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COMMUNICATION

A novel BF_2-chelated azadipyrromethene–fullerene dyad: synthesis, electrochemistry and photodynamics†‡

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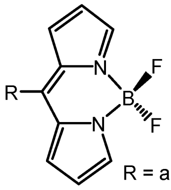
The synthesis, structure, electrochemistry and photodynamics of a BF_2-chelated azadipyrromethene–fullerene dyad are reported in comparison with BF_2-chelated azadipyrromethene without fullerene. The attachment of fullerene resulted in efficient generation of the triplet excited state of the azadipyrromethene *via* photoinduced electron transfer.

Study of photoinduced energy and electron transfer in novel donor–acceptor dyads and polyads (having multiple number of donor and acceptor entities) is of paramount importance due to their significance in mimicking the natural photosynthesis, and also for technological advances in solar energy conversion, a promising solution for global energy demands and environmental issues.[1–3] Consequently, various donor–acceptor architectures have been constructed and light induced electron transfer events have been probed. In most cases, tetrapyrroles such as porphyrin and phthalocyanine have been commonly employed as donors due to their close resemblance to the natural chlorophyll pigment.[1–3] In a few selected cases, donors other than tetrapyrroles but structurally related have been employed and novel features that are otherwise not attainable using normal tetrapyrroles have been accomplished.[4,5] Thus, exploration of novel donors with relatively different spectral and electrochemical properties is highly attractive since the constructed new dyads could exhibit novel photochemical properties useful for energy harvesting and optoelectronic applications.



R = aryl or alkyl

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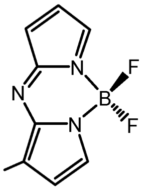

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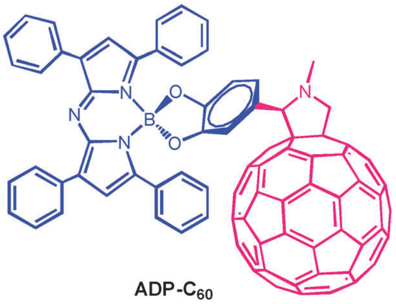
Difluoroboron chelated dipyrromethene, **1** (also known as BODIPY or BDP), a bidentate Lewis base, is one of the commonly used fluorophores in developing sensors and tags to detect biomolecules owing to its superior fluorescent properties that include lifetimes of ∼4 ns and quantum yields exceeding 80%.[6] BDP has also been used in building photosynthetic antenna and reaction center mimics.[1–3] Interestingly, BF_2-chelated azadipyrromethene, **2** (abbreviated as ADP), a structural analog of BDP, has recently gained much attention for its photochemical properties.[7] ADP absorbs near 300 and 600 nm regions with very high molar absorptivities, that is, at spectral regions of solar energy capture and photodynamic therapy interests. Like BDP, ADP is also fluorescent, however with desirable emission in the red region (660–700 nm) with quantum yields exceeding 40%. However, usage of ADP in building donor–acceptor dyads has been limited due to the associated synthetic challenges.[8] In the present study, we report a novel dyad featuring ADP covalently linked to the well-known electron acceptor, [60]fullerene, (abbreviated as ADP–C_{60}) and report photoinduced electron transfer originating in this dyad.



ADP-C_{60}

The synthesis of the ADP–C_{60} dyad involved a multi-step procedure. First, the BF_2 chelate of (3,5-diphenyl-1*H*-pyrrol-2-yl)(3,5-diphenylpyrrol-2-ylidene)-amine was

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‡ Electronic supplementary information (ESI) available: Synthetic and experimental details along with mass and NMR spectra, femtosecond and nanosecond transient spectra of the control ADP compound in PhCN. See DOI: 10.1039/c1cc16071k

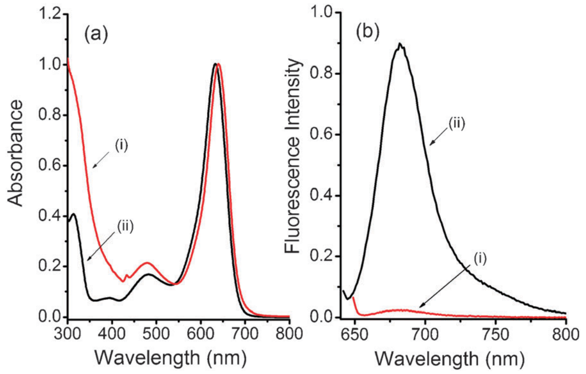

Fig. 1 (a) Optical absorbance and (b) fluorescence emission spectra of (i) ADP–C_{60} dyad and (ii) ADP-control in benzonitrile.

synthesized by literature methods.[7a] This compound was further reacted with 3,4-dihydroxybenzaldehyde in the presence of $AlCl_3$ to obtain the formyl phenyl dioxyboron derivative. Finally, the electron acceptor was appended by reacting it with fullerene and *N*-methylglycine in toluene (see ESI‡ for synthetic and experimental details along with a scheme).[9] The newly synthesized compounds were fully characterized by NMR, mass and other spectroscopic methods.

Fig. 1a and b show the optical absorption and emission spectra of the dyad and the control ADP having no fullerene entity in benzonitrile. The ADP peaks in the control compound were located at 313, 482 and 632 nm, respectively. Upon appending fullerene these bands were shifted to 312, 479 and 640 nm, respectively. The band at 312 nm was much higher in intensity due to overlap of the fullerene absorption band. A sharp peak at 434 nm characteristic of fulleropyrrolidine was also observed for the dyad. The 8 nm red shift of the 632 nm peak of ADP can be attributed to the electronic interactions between the donor and acceptor entities in the dyad. As shown in Fig. 1b, the ADP control exhibited an emission band at 682 nm, over 150 nm red shifted to the structural analog, BDP. However, in the ADP–C_{60} dyad, intensity of this band was found to be quenched over 98% indicating very efficient photochemical events. Energy transfer as a quenching mechanism could be ruled out due to the absence of spectral overlap between ADP emission and C_{60} absorption. The quenching of ^{1}ADP*-emission in the ADP–C_{60} dyad suggests the formation of either $\mathrm{ADP}^{\bullet-}$–$C_{60}^{\bullet+}$ or $\mathrm{ADP}^{\bullet+}$–$C_{60}^{\bullet-}$ charge-separation products.

The structure of the dyad was visualized by performing computational calculations at the B3LYP/6-31G* level.[10] Fig. 2a and b show optimized structure on the Born–Oppenheimer potential energy surface and the molecular electrostatic potential map of the dyad. The center-to-center distance between the boron atom and the center of the fullerene was found to be ~10 Å, indicating close positioning of the donor and acceptor entities. The HOMOs were found to be on the ADP part of the dyad, while the LUMO and LUMO + 1 were on the ADP and the fullerene entities, respectively. The gas phase HOMO–LUMO gap was found to be 1.84 eV, smaller than that reported for porphyrin–fullerene dyads.[2,3] The presence of LUMO on the ADP suggests that it is electron deficient. To confirm this computational prediction, electrochemical studies were performed to evaluate the redox potentials of the ADP and C_{60} entities of the dyad.

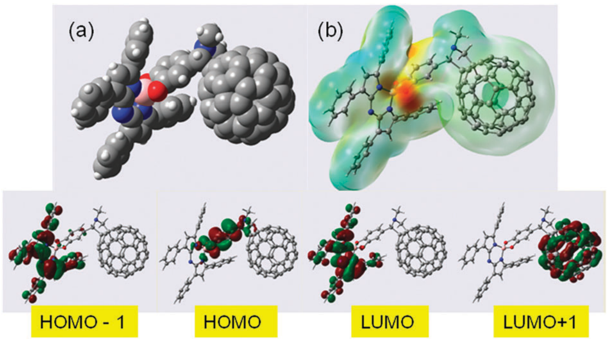

Fig. 2 (a) Space filling model and (b) molecular electrostatic potential map of the ADP–C_{60} dyad calculated at the B3LYP/6-31G* level. The frontier HOMO − 1, HOMO, LUMO and LUMO + 1 of the dyad are also shown.

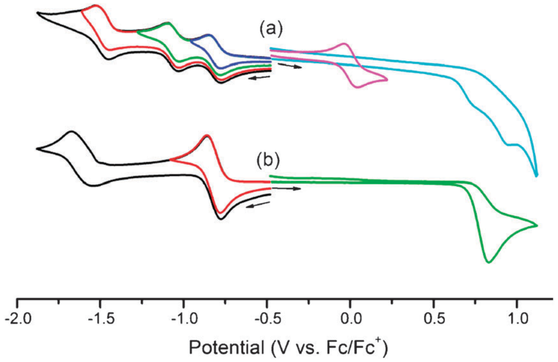

Fig. 3 Cyclic voltammograms of (a) ADP–C_{60} dyad and (b) ADP-control compound in benzonitrile, 0.1 M $(TBA)ClO_4$. Scan rate = 100 mV s^{-1}. The peak at 0.0 V in (a) represents ferrocene oxidation used as an internal standard.

The cyclic voltammogram of the dyad revealed reduction peaks at $E_{1/2} = -0.81$, -1.06 and -1.49 V *vs.* Fc/Fc$^+$, while irreversible oxidation peaks at $E_{pa} = 0.76$ and 0.94 V *vs.* Fc/Fc$^+$ (Fig. 3a) were also observed. By comparison with the ADP control (Fig. 3b), the first reversible reduction has been attributed to the reduction of ADP macrocycle, while the second reduction to the reduction of fullerene spheroid. The third reduction wave is an overlap of the second reduction of ADP and fullerene entities. Importantly, the easy reduction of ADP compared to fullerene is evident from these studies. Based on the redox potential measurements, the formation of $\mathrm{ADP}^{\bullet-}$–$C_{60}^{\bullet+}$ (~2 eV) is excluded because of its higher energy compared with the ^{1}ADP* (1.91 eV) and $^1C_{60}$* (1.75 eV) excited states.[11]

The photodynamics of ADP–C_{60} dyad *via* the singlet excited ADP was examined by femtosecond transient measurements by using 480 nm excitation, as shown in Fig. 4. The transient spectrum of the ADP control following excitation with 130 fs flash at 460 nm in benzonitrile showed the absorption of the singlet ADP in the visible region with a maximum at 520 nm and a decay rate constant of 7.8×10^8 s^{-1} (see ESI‡ for the spectra). In contrast, the transient spectrum of ADP–C_{60} dyad exhibited the NIR absorption at 1000 nm, which is diagnostic of $C_{60}^{\bullet-}$, with a rate of formation of 1.0×10^{12} s^{-1}, followed by a decay rate constant of 5.0×10^9 s^{-1} (lifetime: 200 ps). This indicates that ultrafast electron transfer from ^{1}ADP* to C_{60}

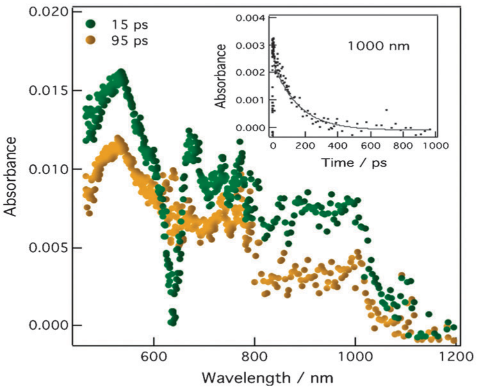

Fig. 4 Femtosecond transient absorption spectra of the ADP–C_{60} dyad in deaerated benzonitrile. λ_{ex} = 480 nm.

occurs in spite of the slightly positive driving force of electron transfer (0.07 eV) and desirable short distance between the ADP and C_{60} moieties. The energy level of charge separated state, $C_{60}^{\bullet -}$–$\mathrm{ADP}^{\bullet +}$ (1.84 eV), is significantly higher than the low-lying triplet state of ADP. In such a case the charge recombination is expected to afford the triplet excited state of ADP (^{3}ADP*).

The formation of ^{3}ADP* was confirmed by the complementary nanosecond transient spectra in the microsecond region as shown in Fig. 5, where the absorption bands due to the triplet ^{3}ADP* are clearly observed in the visible region with a maximum at 430 nm and also in the NIR region with a maximum at 850 nm. The triplet ADP decayed to the ground state with a rate of 1.2×10^4 s^{-1}, slightly faster than the ADP control compound, being 4.5×10^3 s^{-1}.

In summary, utilization of BF_2 chelated azadipyrromethene, a structural analog of BF_2-chelated dipyrromethene, having absorption and emission maxima well into the red region, in building donor–acceptor dyads is explored. The target molecule, ADP–C_{60} dyad, was synthesized *via* a multi-step synthetic procedure. Computational studies predicted the ADP to be electron deficient, while electrochemical studies proved that this is indeed the case, where the ADP macrocycle is electron deficient by 250 mV compared to fullerene. Photoinduced electron transfer was observed from femtosecond transient absorption studies. Excitation of the ADP entity of the dyad resulted in the electron transfer from the singlet excited ADP to the attached C_{60} forming $\mathrm{ADP}^{\bullet +}$–$C_{60}^{\bullet -}$. Production of the triplet ADP state *via* charge recombination of ADP–C_{60} is the likely pathway, taking into consideration that the energy of $\mathrm{ADP}^{\bullet +}$–$C_{60}^{\bullet -}$ is significantly higher than the triplet ADP. The present study opens up a venue for utilization of difluoroborane chelated azadipyrromethene in light energy harvesting donor–acceptor systems.

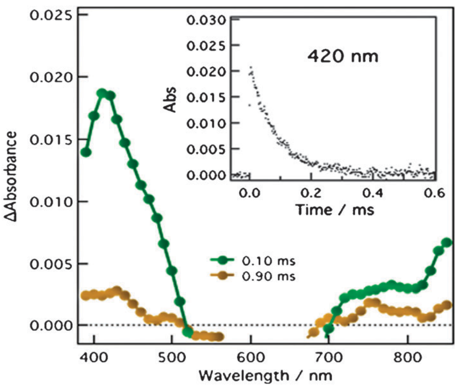

Fig. 5 Nanosecond transient absorption spectra of the ADP–C_{60} dyad in deaerated benzonitrile. λ_{ex} = 460 nm.

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11 $-\Delta G_{CR} = e(E_{ox} - E_{red}) + \Delta G_S$; $-\Delta G_{CS} = \Delta E_{00} - (-\Delta G_{CR})$, where ΔE_{00} and ΔG_S are the energy of ^{1}ADP* and the static energy, respectively.