entities in compounds **2** and **3** had minor effects on the first oxidation potential while in the case of **4**, an anodic wave corresponding to ferrocene oxidation was observed prior to BODIPY oxidation.

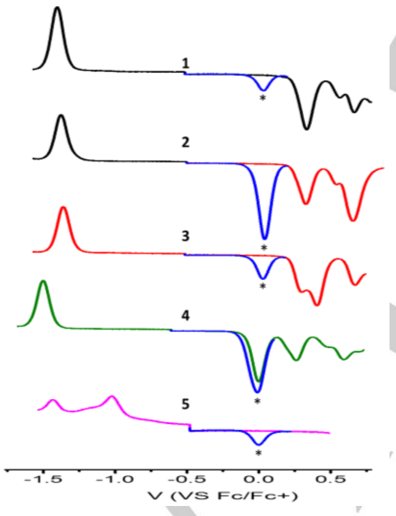


Figure 5. Differential pulse voltammograms of compounds **1-5** in benzonitrile, 0.1 M (n-Bu_4N)ClO_4. Scan rate = 50 mV/s, pulse width = 50 ms, pulse height = 0.025 V. The '*' corresponds to the oxidation of ferrocene used as an internal standard.

Table 1 lists the first oxidation and first reduction potentials of these investigated compounds. Upon forming the supramolecular complex, the BODIPY oxidation waves revealed a small anodic shift while the potential for C_{60} reduction had no appreciable effect (see Table 1 and Figure S3). The currents for redox peaks were lower upon forming the supramolecular complex that could be ascribed to smaller diffusion coefficient as a result of increased mass of the supramolecular complex.

The free energy change for charge recombination (ΔG_{CR}) and charge separation (ΔG_{CS}) from the singlet excited state of the bis-styryl BODIPY within the donor-acceptor system was calculated using spectroscopic, computational and electrochemical data using equations described in Table 1 footnote.[29] These results reveal thermodynamic feasibility of charge separation and recombinaion in the studied conjugates

Table 1. Redox potentials (V vs. Fc/Fc^+), free-energy change[30] for charge separation (ΔG_{CS}) and recombination (ΔG_{CR}) for the donor-acceptor conjugates in benzonitrile.

Compound	**1st and 2nd oxidations**	**1st reduction**	**$-\Delta G_{CR}{}^{a}$, eV**	**$-\Delta G_{CS}{}^{b}$, eV**
1	0.30	-1.42	--	--
2	0.29, 0.60	-1.41	--	--
3	0.27, 0.38	-1.39	--	--
4	0.01, 0.26	-1.45	--	--
5	--	-1.02	--	--
1+5	0.32	-1.01	1.27	0.58
2+5	0.31	-1.02	1.27	0.58
3+5	0.30	-1.01	1.25	0.60
4+5	0.02	-1.02	1.00	0.85

[a] $-\Delta G_{CR} = e(E_{ox} - E_{red}) - \Delta G_S$

[b] $-\Delta G_{CS} = E_{0,0} - (-\Delta G_{CR})$

where the solvation energy ΔG_S is given as

$$\Delta G_S = e^2 / 4 \pi \varepsilon_0 \varepsilon_R R_{CC})$$

where ΔG_S is, E_{ox} is the first oxidation potential of the donor in the conjugate, E_{red} is the first reduction potential of the acceptor in the conjugate, $E_{0,0}$ is the energy associated with the 0,0 optical transition (midpoint of absorption and emission corresponding to 0,0 transition) being, 1.85 eV. ε_0 and ε_R refer to vacuum permittivity and dielectric constant of the employed solvent, respectively. R_{CC} is the center-to-center distance (distance between boron and center of fullerene) being 11.5 Å for the donor-acceptor conjugates. The calculated ΔG_S was found to be 0.06 eV for the conjugates in benzonitrile.

Further, spectroelectrochemical studies were performed to spectrally characterize the one-electron oxidation products of bis-styrylBODIPYs, **1-4**. The spectral changes observed for compounds **1-3** were quite similar. That is, the peaks located in the 385 and 655 nm range revealed diminished intensity with the appearance of new peaks in the 518, 545 and 586 nm range corresponding to their radical cation formation (see Figure S4). One or two isosbestic points were also observed. The spectral changes were reversible, that is, applying a voltage of -0.10 V quantitatively recovered the spectrum of the initial neutral compound. For compound **4**, however, these spectral changes were subtle due to facile oxidation of ferrocene over bis-styrylBODIPY entity. The small spectral change of bis-styrylBODIPY peaks suggests communication between the *meso*-substituted ferrocene with the bis-styrylBODIPY π-system.

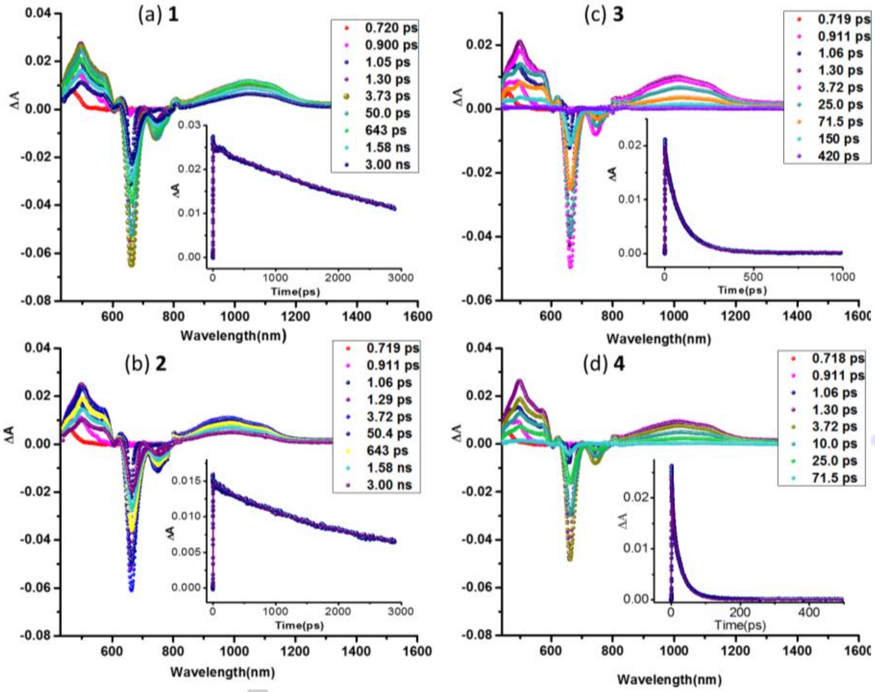


Figure 7. Femtosecond transient spectra (100 fs pulse width at 654 nm) of compounds **1-4** in Ar-saturated benzonitrile at the indicated delay times. The time profiles of the 500 nm are shown in the corresponding figure insets.

An energy level diagram was constructed to visualize the different photochemical events occurring in the donor-acceptor conjugates. Figure 6 shows such a diagram wherein formation of $D^{\bullet+}$-$C_{60}^{\bullet-}$ charge separated state from $^1D^*$ (where D-C_{60} refers to the supramolecular complex formed between compounds **1** – **4**, abbreviated as D, and C_{60} in Figure 1). through an intermediate exciplex state, [D-C_{60}]* (excited state complex) is feasible. Formation of $D^{\bullet+}$-$C_{60}^{\bullet-}$ from $^1C_{60}^*$ is also a possibility, however, at the excitation wavelength of bis-styryl BODIPY absorption peak maxima (654 nm), no C_{60} was excited thus safely ruling out this possibility. The [D-C_{60}]* exciplex state competitively could also populate either the $^3D^*$ or $^3C_{60}^*$ in addition to charge transfer process (see Figure 6). The energy of the charge separated state in **1+5**, **2+5** and **3+5** are almost the same (1.25-1.27 eV) while that of **4+5** is about 1.00 eV. Under such circumstances, the $D^{\bullet+}$-$C_{60}^{\bullet-}$ (where D = **1** - **3**) could populate the $^3D^*$ (E_T ~ 1.35 eV)[21a] prior to returning to the ground state. However, populating $^3C_{60}^*$ (E_T = 1.50 eV)[30] would be thermodynamically not a feasible process. However, in the case of **4+5** due to low energy of the charge separated state, population of neither $^3D^*$ or $^3C_{60}^*$ is anticipated. In such a case, the charge separated state would charge recombine directly to the ground state. In order to further understand these mechanistic routes and to secure evidence for charge separation, transient absorption studies using femtosecond and nanosecond transient techniques were systematically performed and summarized in the following section.

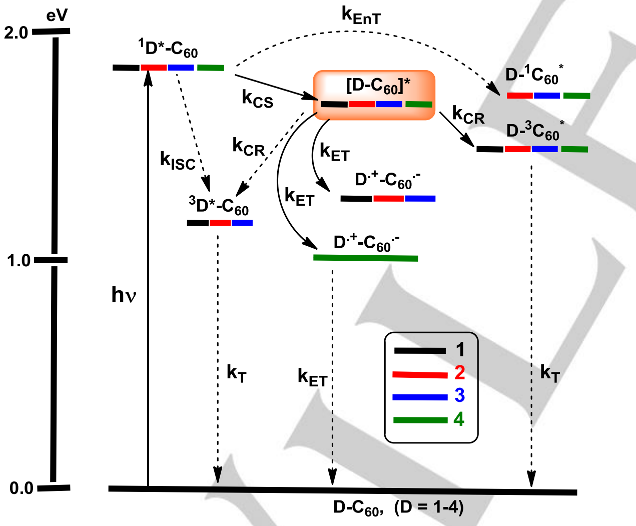


Figure 6. Energy level diagram showing the different photochemical events of 'two-point' bound bis-styrylBODIPY-C_{60} conjugates (D = **1-4**) in benzonitrile. Energies of different states were evaluated from spectral and electrochemical studies. Energy of ^{3}bis(styryl)BODIPY* was taken from Ref. 21a. Solid arrow indicates major photo processes, dashed arrow indicates minor photo processes. Abbreviations: CS = charge separation, CR = charge recombination T = triplet state. The exciplex state is abbreviated as [D-C_{60}]*.

Femtosecond transient absorption studies

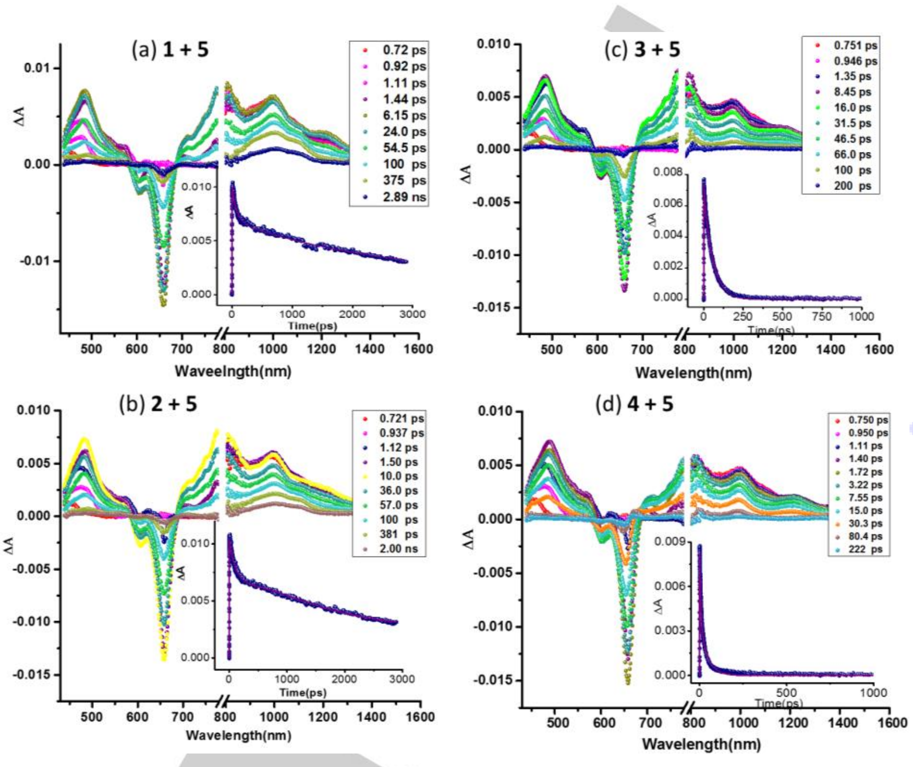


Figure 8. Femtosecond transient spectra (100 fs pulse width at 654 nm) of donor-acceptor conjugates formed by complexing compounds **1-4** with compound **5** in Ar-saturated benzonitrile at the indicated delay times. The time profiles of the 1010 nm are shown in the corresponding figure insets.

First, femtosecond transient absorption spectral studies of the bis-styrylBODIPY compounds were performed. The compounds were excited at the most intense visible peak maxima corresponding to the $S_o \rightarrow S_1$ transition using 100 fs laser pulses in deaerated benzonitrile. The instantaneously formed singlet excited state of compound **1** having only a toluyl group at the *meso* position, revealed peaks at 500, 628 and 1044 nm corresponding to transitions originating from the singlet excited state of **1**. In addition, negative peaks at 660 and 745 nm having contributions from ground state bleaching and stimulated emission were observed. The decay of the positive peaks and the recovery of the negative peaks was rather slow extending beyond 3 ns, monitoring time window of our instrumental setup. This is consistent with relatively long lifetime of (3.73 ns) of **1**, discussed earlier.

The spectral features for compounds **2-4** were almost similar but with one exception (see Figure 7b-c). That is, the time constants for the decay of the positive peaks and recovery of the negative peaks were different, as shown by the time profile plots in the respective figure inset. The time constants observed the following trends: **1**>**2**>**3**>**4** (see Table 2) which tracked the earlier discussed excited state lifetime of these compounds. The short time constants in the case of **3** and **4** suggest excited state interactions, especially in the case of ferrocene functionalized bis-styrylBODIPY, **4**, and to a lesser extent in the case of **3**.

Table 2. Time constants of the 1040 nm peak corresponding to the $S_1 \rightarrow S_n$ transition and 660 nm peak corresponding to ground state recovery of *meso*-donor functionalized bis-styrylBODIPY, **1-4** and the estimated rates of charge separation, k_{CS} and charge recombination, k_{CR} of the supramolecular complexes formed by complexing **1-4** by **5** in benzonitrile.

Compound	Decay/recovery time constants, ps	k_{CS}, s^{-1}	k_{CR}, s^{-1}
1	4057, 4050	--	--
2	3515, 3250	--	--
3	104, 93	--	--
4	30, 23	--	--
1+5	2632	6.1×10^8	3.4×10^8
2+5	1478	5.8×10^8	5.7×10^8
3+5	276	7.2×10^9	1.8×10^9
4+5	30	2.6×10^{10}	1.7×10^9

Next, the femtosecond transient spectra of the donor-acceptor conjugates formed by self-assembling **5** to compounds **1-4** in benzonitrile were investigated. From spectroelectrochemical studies bis-styrylBODIPY$^{\bullet +}$ is expected to reveal a peak at 580 nm range where strong negative peaks of ^{1}bis-styrylBODIPY* exist. The $C_{60}^{\bullet -}$ is expected to reveal its characteristic peak at 1020 nm. Presence of these transient peaks would provide direct spectral evidence of charge separation in the donor-acceptor conjugates. Alternatively, singlet-singlet energy transfer from ^{1}bis-styrylBODIPY* to C_{60} to produce $^1C_{60}^*$ could also occur. The $^1C_{60}^*$ exhibits transient peaks in the near-IR region at 880 and 1010 nm.

As shown in Figure 8, the recorded transient spectral features of the donor-acceptor conjugates were supportive of the formation of an initial intermediate exciplex state followed by generating the electron transfer products. As expected, the decay and recovery of the peaks originated from ^{1}bis-styrylBODIPY* were faster than that observed for pristine **1-4** due to the occurrence of competitive exciplex or charge transfer process (see Table 2). Importantly, in these conjugates a strong peak in the 790-800 nm range was observed whose peak position was different from that of either ^{1}bis-styrylBODIPY* or $^1C_{60}^*$ (product of rapid energy transfer). The decay of this peak concurrently developed the growth of $C_{60}^{\bullet -}$ suggesting that it

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would be due to an intermediate exciplex state, [D-C_{60}]* (D = **1-4**), as is previously shown for porphyrin-fullerene donor-acceptor systems.[31]

The decay profile of the 1016 nm peak corresponding to $C_{60}^{\bullet-}$ was monitored to evaluate the charge recombination kinetics. In all of the studied systems, the decay of this peak was found to be biexponential with short and long-lived components. From spectral observations, the short lived component was ascribed to peak associated with ^{1}bis-styrylBODIPY* (see Figure 7) while the long-lived component was ascribed to $C_{60}^{\bullet-}$ involving charge recombination process. The time constants for the long-lived component were found to be 2950, 1753, 547 and 572 ps, respectively, for **1+5, 2+5, 3+5** and **4+5**. The k_{CR} derived from these time constants are given in Table 2. The difference in k_{CS} and k_{CR} for **1+5, 2+5, 3+5** having almost the same energies for charge separation and charge recombination could be due to the intermediate exciplex governing the degree of charge separation to some extent, although additional experimental evidence are needed to verify this fact.

Further, nanosecond transient spectra of the donor-acceptor conjugates were recorded, initially, at the excitation wavelength of 654 nm corresponding to ^{1}bis-styrylBODIPY* formation. However, at this excitation wavelength the transient signal strength was too weak to measure. When the excitation wavelength was changed to 355 nm, triplet spectra of ^{3}bis-styrylBODIPY* were observed for **1-3** but not for **4** as shown in Figure S6a-c. The most intense peak was located around 510 nm with another broader peak centered around 790 nm. The determined decay time constants (see figure inset for time profiles) were found to be 127, 158, and 356 μs, respectively, for **1**, **2** and **3**. The nanosecond transient spectra of the fullerene derivative, **5** revealed peaks at 400, 700 and 825(sh) nm in agreement with earlier studies on fulleropyrrolidine (see Figure 6d).[22a] The decay time constant for this peak was 16 μs. The nanosecond transient spectra of the donor-acceptor hybrids were better defined compared to the corresponding pristine bis-styrylBODIPY derivatives, as shown in Figure S7. In all these hybrids, transient peaks originated from $^3C_{60}$* and to a lesser extent that from ^{3}bis-styrylBODIPY* were obvious. In the energy level diagram in Figure 6, population of the ^{3}bis-styrylBODIPY* state from the radical ion-pair state, $D^{\bullet+}$-$C_{60}^{\bullet-}$ in the case of hybrids formed by **1-3** with **5** is feasible, however, not that of $^3C_{60}$*. In such an instance, population of $^3C_{60}$* (and ^{3}bis-styrylBODIPY* to lesser extent) could competitively occur from the intermediate exciplex state, [D-C_{60}]*. That is, [D-C_{60}]* could either undergo electron transfer to yield the radical ion-pair or could populate either the donor or acceptor triplet levels. It may also be mentioned here that at the excitation wavelength of 355 nm, direct excitation of C_{60} is also possible, contributing to the overall triplet spectra shown in Figure S7. The decay time constants of the fulleropyrrolidine peak at 770 nm (see figure inset for time profiles) were found to be 236, 286, 218, and 16 μs, respectively, for the **1+5, 2+5, 3+5** and **4+5** supramolecular donor-acceptor hybrids. The growth of the $^3C_{60}$* time profiles in Figure S7a-c insets were slow (5-20 μs) suggesting that the formation of $^3C_{60}$* could be through the routes discussed in Figure 6 and not from directly excited fulleropyrrolidine.

Summary

A 'two-point' crown ether – alkyl ammonium binding strategy has been successfully developed to build supramolecular donor-acceptor conjugates to yield structurally well-defined, bis(styryl crown ether)BODIPY - bis(alkyl ammonium) fulleropyrrolidine donor-acceptor conjugates. Further, the *meso*-position of the bis-styrylBODIPY carried a secondary electron donor. The geometry and electronic structure derived from B3LYP/6-31G(d,p) method revealed stable self-assembled structures demonstrating no steric hindrance between the entities. The established energy level diagram using spectral, electrochemical and computational results helped in understanding the mechanistic details of excited state processes originating from the initial ^{1}bis-styrylBODIPY* state. Femtosecond transient absorbance studies were indicative of the formation of an exciplex state prior to the charge transfer state to yield bis-styrylBODIPY$^{\bullet+}$-$C_{60}^{\bullet-}$ charge separated state. The time constants for charge separation were generally lower compared to charge recombination process. The secondary electron donor present at the *meso*-position of bisstyrylBODIPY did not much help in stabilizing the charge separated state appreciably.

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. Tetra-*n*-butylammonium perchlorate, (*n*-$Bu_4N)ClO_4$, used in electrochemical studies was from Fluka Chemicals. Synthesis of **5** is given elsewhere.[23]

Synthesis of 3,5-bis(benzo-18-crown-6 styryl)BODIPY, **1**

Synthesis of 4'-formyl benzo-18-crown-6: Benzo-18-crown-6 (2.52 g, 8.07 mmol) and hexamethylenetetramine (1.2 g, 8.56 mmol) were kept in a 50 mL round bottom flask and refluxed with trifluoroacetic acid (6.1 mL, 79.66 mmol) for 24 hours under nitrogen. The resulting dark-red mixture was cooled in ice bath for 20 min. After cooling ice and hydrochloric acid (2 drops) were added to the mixture. The ice bath was removed, and the mixture was stirred for 2.5 h. The mixture was then extracted with dichloromethane and the organic layer was dried over anhydrous Na_2SO_4 The solvent was removed and the crude product was purified over a silica column. The product was eluted with CH_2Cl_2/EtOAc (90:10, v/v). After evaporated the solvent, the product, as light yellow oil, was mixed with diethyl ether and refrigerated overnight. The desired compound was obtained as a white solid. Yield:1.92 g (70%); ^{1}H NMR ($CDCl_3$;400 MHz): δ = 3.66–3.78 (m, 12H, crown ethylene-H), 3.88–3.96 (m, 4H,crownethylene-H), 4.16–4.24 (m, 4H,crown ethylene-H), 6.93 (d, J =8.2 Hz, 1H,Ar-H), 7.36 (d, J = 1.8 Hz, 1H,Ar-H), 7.42 (d,d, J = 8.2, 1.8 Hz,1H,Ar-H) 9.81 ppm (s, 1H,-CHO).

Synthesis *meso*-phenyl BODIPY, 1a: Benzaldehyde (1.06 g, 10 mmol) and 2,4-dimethylpyrrole (1.75 mL,17 mmol) were kept in a 1000 mL round-bottom flask with dichloromethane (650 mL) under nitrogen at room temperature. After stirred for 15 min, trifluoroacetic acid (154 uL, 2 mmol) was added to the mixture. After 2h, the resulting solution was washed by 0.1M NaOH (160 mL) and then deionized water (160 mL). The organic layer was dried over anhydrous Na_2SO_4 and then the solvent was removed. The residue was transferred to a 100 mL round-bottom flask and dissolved in toluene (40 mL) under nitrogen at room temperature. After 15 min, p-chloranil (2.213 g, 9 mmol) was added to the mixture, then after 15 min, Et_3N (6 mL) was added. After that $BF_3{\cdot}Et_2O$ (5.6 mL) was added dropwise to the solution. The mixture was stirred for 2h and then washed with deionized water (160 mL) and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4.The solvent was removed under reduced pressure and the crude product was purified over silica column. The desired compound which has an orange color was eluted by Hexanes/CH_2Cl_2 (40:60, v/v). Yield: 445 mg (16.1%); ^{1}H NMR ($CDCl_3$;400 MHz): δ = 1.37 (s, 6H, CH_3-H), 2.55 (s, 6H,CH_3-H), 5.97 (s, 2H,pyrrole-H), 7.23–7.31 (m, 2H,Ar-H), 7.40-7.56 ppm (m, 3H,Ar-H).

Synthesis of 3,5-bis(benzo-18-crown-6 styryl) BODIPY, 1: *meso*-phenyl BODIPY (300 mg, 0.925 mmol), 4'-formyl benzo-18-crown-6 (1.57 g, 4.625 mmol), piperidine (1 ml) and acetic acid (1 ml) were kept in a 50 ml round bottom flask and refluxed with benzene (20 ml) for 48 hours under nitrogen by using Dean-Stark apparatus. This reaction was monitored by UV-Vis spectrum (500 nm peak was consumed, and 649.6 nm peak was generated in DCM). After that the mixture was washed by DI water (70 ml) and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, then the solvent was removed under reduced pressure. The crude product was purified over silica as the first column and over basic alumina as the second column. The desired compound as green-blueish color was eluted by CH_2Cl_2-MeOH (98:2, v/v). Yield- 322 mg (35.8%). ^{1}H NMR ($CDCl_3$; 400MHz), δ = 1.43 (s, 6H, CH_3-H), 3.69-3.81 (m, 24H, crown ethylene-H), 3.93-3.98 (m, 8H, crown ethylene-H), 4.18-4.28 (m, 8H, crown ethylene-H), 6.60 (s, 2H, pyrrole-H), 6.87-6.90 (d, J = 8.2Hz, 2H, Ar-H), 7.13-7.15 (d, J = 1.8Hz, 2H, Ar-H), 7.15-7.22 (m, 4H, CH-H, Ar-H), 7.31-7.34 (m, 2H, Ar-H), 7.47-7.50 (m, 3H, Ar-H), 7.53-7.59 ppm (d, J = 16.2Hz, 2H, CH-H). ^{13}C NMR ($CDCl_3$; 100MHz), δ = 14.20, 14.61, 21.07, 29.70, 60.40, 68.94, 69.42, 69.49, 69.56, 69.67, 70.56, 70.74, 70.82, 70.89, 113.10, 113.15, 113.56, 113.59, 117.45, 117.65, 121.87, 128.51, 128.89, 129.02, 130.18, 133.23, 135.24, 136.08, 138.18, 141.78, 148.95, 150.16, 152.65 ppm. MALDI-MS, calculated = 968.88, found – 968.5(M^+), 991.5 (M^++ Na^+).

Synthesis of *meso*-triphenylamino (3,5-bis(benzo-18-crown-6 styryl)) BODIPY, 2

Synthesis meso-triphenylamine BODIPY, 2a: 4-(Diphenyl amino)-benzaldehyde (970 mg, 3.54 mmol) and 2,4-dimethylpyrrole (621 uL, 6.03 mmol) were kept in a 500 mL round-bottom flask with dichloromethane (230 mL) under nitrogen at room temperature. After stirred for 15 min, trifluoroacetic acid (55 uL, 0.71 mmol) was added to the mixture. After 2h, the resulting solution was washed by 0.1m NaOH (60 mL) and then deionized water (60 mL). The organic layer was dried over anhydrous Na_2SO_4 and then the solvent was removed. The residue was transferred to a 50 mL round-bottom flask and dissolved in toluene (14 mL) under nitrogen at room temperature. After 15 min, p-chloranil (784.36 mg, 3.19 mmol) was added to the mixture, then after 15 min, Et_3N (2.27 mL) was added. After that $BF_3{\cdot}Et_2O$ (2 mL) was added dropwise to the solution. The mixture was stirred for 2h and then washed with deionized water (60 mL) and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4.The solvent was removed under reduced pressure and the crude product was purified over silica column. The desired compound which has an orange color was eluted by Hexanes/CH2Cl2 (30:70, v/v). Yield:338 mg (22.8%); ^{1}HNMR ($CDCl_3$;400 MHz): δ = 1.59 (s, 6H, CH_3-H), 2.55 (s, 6H, CH_3-H), 6.00 (s, 2H, pyrrole-H), 7.04–7.09 (m, 2H, Ar-H), 7.09–7.13 (m, 6H, Ar-H), 7.19–7.15 (m, 2H, Ar-H), 7.27-7.32 ppm (m, 4H, Ar-H).

Synthesis of *meso*-triphenylamino (3,5-bis(benzo-18-crown-6 styryl)) BODIPY, 2: *meso*-Triphenylamino BODIPY, **2a** (300 mg, 0.61 mmol), 4'-formyl benzo-18-crown-6 (1.04 g, 3.05 mmol), piperidine (0.7 ml) and acetic acid (0.7 ml) were kept in a 50 ml round-bottom flask and refluxed with benzene (13 ml) for 48 hours under nitrogen by using Dean-Stark apparatus. This reaction was monitored by UV-Vis spectrum (500 nm peak was consumed, and 649 nm peak was generated in DCM). After that the mixture was washed by DI water (50 ml) and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, then the solvent was removed under reduced pressure. The crude product was purified over silica as the first column and over basic alumina as the second column. The desired compound as green-blueish color was eluted by CH_2Cl_2-MeOH (95:5, v/v). Yield- 307 mg (44.3%). ^{1}H NMR ($CDCl_3$; 400MHz), δ = 1.65 (s, 6H, CH_3-H), 3.69-3.81 (m, 24H, crownethylene-H), 3.93-3.98 (m, 8H, crownethylene-H), 4.18-4.28 (m, 8H crownethylene-H), 6.63 (s, 2H, pyrrole-H), 6.87-6.90 (d, J = 8.2Hz, 2H, Ar-H), 7.05-7.09 (m, 2H, Ar-H), 7.11-7.15 (m, 6H, Ar-H), 7.15-7.22 (m, 8H Ar-H, CH-H), 7.27-7.32 (m, 4H, Ar-H), 7.53-7.58 ppm (d, J = 16.2Hz, 2H, CH-H). ^{13}C NMR ($CDCl_3$; 100MHz), δ = 14.85, 53.42, 68.99, 69.51, 69.58 69.69, 70.75, 70.80, 70.84, 70.91, 113.24, 113.69, 117.51, 117.63, 121.86, 123.27, 123.43, 124.70, 128.51, 129.42, 129.45, 130.25, 133.54, 135.97, 138.39, 141.63, 147.37, 148.52, 148.99, 150.19, 152.53 ppm. MALDI-MS, calculated = 1136.09, found – 1135.7(M^+), 1158.7 (M^++ Na^+).

Synthesis of *meso*-phenothiazine (3,5-bis (benzo-18-crown-6 styryl)) BODIPY, 3

Syntheses of 3-formyl-10-methylphenothiazine: Phosphorus(V) oxychloride (1.31 mL, 14.05 mmol) and DMF (10 mL) were kept in a 100 mL round-bottom flask under nitrogen at 0℃. The solution of 10-methylphenothiazine (1 g, 4.69 mmol) in DMF (10 mL) was added dropwise to the mixture. After the mixture had been stirred for 30 min, the mixture was refluxed overnight. After cooling at room temperature, the round-bottom flask was kept in the ice bath, and a saturated solution of sodium hydroxide was added dropwise until the pH of the solution was in the 7–8 range (litmus paper detection). The mixture was then extracted with dichloromethane and the organic layer was dried over anhydrous Na_2SO_4.The solvent was removed under reduced pressure, and the crude product was purified over a silica column. The desired compound was obtained as a lemon-yellowish color and was eluted by hexanes/CH_2Cl_2 (50:50, v/v). Yield: 446.2 mg (39.5%); ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 3.30 (s, 3H,CH_3-H), 6.69–6.78 (m, 2H,Ar-H), 6.89–6.97 (m 1H,Ar-H), 7.01–7.07(dd, J =7.6, 1.1 Hz, 1H,Ar-H), 7.09–7.16 (m, 1H,Ar-H), 7.44–7.50 (d, J = 1.6Hz,1H,Ar-H), 7.51–7.58 (dd, J = 8.4, 1.7 Hz, 1H,Ar-H), 9.72 ppm (s, 1H,CHO).

Synthesis *meso*-phenothiazine BODIPY, 3a: 3-Formyl-10-methyl phenothiazine (950 mg, 3.94 mmol) and 2,4-dimethylpyrrole (690 uL, 6.7 mmol) were kept in a 500 mL round-bottom flask with dichloromethane (260 mL) under nitrogen at room temperature. After stirred for 15 min, trifluoroacetic acid (60 uL, 0.79 mmol) was added to the mixture. After 2h the resulting solution was washed by 0.1m NaOH (70 mL) and then deionized water (70 mL). The organic layer was dried over anhydrous Na_2SO_4 and then the solvent was removed. The residue was transferred to a 50 mL round-bottom flask and dissolved in toluene (16 mL) under nitrogen at room temperature. After 15 min, p-chloranil (871.3 mg, 3.54 mmol) was added to the mixture, then after 15 min, Et_3N (2.52 mL) was added. After that $BF_3{\cdot}Et_2O$ (2.2 mL) was added dropwise to the solution. The mixture was stirred for 2 h and then washed with deionized water (70 mL) and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4.The solvent was removed under reduced pressure and the crude product was purified over silica column. The desired compound which has an orange color was eluted by Hexanes/CH_2Cl_2 (30:70, v/v). Yield:364 mg (23.7%); ^{1}H NMR ($CDCl_3$; 400 MHz): δ = 1.50 (s, 6H, CH_3-H), 2.55 (s, 6H,CH_3-H), 3.42 (s, 3H,CH_3-H), 5.97 (s, 2H, pyrrole-H), 6.84–6.89 (m, 2H, Ar-H), 6.95–7.00 (m, 1H, Ar-H), 7.01–7.07 (m, 2H, Ar-H), 7.12–7.16 (d, J=7.6, 1.4 Hz, 1H, Ar-H), 7.19-7.24 ppm (m, 1H, Ar-H).

Synthesis of *meso*-phenothiazine (3,5-bis (benzo-18-crown-6 styryl)) BODIPY, 3: A mixture of **3a** (300 mg, 0.653 mmol), 4’-formyl benzo-18-crown-6 (1.111 g, 3.265 mmol), piperidine (0.7 ml) and acetic acid (0.7 ml) were kept in a 50 ml round bottom flask and refluxed with benzene (13 ml) for 48 hours under nitrogen by using Dean-Stark apparatus. This reaction was monitored by UV-Vis spectrum (500 nm peak was consumed, and 651.87 nm peak was generated in DCM). After that the mixture was washed by DI water (50 ml) and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, then the solvent was removed under reduced pressure. The crude product was purified over silica as the first column and over basic alumina as the second column. The desired compound as green-blueish color was eluted by CH_2Cl_2-MeOH (95:5, v/v). Yield- 112 mg (15.5%). ^{1}H NMR ($CDCl_3$; 400 MHz), δ = 1.54 (s, 6H, CH_3-H), 3.41 (s, 3H, CH_3-H), 3.67-3.79 (m, 24H, crown ethylene-H), 3.92-3.97 (m, 8H, crown ethylene-H), 4.17-4.26 (m, 8H, crown ethylene-H), 6.59 (s, 2H, pyrrole-H), 6.83-6.88 (m, 4H, Ar-H), 6.94-6.98 (m, 1H, Ar-H), 7.04-7.11 (m, 4H, CH-H, Ar-H), 7.12-7.15 (m, 2H, Ar-H), 7.16-7.22 (m, 4H, Ar-H), 7.50-7.55 ppm (d, J = 16.2Hz, 2H, CH-H). ^{13}C NMR ($CDCl_3$; 100MHz), δ = 14.14, 15.28, 15.45, 22.70, 24.64, 29.37, 29.70, 31.92, 35.47, 68.71, 68.91, 69.15, 69.42, 69.52, 69.80, 69.85, 70.04, 70.15, 70.62, 70.71, 70.74, 71.00, 112.63, 112.65, 112.71, 112.74, 112.93, 113.23, 113.28, 114.24, 114.27, 117.41, 117.66, 117.83, 120.21, 121.80, 122.73, 122.81, 124.29, 126.80, 127.23, 127.42, 127.48, 127.59, 127.66, 127.71, 129.00, 130.12, 133.44, 136.11, 137.24, 141.73, 145.28, 146.27, 148.74, 149.71, 149.93, 152.62 ppm. MALDI-MS, calculated = 1104.07, found – 1103.4(M$^+$), 1126.2 (M$^+$+ Na$^+$).

Synthesis of *meso*-(4’-ferrocenylphenyl)-3,5-bis (benzo-18-crown-6 styryl) BODIPY, 4

Synthesis of 4-ferrocenylbenzonitrile: 4-Ferrocenylbenzonitrile was synthesized by Coe et al.[32] Briefly, ferrocene (3.8 g, 20.4 mmol) and sulfuric acid (25 ml) mixed in a 100ml round-bottomed flask, and this resulting deep blue ferrocenium solution was stirred at room temperature for 2 hours under nitrogen. Sodium nitrite (0.91 g, 13.2 mmol) and water (5 ml) was mixed at 0 ºC in a 50ml beaker, and then this mixture was added dropwise to a stirred 4-aminobenzonitrile (1.42 g, 12.0 mmol) and 1:1 water/HCl (10 ml) solution in a 100 ml round-bottomed flask. This mixture was stirred at 0 ºC on an ice bath for 30 mins under nitrogen in order to form diazonium solution. The ferrocenium solution was poured in to a 500 ml round-bottomed flask which contained ice/water (100 ml) at 0 ºC on an ice bath under nitrogen. After 15 mins, copper powder (1.0 g) was added to this 500 ml round-bottomed flask, and then the diazonium solution was added dropwise with the vigorous stirring. After 30 mins, the ice bath has removed, and the mixture was stirred at room temperature for 24 hours under nitrogen. After that, ascorbic acid (5 g) was added to the 500 ml round-bottomed flask to reduce any remaining ferrocenium to ferrocene, and then the mixture was stirred 1 hour. After that the mixture was washed by DI water (100 ml) and extracted with DCM. The organic layer was filtered through Celite, and then was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified over a silica column. The desired compound was obtained as an orange-red color was eluted by Hexanes/CH_2Cl_2 (40:60, v/v). Yield: 1.6g (46.6%). ^{1}H NMR ($CDCl_3$; 500 MHz): δ= 4.05 (s, 5H, C_5H_5-H), 4.40-4.45 (t, J = 1.95 Hz, 2H, C_5H_4-H), 4.67-4.72 (t, J = 1.95 Hz, 2H, C_5H_4-H), 7.50-7.53 (d, J = 8.3 Hz, 2H, Ar-H), 7.54-7.57 ppm (d, J = 8.3 Hz, 2H, Ar-H).

Synthesis of 4-ferrocenylbenzaldehyde: 4-Ferrocenylbenzaldehyde was synthesized by Coe et al.[32] Briefly, diisobutylaluminum hydride (DIBAL, 0.96 ml, 5.37 mmol) was added very slow dropwise to a stirred solution of 4-ferrocenylbenzonitrile (1.4 g, 4.88 mmol) in dry toluene (28 ml) at 0 ºC in 100 ml round-bottomed flask on an ice bath under nitrogen. After 30 mins, the ice bath has removed. The solution was stirred for 2 hours, and then MeOH (7 ml) was added to destroy any residual DIBAL. Aqueous sulfuric acid (sulfuric acid: water = 1:3 28 ml) was added to solution. The solution was stirred 1 hour, then was washed by deionized water (100 ml) and extracted with DCM. The organic layer was dried over anhydrous Na_2SO_4, and then the solvent was removed under reduced pressure. The crude product was purified over a silica column. The desired compound was obtained as a red color was eluted by Hexanes/CH_2Cl_2 (20:80, v/v). Yield: 1.28 g (90.4%). ^{1}H NMR ($CDCl_3$; 500 MHz): δ = 4.05 (s, 5H, C_5H_5-H), 4.42-4.45 (t, J = 1.95 Hz, 2H, C_5H_4-H), 4.73-4.76 (t, J = 1.95 Hz, 2H, C_5H_4-H), 7.57-7.62 (d, J = 8.3 Hz, 2H, Ar-H), 7.77-7.81 (d, J = 8.3 Hz, 2H, Ar-H) 9.97 ppm (s, 1H, CHO).

Synthesis *meso*-ferrocenylphenyl BODIPY, 4a: 4-Ferrocenyl benzaldehyde (840 mg, 2.89 mmol) and 2,4-dimethylpyrrole (510 uL,4.91 mmol) were kept in a 500 mL round-bottom flask with dichloromethane (220 mL) under nitrogen at room temperature. After stirred for 15 min, trifluoroacetic acid (44 uL, 0.578 mmol) was added to the mixture. After 2h, the resulting solution was washed by 0.1M NaOH (50 mL) and then deionized water (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and then the solvent was removed. The residue was transferred to a 50 mL round-bottom flask and dissolved in toluene (12 mL) under nitrogen at room temperature. After 15 min, p-chloranil (640 mg, 2.6 mmol) was added to the mixture, then after 15 min, Et_3N (1.85 mL) was added. After that $BF_3{\cdot}Et_2O$ (1.62 mL) was added dropwise to the solution. The mixture was stirred for 2h and then washed with deionized water (50 mL) and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4.The solvent was removed under reduced pressure and the crude product was purified over silica column. The desired compound which has an orange color was eluted by Hexanes/CH_2Cl_2 (40:60, v/v). Yield:160 mg (12.7%); ^{1}H NMR ($CDCl_3$;400 MHz): δ = 1.50 (s, 6H, CH_3-H), 2.57 (s, 6H,CH_3-H), 4.00 (s, 5H, C_5H_5-H), 4.37-4.40 (t, J = 1.9 Hz, 2H, C_5H_4-H), 4.73-4.76 (t, J = 1.9 Hz, 2H, C_5H_4-H), 5.99 (s, 2H,pyrrole-H), 7.16–7.21 (d, J=8.1 Hz, 2H,Ar-H), 7.57–7.62 ppm (d, J=8.1 Hz, 2H,Ar-H).

Synthesis of *meso*-(4’-ferrocenylphenyl)-3,5-bis (benzo-18-crown-6 styryl)BODIPY, 4: To a mixture of **4a** (150 mg, 0.295 mmol), 4’-formyl benzo-18-crown-6 (502.05 mg, 3.265 mmol), piperidine (0.5 ml) and acetic acid (0.5 ml) were kept in a 50 ml round bottom flask and refluxed with benzene (7 ml) for 48 hours under nitrogen by using Dean-Stark apparatus. This reaction was monitored by UV-Vis spectrum (500 nm peak was consumed, and 647.87 nm peak was generated in DCM). After that the mixture was washed by DI water (50 ml) and extracted with DCM The organic layer was dried over anhydrous Na_2SO_4, then the solvent was removed under reduced pressure. The crude product was purified over silica as the first column and over basic alumina as the second column. The desired compound as purple color was eluted by CH_2Cl_2-MeOH (95:5, v/v). Yield- 77 mg (22.6%). ^{1}H NMR ($CDCl_3$; 400 MHz), δ = 1.54 (s, 6H, CH_3-H), 3.68-3.81 (m, 24H, crown ethylene-H), 3.92-4.01 (m, 13H, crown ethylene-H, C_5H_5-H), 4.17-4.27 (m, 8H, crown ethylene-H), 4.36-4.39 (t, J = 1.9 Hz, 2H, C_5H_4-H), 4.73-4.76 (t, J = 1.9 Hz, 2H, C_5H_4-H), 6.61 (s, 2H, pyrrole-H), 6.86-6.90 (d, J = 8.3Hz, 2H, Ar-H), 7.11-7.22 (m, 8H, CH-H, Ar-H), 7.53-7.60 ppm (m, 4H, CH-H, Ar-H). ^{13}C NMR ($CDCl_3$; 100MHz), δ = 14.76, 66.38, 69.04, 69.48 69.57, 69.69, 69.78, 69.92, 70.57, 70.81, 70.89, 70.97, 112.91, 113.02, 113.11, 113.62, 117.45, 117.73, 121.89, 126.12, 128.57, 130.17, 132.38, 133.28, 136.14, 138.41, 140.38, 141.74, 148.90, 150.10, 152.59 ppm. MALDI-MS, calculated = 1152.90, found – 1175.5 (M$^+$+ Na$^+$).

Spectral Measurements

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 Varian Eclipse spectrometer. A right angle detection method was used. The ^{1}H NMR studies were carried out on a Varian 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Differential pulse voltammograms were recorded on an EG&G 263A potentiostat/galvanostat using a three electrode system. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using nitrogen gas.

Femtosecond pump-probe transient spectroscopy

Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent incorporating diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with femtosecond harmonics generator both provided by Ultrafast Systems LLC was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into a TOPAS-Prime-OPA system with 290-2600 nm tuning range from Altos Photonics Inc., (Bozeman, MT), while the rest of the output was used for generation of white light continuum. In the present study, the second harmonic 400 nm excitation pump was used in all the experiments. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K.

Nanosecond laser flash photolysis

The studied compounds were excited by a Opolette HE 355 LD pumped by a high energy Nd:YAG laser with second and third harmonics OPO (tuning range 410-2200 nm, pulse repetition rate 20 Hz, pulse length 7 ns) with the powers of 1.0 to 3 mJ *per* pulse. The transient absorption measurements were performed using a Proteus UV-Vis-NIR flash photolysis spectrometer (Ultrafast Systems, Sarasota, FL) with a fibre optic delivered white probe light and either a fast rise Si photodiode detector covering the 200-1000 nm range or a InGaAs photodiode detector covering 900-1600 nm range. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing Tektronix oscilloscope.

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Keywords: Bis-styryl crown ether BODIPY • fullerene • self-assembly • electron transfer • two-point binding

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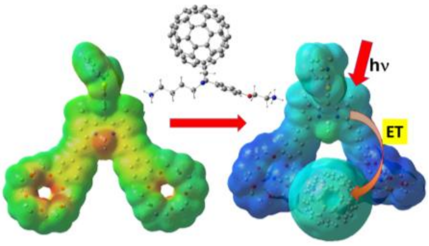
Self-assembled Donor-Acceptor

FULL PAPER

'Two-Point' Self-Assembly and Photoinduced Electron Transfer in *meso*-Donor Carrying Bis(Styryl Crown Ether)BODIPY-Bis(Alkyl Ammonium)Fullerene Donor-Acceptor Conjugates



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Formation of stable self-assembled hybrids and occurrence of photoinduced electron transfer *via* an intermediate exciplex state in bis(styryl crown ether)BODIPY-fullerene donor-acceptor conjugates is demonstrated.