Excited State Charge Separation in Solution and in Electropolymerized Films of Terthiophene-Fullerene Dyad and Phenothiazine-Terthiophene-Fullerene Triad

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A covalently linked molecular dyad comprised of terthiophene and C60, and a molecular triad comprised of phenothiazine, terthiophene and C60 have been newly synthesized to probe photoexcited events in solution and at the electropolymerized film. The X-ray structure of the dyad revealed spatial disposition of the donor-acceptor entities without significant intermolecular type interactions. Optical absorbance, fluorescence, and the electrochemical studies were consistent with the structural integrity of the dyad and triad. Further, the TT-C60 dyad (TT = terthiophene) was found to electropolymerize during multi-cycling of voltammograms. The frontier HOMO and LUMO orbitals of the phenothiazine-terthiophene-C60 triad (PTZ-TT-C60; PTZ = phenothiazine) were found to be located respectively on the phenothiazine-terthiophene and C60 entities. Free-energy calculations revealed that the excited state charge transfer resulting into the formation of TT•+ C60•− in the case of the dyad, and (PTZ-TT)•+ C60•− charge separated state in the case of triad to be thermodynamically feasible. Evidence for the occurrence of excited state singlet-singlet energy transfer from 1TT to form 1C60 followed by charge transfer was secured from studies involving femtosecond transient absorption studies in polar benzonitrile. Charge stabilization to some extent in the triad compared to that in the dyad was obtained. Attempts were also made to secure evidence of charge separation in the terthiophene-fullerene drop-cast and electropolymerized films on FTO surface.

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Covalent combination of suitable electron donor and acceptor building blocks, capable of mimicking photoinduced electron transfer that occurs in photosynthesis, has been one of the active areas of research in modern time.1–37 Such donor-acceptor systems with an ability to produce charge separated states upon photoexcitation are found to be useful for photovoltaic applications.38–41 Fullerene,42–45 C60 due to its extraordinary electron-acceptor character46–48 and fascinating chemical versatility, has been one of the most studied electron-acceptor building blocks.49 Several efficient artificial photosynthetic C60-based systems have been reported, using different chromophores as photoexcitable electron-donor counterparts. Further improvements in charge separation has been achieved by multi-modal approach having more than one electron donor entities engineered to achieve sequential electron transfer resulting in long-lived charge separated states.1–37

It is well known that oligo/polythiophenes possesses advantageous electronic properties and thus, thiophene-based materials are promising candidates for applications in organic electronics.49 Thiophene-chains/polymer have been used as π-bridges, due to their significant charge carrier ability50 and to connect electron donor and electron acceptor moieties.22 In addition, thiophene-based oligomers and polymers, are p-type semiconductors in light-emitting diodes, field effect transistors and sensors51–55 and photovoltaic cells.53 Hence, probing photoinduced charge separation in oligo/polythiophene based donor-acceptor systems is important. In the present study, we have undertaken this task and report synthesis, X-ray structure and excited state events occurring in a terthiophene-C60 dyad (TT-C60), and a phenothiazine-terthiophene-C60 triad (PTZ-TT-C60) (see Figure 1 for structures). The triad has been synthetized to realize charge stabilization due to delocalization of radical cation over the PTZ and TT entities of the triad. Additionally, the dyad was electropolymerized to form thin films, and charge separation in these films and drop-cast film electrodes has been studied using femtosecond transient absorption spectrosopic technique.

Syntheses and X-ray structure.—The synthesis of TT-C60 dyad is given elsewhere.38 The triad, PTZ-TT-C60 was synthesized according to a multi-step procedure shown in Scheme 1 below. Details of the synthesis are given in the Experimental section. Briefly, this involved first synthesis of 4-iodo-[2,2',5',2’]-terthiophene-5-carboxaldehyde (2a) by reacting commercially available terthiophene-5-carboxaldehyde

Figure 1. Structures of terthiophene-C60 dyad (TT-C60), and a phenothiazine-terthiophene-C60 triad (PTZ-TT-C60) investigated in the present study.

TOC Figure

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with N-iodosuccinamide (NIS) in glacial acetic acid/chloroform mixture, followed by chromatographic purification (yield = 81%). Next, 2a was treated with phenothiazine in the presence of Cu powder and potassium carbonate in dichlorobenzene to yield 10-[(2,2';5',2'')terthiophene-5-carboxaldehyde]phenothiazine (2b) in 78% yield. Finally, the target triad (PTZ-TT-C60), 2 was synthesized by reacting 2b with sarcosine and C60 in toluene according to fulleropyrrolidine preparation procedure.54 The yield of the final purified compound was 4.2%. The structural integrity of the newly synthesized compound was obtained from 1H and 13C NMR, MALDI-TOF-Mass, optical and electrochemical studies (see supporting information for relevant spectra). Both the triad and dyad were stored in dark prior performing photochemical studies.

Figure 2 shows the crystal structure and crystal packing diagram of the TT-C60 dyad. The dyad crystallized in the monoclinic crystal system, P 21/c. There were two independent molecules that have slightly different geometry and a half of a molecule of hexane that occupied a special position in the asymmetric unit. In one structure the three thiophene rings were facing the same side as shown in Figure 2a and in other the central thiophene ring was facing the opposite side. The fullerene fragment (C1A...C60A) of one independent molecule had several C atoms with enlarged ADP(S) values indicating the presence of a disorder. Due to the weakness of the crystal, it was impossible to find the second position for all C atoms of the disordered fullerene fragment. In the crystal packing, no significant intermolecular type association was noticed. Refinement details and structural parameters are summarized in Table I.

**Table I. Structure determination summary for the TT-C60 dyad.**

| Parameter | Value |
|-----------|-------|
| CCDC entry No. | 1514198 |
| Empirical formula | C153 H33 N2 S6 |
| Formula weight | 2091.17 |
| Temperature, K | 200(2) |
| Radiation type | Mo |
| Crystal system | Monoclinic |
| Space group; Z | P 21/c; 4 |
| a, Å | 13.7748(5) |
| b, Å | 18.7664(7) |
| c, Å | 33.3291(13) |
| α, deg | 90 |
| β, deg | 100.689(1) |
| γ, deg | 90 |
| Volume, Å³ | 8466.2(6) |
| Density (Mg/m³) | 1.641 |
| Crystal size (mm) | 0.23 × 0.08 × 0.04 |
| θ scan range (°) | 1.50 - 26.00 |
| F(000) | 4244 |
| Crystal color, shape | black, needle |
| Absorption coeff. (mm⁻¹) | 0.237 |
| Absorption correction | Multi-scan |
| R(int) | 0.0657 |
| Indep. refls. | 78532 |
| Obs. refls. [Fo > 4sig(Fo)] | 16616 |
| Final R₁ | 0.1093 |
| Final wR₂ | 0.2560 |
| Goodness of Fit | 1.063 |
| Δρmax, Δρmin (e Å⁻³) | 1.688, -1.093 |

Absorbance and fluorescence studies.—Figure 3a shows the absorption spectrum of TT-C60, and PTZ-TT-C60 along with control compounds in benzonitrile. Most of the absorption was in the 300–500 nm range for both the dyad and triad due to different entities. The absorption bands of TT-C60 were located at 334 with a shoulder in the 380 nm range. Peaks corresponding to PTZ-TT-C60 were located at 327, 380 and 415(sh) nm. A sharp peak at 430 nm characteristic of fulleropyrrolidine was also observed in both the dyad and triad.
Figure 3. (a) Absorption spectrum of (i) TT-C60, (ii) PTZ-TT-C60, (iii) 2a and (iv) 2b used as control compounds, and (b) fluorescence spectrum of (i) terthiophene and (ii) the triad ($\lambda_{ex} = 380$ nm) in benzonitrile.

Substantial blue-shift of the absorption band of terthiophene upon appending fullerene was observed. As shown in Figure 3b, fluorescence of terthiophene was located at 500 nm and was fully quenched both in the dyad and triad indicating occurrence of excited state events from the singlet excited state of TT.

**Electrochemical studies.—** Next, electrochemical studies using cyclic voltammetric technique were performed to evaluate the redox potentials and to check the ability of the dyad and triad to form polymers upon oxidation of the terthiophene entity. As shown in Figure 4, the first three reductions involving C60 were found to be fully reversible and were located at $-0.53$, $-0.94$ and $-1.50$ V vs. Ag/AgCl. During the anodic scan of the dyad, two irreversible peaks at 1.12 and 1.25 V vs. Ag/AgCl were observed. For the triad, three irreversible anodic peaks at 1.09, 1.17 and 1.42 V vs. Ag/AgCl were observed. From the control experiments, the first oxidation process of the triad was ascribed to the phenothiazine entity of the triad and the latter to the terthiophene entity.

During anodic multi-cycling of the voltammograms, only the TT-C60 was capable of electropolymerize. A film on Pt working electrode was generated after 10 cycles (brown colored film, see Figure S6 in the supporting information for voltammograms). Further, the electrochemical behavior of the film on the Pt surface was investigated by recording the voltammogram in a fresh solution of benzonitrile containing 0.1 M (TBA)ClO4 as shown in Figure 5. The voltammograms revealed C60 reductions implying during anodic electropolymerization of the dyad, the structure of C60 was not compromised. A scan rate study yielded a linear plot for peak current versus scan rate (see Figure 5 inset) confirming the redox process is due to surface confined fullerene entity.

**Computational studies.—** In order to visualize the geometry and electronic structure of the PTZ-TT-C60 triad, computational studies were performed using B3LYP/6-31G* basis set. In agreement with the earlier reported X-ray structure of phenothiazine derivatives, the optimized structure the phenothiazine ring was found to be slightly puckered due to presence of sulfur atom (Figure 6a). The three thiophene rings of terthiophene entity were facing the same side, similar to that seen in the earlier discussed X-ray structure, however, forcing the central thiophene ring in the opposite side was also energetically feasible. Cyclic voltammogram of the triad revealed that the oxidation potentials of phenothiazine and terthiophene entities were to be close. This was also implied by the location of frontier HOMO which was spread throughout the phenothiazine and terthiophene entities. As predicted by voltammetry data, the frontier LUMO was found to be exclusively on the C60 entity (Figure 6b). These results reveal the

**Figure 4.** Cyclic voltammogram of (a) TT-C60, and (b) PTZ-TT-C60 in benzonitrile containing 0.1 M (TBA)ClO4 at a scan rate of 100 mV/s.

**Figure 5.** Cyclic voltammograms of electropolymerized TT-C60 film on Pt surface at different scan rates (10-100 mV/s with 10 mV increments) in benzonitrile containing 0.1 M (TBA)ClO4. The figure inset shows a plot of peak current for the first reduction of C60 versus scan rate confirming the redox process is due to surface confined redox-active polymer film.
PTZ-TT entity to be the electron donor segment and C$_{60}$ entity to be electron acceptor entity during photoinduced electron transfer events. That is, formation of (PTZ-TT)$^*$-C$_{60}$$^-$ is predicted. The delocalization of the radical cation on PTZ-TT entity is expected to stabilize the charge separated state in the triad as compared to that in the TT-C$_{60}$ dyad.58-59

Using the spectral and electrochemical data, free-energy change for charge separation from singlet excited '1TT' ($E_{0,0} = 2.73$ eV) and '1C$_{60}^+$ ($E_{0,0} = 1.76$ eV) were evaluated according to Rehm-Weller approach$^{60}$ by neglecting solvation term (Equation 1).

$$\Delta G_{CS} = E_{ox} - E_{red} - E_{0,0}$$  \hspace{1cm} [1]

where $E_{ox}$ is the oxidation potential of the donor, $E_{red}$ is the reduction potential of the acceptor. The estimated $\Delta G_{CS}$ values for the occurrence of photoinduced charge separation in TT-C$_{60}$ was found to be $-1.08$ eV while this value for the PTZ-TT-C$_{60}$ from '1TT' was $-1.11$ eV. Similarly, the estimated $\Delta G_{CS}$ values for the occurrence of photoinduced charge separation in TT-C$_{60}$ was $-0.11$ eV, and in PTZ-TT-C$_{60}$ was $-0.14$ eV from '1C$_{60}^+$'. These results revealed thermodynamic feasibility for the occurrence of photoinduced electron transfer leading to charge separated states from both '1TT$^*$ and '1C$_{60}^+$ both in the dyad and triad.

**Femtosecond transient absorption studies.**—In the present study, the samples were excited at 400 nm (100 fs pulse width) that mainly excited the terthiophene entity of the dyad and triad. Figure S1 shows the femtosecond transient absorption spectra of the control compound terthiophene in benzonitrile. Immediately after excitation, the instantaneously formed '1TT' revealed a positive peak at 608 nm corresponding to the transitions involving the singlet-singlet excited state. A depleted band at 500 nm corresponding to stimulated emission of '1TT' was observed. $^{61}$ The decay and recovery of the positive and depleted peaks was accompanied by a new peak in the 520–590 nm range that was assigned to the '1TT' transitions from nanosecond transient absorption studies. $^{61}$ The decay rate constant of the 608 nm peak was found to be $1.37 \times 10^9$ s$^{-1}$.

Figure 7a shows the femtosecond transient absorption spectra of the TT-C$_{60}$ dyad in benzonitrile. The instantaneous formation of '1TT$^*$ within the dyad was clear in the spectrum recorded at 1.2 ps. However, the decay of this signal was much more rapid and the stimulated emission peak of '1TT' expected at 500 nm was absent compared to that observed in the control pristine terthiophene implying involvement of '1TT$^*$-C$_{60}$ in additional photochemical events (see Figure 7b for '1TT$^*$ decay curve). New peaks at 500, 880 and 1020 nm characteristic of singlet excited fulleropyrrolidine ('1C$_{60}^+$) were observed within 5 ps. $^{45}$ This implies rapid singlet-singlet energy transfer from '1TT' to C$_{60}$ to from TT-'1C$_{60}^+$ within the dyad. Additional contributions could also come from the direct excitation of fulleropyrrolidine at the excitation wavelength of 400 nm. Subsequent decay of the '1C$_{60}^+$ peaks revealed generation of new peaks at 485 and 1015 nm (see spectrum recorded at 750 ps). The 480 nm peak could be ascribed to TT$^{**}$ based from the spectra recorded for oxidized TT-C$_{60}$ dyad in benzonitrile while the 1015 nm peak is due to C$_{60}$$^{**}$ (see Figure S2 in the supporting information). These results support formation of TT$^{**}$-C$_{60}$$^{**}$ charge separated state. From the time profile of the 1016 nm peak (Figure 7c), the rate of charge recombination, $k_{CR}$ was found to be $4.27 \times 10^9$ s$^{-1}$. Due to spatial close proximity, the observed faster charge recombination is conceivable. The decay of the TT$^{**}$-C$_{60}$$^{**}$ peaks resulted in populating the '1TT' as evidenced from a broad peak in the 620 nm range that was confirmed by recording nanosecond transient absorption spectra in benzonitrile. $^{61}

Figure 8a shows the transient absorption spectra of PTZ-TT-C$_{60}$ triad in benzonitrile. Successful singlet state population of TT in the PTZ-TT-C$_{60}$ triad was clear with characteristic peaks of '1TT' at 600 nm (see spectrum recorded at 1.5 ps). Rapid decay of this peak resulted in the formation of new peaks at 505, 890 and 1015 nm characteristic of '1C$_{60}^+$ within 3 ps implying occurrence of singlet-singlet energy transfer from PTZ-'1TT-C$_{60}$ to form PTZ-TT-'1C$_{60}^+$ (see Figure 8b for decay curve) The spectrum recorded at higher delay times revealed additional changes, that is, diminishing of '1C$_{60}^+$ with the survival of the peak at 1020 nm characteristic of C$_{60}$' (see spectrum recorded at 1 ns). The 505 nm peak was broadened and red-shifted. These observations showed the formation of (PTZ-TT)$^{**}$-C$_{60}$$^{**}$ charge separated state in which the radical cation is delocalized over the PTZ-TT entity. If such is the case, one would expect the decay of the radical ion-peaks to be slower than that observed in TT-C$_{60}$. This is indeed the case as shown in the decay time profile of C$_{60}$$^{**}$ in Figure 8c. The rate of charge recombination, $k_{CR}$ estimated was found to be $1.08 \times 10^9$ s$^{-1}$ which was much slower than that observed for the dyad. At higher decay times, a new peak at 700 nm range started to develop suggesting that the charge separated state to populate the '1C$_{60}^+$ state prior returning to the ground state (see spectrum recorded at 3 ns).

In summary, in benzonitrile, the femtosecond transient absorption studies of both the dyad and triad revealed that upon excitation, singlet-
Figure 8. (a) Femtosecond transient absorption spectra of PTZ-TT-C60 at the indicated delay times in Ar-saturated benzonitrile (400 nm of 100 fs laser excitation). (b) time profile of the 600 nm peak corresponding to decay of 1TT∗ of the triad. (c) time profile of the 1020 nm peak corresponding to the delay of C60•−.

Singlet energy transfer from the initial 1TT∗ occurred to populate the 1C60∗. Subsequent electron transfer leading to charge separated state was observed. Relatively long-lasting charge separated state in the case of the triad was observed due to delocalization of the radical cation electron density over the PTZ and TT entities of the triad.

Finally, we also made an attempt to seek evidence of charge separation in electropolymerized TT-C60 dyad films. For this, a film of the dyad was grown on fluorinated tin oxide (FTO) transparent electrode surface by multi-cyclic voltammetry (90 cycles). In another experiment TT-C60 was drop casted on FTO as a control wherein the TT retained its molecular characteristics. Figure 9 shows the femtosecond transient absorption spectra of the dyad drop casted and electropolymerized on ITO surface. For the drop-casted electrode, the peak position of the instantaneously formed 1TT∗ was at almost the same wavelength although appreciable spectral broadening was observed. Relaxation of these peaks was much slower compared to that observed in solution studies. Although much weaker, growth of C60•− at 1020 nm and that of TT•+ in the 520 nm range was evident in the spectrum recorded at the delay time of 1 ps thus establishing charge separation in the drop-casted film electrode. The decay of the C60•− was biexponential with time constants of 25 and 297 ps resulting in kCR values of 4.0 × 10^10 s^-1 and 3.36 × 10^9 s^-1, respectively (see Figure 9b for decay curves).

Interestingly, for the electropolymerized film electrode, the peak corresponding to singlet excited TT polymer was much broader and was red-shifted to 626 nm. This could be due to increased π-conjugation of the thiophene entities in the polymer. The peak corresponding to C60•− was slightly better developed than the drop-casted electrode surface (see Figure 9c) meaning higher quantum yields of charge separated states. The decay of the C60•− was triexponential with time constants of 2.46, 33.0 and 571.0 ps resulting in kCR values of 4.11 × 10^11 s^-1, 3.0 × 10^10 s^-1 and 1.75 × 10^9 s^-1, respectively (see Figure 9d for decay curves).

Experimental

Chemicals.—Buckminsterfullerene, C60 (99.95% purity), was obtained from SES Research (Houston, TX). Tetra-n-butyl ammonium perchlorate, (n-C4H9)4NClO4, and terthiophene-5-carboxaldehyde were obtained from Sigma Chemicals. All chromatographic materials
and solvents were procured from Fisher Scientific and were used as received. The synthesis of TT-C60 dyad is given elsewhere.38

**Synthesis of PTZ-TT-C60 triad.**—Synthesis of 4-iodo-[2,2';5',2"] Terthiophene-5-carboxaldehyde.—[2,2';5',2"] Terthiophene-5-carboxaldehyde (505 mg, 1.82 mmol), N-iodo succinimide (NIS, 411 mg, 1.82 mmol) and a 1:1 ratio of glacial acetic acid to chloroform (15 mL each) was stirred for 17 hours in dark conditions in an ice bath and let warm to room temperature under nitrogen atmosphere. Dichloromethane was added to the wash mixture (75 mL). The mixture was neutralized with a saturated sodium bicarbonate solution (2 × 55 mL) and then washed with deionized water (3 × 150 mL). The organic layer (yellow-orange liquid) was collected and dried over sodium sulfate. After removing solvent under reduced pressure, the crude product was purified over silica gel column and eluted with hexanes/chloroform (1:3) v/v). Yield: 596 mg (80.78% yield). *1H NMR (CDCl3; 500 MHz): δ = 8.68-8.69 (d, J = 3.8Hz, 1H, Thiophene-H), 7.18-7.20 (d, J = 3.8 Hz, 1H, Thiophene-H), 7.25-7.27 (m, 2H, Thiophene-H), 7.67-7.69 (d, J = 4.0 Hz, 1H, Thiophene-H), 9.86 ppm (s, 1H, CHO-H).

**Synthesis of 10-[{2,2';5',2"} terthiophene-5-carboxaldehyde]-phenothisanne.**—Into a 100 mL round bottom flask was added 4-iodo-[2,2';5',2"] terthiophene-5-carboxaldehyde (250 mg, 0.62 mmol), phenothisanine (247 mg, 1.24 mmol), copper powder (118 mg, 1.86 mmol), potassium carbonate (514 mg, 3.72 mmol), o-dichlorobenzene (25 mL) was stirred and refluxed for 48 hours under nitrogen atmosphere. After cooling to room temperature, DCM was added to the compound and was separated with a water wash. Organic layer was collected and dried over sodium sulfate. After removing solvent under reduced pressure, the crude product was purified over a silica gel column. Product eluted with hexanes/DCM (3:7 v/v). Yield: 231 mg (78.4% yield); *1H NMR (CDCl3; 500 MHz): δ = 8.68-8.69 (d, J = 3.8Hz, 1H, Thiophene-H), 7.26-7.27 (m, 1H, Thiophene-H), 7.29-7.30 (d, J = 3.8Hz, 1H, Thiophene-H), 7.18-7.20 (d, J = 3.8 Hz, 1H, Thiophene-H), 7.25-7.27 (m, 2H, Thiophene-H), 7.67-7.69 (d, J = 4.0 Hz, 1H, Thiophene-H), 9.86 ppm (s, 1H, CHO-H).

**Synthesis of 10-{[2,2';5',2"] terthiophene-5-fulleropyrrolidine]-phenothisanne.**—A mixture of 10-{[2,2';5',2"] terthiophene-5-carboxaldehyde} phenothisanine (100 mg, 0.21 mmol), sarcosine (175 mg, 0.84 mmol), fullerene C60 (303 mg, 0.42 mmol) in toluene (300 mL) was stirred and refluxed for 48 hours under nitrogen atmosphere. After removing solvent under reduced pressure, the crude product was purified over a silica gel column. Product eluted with heated toluene/ethyl acetate (5:5 v/v) yield: 15 mg (5.8% yield); *1H NMR (CDCl3; 500 MHz): δ = 2.94 (s, 3H, Pyrollidine-CH3), 4.22-4.31 (d, J = 9.6 Hz, 1H, Pyrollidine-CH3), 4.97-5.03 (d, J = 9.6 Hz, 1H, Pyrollidine-CH3), 5.21-5.29 (d, J = 3.8 Hz, 1H, Pyrollidine-CH3), 6.77-6.81 (dd, J = 8.2, 1.3 Hz, 2H, Ar-H), 6.87-6.93 (dd, J = 7.5, 1.3 Hz, 2H, Ar-H), 6.97-7.02 (m, 3H, 1H-Thiophene-H, 2H-Ar-H), 7.04-7.06 (d, J = 1.6 Hz, 1H, Ar-H), 7.06-7.07 (d, J = 1.6 Hz, 1H, Ar-H), 7.08-7.10 (d, J = 1.6 Hz, 1H, Ar-H), 7.14-7.16 (d, J = 3.8Hz, 1H, Thiophene-H), 7.22-7.24 (d, J = 3.8 Hz, 1H, Thiophene-H), 7.26-7.27 (m, 1H, Thiophene-H), 7.29-7.30 (d, J = 3.9 Hz, 1H, Thiophene-H), 7.68-7.70 (d, J = 4.0 Hz, 1H, Thiophene-H), 9.87 ppm (s, 1H, CHO-H).

**Fluorescence measurements.**—The UV-visible and near-IR spectral measurements were carried out with a Shimadzu 2550 UV-Vis spectrophotometer or Jasco V-670 spectrophotometer. The steady-state fluorescence emission was monitored by using a Varian ( Cary Eclipse) Fluorescence Spectrophotometer or a Horiba Jobin Yvon Nanolog spectrofluorimeter equipped with PMT (for UV-visible) and InGaAs (for near-IR) detectors. A right angle detection method was used for fluorescence measurements at room temperature. All the solutions were purged prior to spectral measurements using argon gas. The *1H NMR studies were carried out on a Varian 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard.

Cyclic voltammetry was recorded on a Princeton Applied Research potentiostat/galvanostat Model 263A using a three electrode system. A platinum button or FTO electrodes were used as the working electrodes, while a platinum wire served as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. All the solutions were purged prior to electrochemical measurements with nitrogen gas.

For drop casting the TT-C60 dyad on FTO electrode, a dyad solution (∼1 mM) in CHCl3 was used and spread evenly on the electrode surface while slowly passing compressed air to evaporate the solvent.

** 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 harmonic generator which produces second and third harmonics of 400 and 267 nm besides the fundamental 800 nm for excitation, 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. The estimated error in the reported rate constants is ±10%.

**Summary**

Photoinduced singlet-singlet excitation transfer followed by charge separation in the investigated molecular dyad and triad comprised of PTZ, TT and C60 entities has been demonstrated. The X-ray structure of the TT-C60 dyad was consistent with the structure obtained from spectroscopic, computational and electrochemical studies. While multi-cycling of anodic voltammograms of TT-C60 dyad resulted in electro- and photo-active films, no such films were formed during multi-cycling of PTZ-TT-C60. Free-energy calculations revealed that photoinduced electron transfer to be thermodynamically feasible in the dyad and triad. Femtosecond transient absorption studies revealed rapid singlet-singlet energy transfer from the instanteneously formed *1TT* to C60, and then charge separation in case of both the dyad and triad. However, in the case of drop-casted and electropolymerized films, occurrence of singlet-singlet energy transfer was found to be bleak, however, evidence for the occurrence of charge separation was observed, more so in the cases of electropolymerized film modified electrode. The present studies bring out the importance of donor-acceptor modified electrodes capable of undergoing photoinduced charge separation and their subsequent applications in light energy harvesting.

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