Millisecond long-lived charge separated state at room temperature in a flexibly linked diphenylaminopolyene-C60 dyad

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Long-lived photoinduced charge separation involving one-step electron transfer is achieved in diphenylaminopolyene based C60-donor dyads with a short, flexible linkage.

Extensive research has been directed towards the synthesis of electron donor–acceptor linked compounds in the hope of finding systems which will form long-lived charge separated (CS) states with high quantum efficiency, as is achieved in the photosynthetic reaction.[1–5] The lifetimes of CS states are sensitive to the energy of the CS state, the type of linkage between the donor and acceptor molecules, and also the molecular topology and distance and orientation of the donor and acceptor moieties.[6–11] Large efforts have been made to achieve a long-lived CS state by tuning these factors with the longest currently reported CS state lifetime of a dyad at room temperature solution being 260 μs for a zinc imidazoporphyrin-C60 dyad.[6] Relatively unexplored is CS lifetime dependence on the flexibility of the linkage between the donor and acceptor in the dyad.

Among a wide variety of donor molecules available for linking covalently to C60, the triphenylamine group is one with good electron donating ability to excited state C60 molecules.[12] We report herein photoinduced intramolecular electron transfer (ET) processes in diphenylaminopolyene (DPAP) based C60-donor dyads (DPAP-C60) with a short, flexible linkage. The decay mechanism of the CS state was elucidated with the use of nanosecond laser flash photolysis. Dual decay components of the CS state were observed, with first order lifetimes of about 300 ns and 1 ms respectively. To our knowledge, this millisecond slow component lifetime is the longest first order lifetime at room temperature ever reported for intramolecular charge recombination (CR) in donor–acceptor dyad systems involving one-step electron transfer. A new method was introduced to simultaneously analyze the backward electron transfer (BET) process which involves both *intra*- (first order) and *inter*molecular (second order) CR.

One and two armed DPAP-C60 dyads (D1 and D2) were synthesized as shown in Scheme 1. Anhydrous tetrahydrofuran (THF) was used freshly distilled from sodium and benzophenone-dried tetrahydrofuran. Other solvents were used as received. Wittig reaction methodologies were used to extend the conjugated lengths of these molecules. The donor chromophores were synthesized with a free OH functionality for attachment to malonyl dichloride. The resulting diester was then coupled to C60 using Hirsh–Bingel methodology, yielding the target dyads as dark solids in high yield.
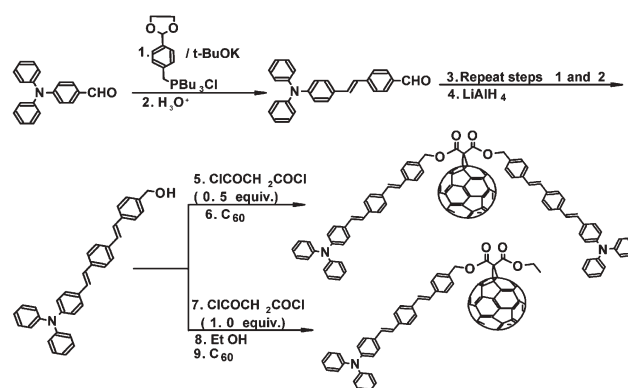
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The successful synthesis of a new kind of Wittig salt (compound 1, Scheme 1) provides an easy way to obtain DPAP-C60 dyads in good yield. The dyads were characterized by ^{1}H NMR, ^{13}C NMR and MALDI-TOF MS apparatus. The absorption bands of the C60 and DPAP moieties are present in the spectra of the linked compounds D1 and D2.

The photoexcitation of both D1 and D2 in deaerated benzonitrile (BN) solution with 360 nm laser light results in fluorescence with the emission maximum at 540 nm. The emission intensities of D1 and D2 are quenched 35- and 9-fold respectively, compared to emission from the reference compound DPAP. This indicates that the excited state of DPAP is quenched efficiently by linked C60. The emission intensity of the single armed D1 is four times smaller than that of D2 at the same DPAP concentration.

The fluorescence decay of the DPAP unit in BN solution was monitored from 415 to 715 nm after excitation with 400 nm light from a frequency doubled ultrafast Ti : sapphire laser (76 MHz, 150 fs pulse width). The fluorescence lifetime of the unlinked DPAP ($\tau_0 = 1.8$ ns) was significantly reduced in D1($\tau_f = 9$ ps). This is likely due to ET from the excited state of DPAP (DPAP*) to C60. The rate constant of forward ET (k_{et}) from DPAP* to C60 was estimated from $k_{et} = 1/\tau_f - 1/\tau_0$, where τ_0 is the fluorescence lifetime of the DPAP unit, and τ_f is that in the linked compound. The k_{et} value of D1 was evaluated to be 1.1×10^{11} s^{-1}.

The time profile of the fluorescence intensity of the DPAP* in D2 shows biexponential decay, with fluorescence lifetimes of 20 and 1800 ps respectively. This may be due to the restriction that only one DPAP* could be quenched by C60 if both arms are photoexcited. The k_{et} value from DPAP* to C60 for D2 was estimated to be 4.9×10^{10} s^{-1}.

Transient absorption spectra of DPAP-C60 were carried out following nanosecond laser excitation at 532 nm. Only absorption

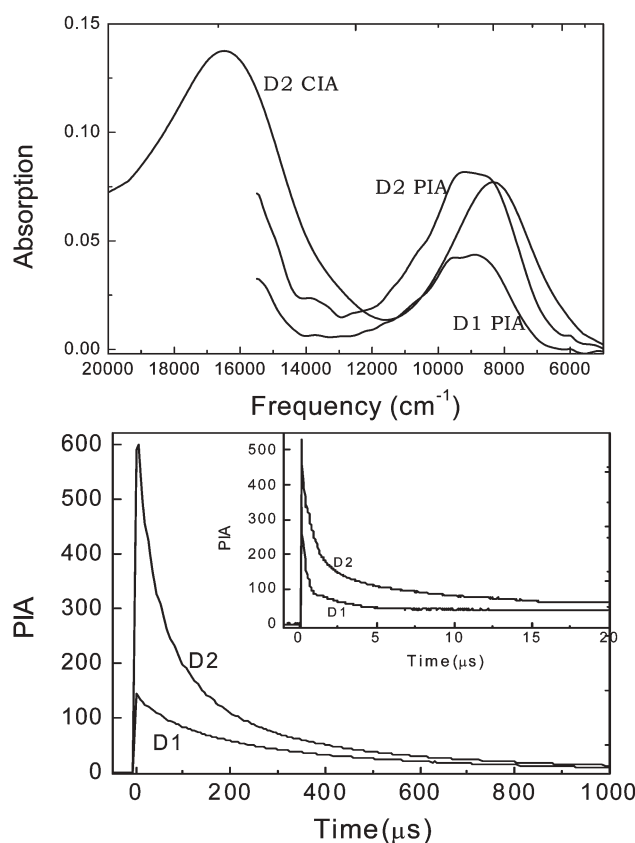**Scheme 1** Synthesis of donor chromophores and dyads.

Fig. 1 Top: photoinduced absorption (PIA) spectra obtained by using 532 nm laser excitation of DPAP-C_{60} in deaerated BN, compared with the chemically induced absorption (CIA) spectrum of the cation generated by doping the donor with $SbCl_5$. Bottom: time profiles (μs range) of DPAP-C_{60} charge separated state decay. Inset are the ns range time profiles.

Fig. 2 Plot of d[CS]/dt *vs.* [CS] for 0.2 mM D2 charge separation state decay in deaerated BN. Circles: experimental data resulting from different pump powers (0.5–5 mJ); solid line: fit with second order polynomial.

of the $^3C_{60}{}^*$ moiety was detected at 740 nm in deaerated toluene. From the decay of the time profile, the lifetime of DPAP-$^3C_{60}{}^*$ was evaluated to be 18 μs, which is close to that of pristine C_{60}. It indicates that the intersystem crossing process from DPAP-$^1C_{60}{}^*$ to DPAP-$^3C_{60}{}^*$ is the predominant one with no charge separation in nonpolar solvents.

The CS state was detected through laser flash photolysis (pumped by a 7 ns 532 nm laser) of DPAP-C_{60} (both D1 and D2) in deaerated benzonitrile (BN) solution as shown in Fig. 1. Following the excitation, an absorption band at 8800 cm^{-1} with a shoulder at 9600 cm^{-1} appears immediately. This is attributable to the DPAP cation and fullerene anion. The transient absorption in the near visible region (15 000 cm^{-1} band) is also due to DPAP$^+$. The photoinduced DPAP$^+$ spectrum is confirmed by doping the donor with a strong oxidizing agent ($SbCl_5$) to chemically generate the cation.

The temporal decay profiles of both D1 and D2 show two obvious components. The time constant of the fast component is about 330 ns, while that of the slow component is about 1 ms. The ratios of populations of the slow and fast components are about 0.15 and 0.2 for D1 and D2 respectively, as shown in Fig. 1.

The CS states decay through back electron transfer (BET) to the ground state. The slow component decays for both D1 and D2 on the μs timescale are neither strictly first order nor second order, as shown in Fig. 1. The BET occurs through two processes: it is close
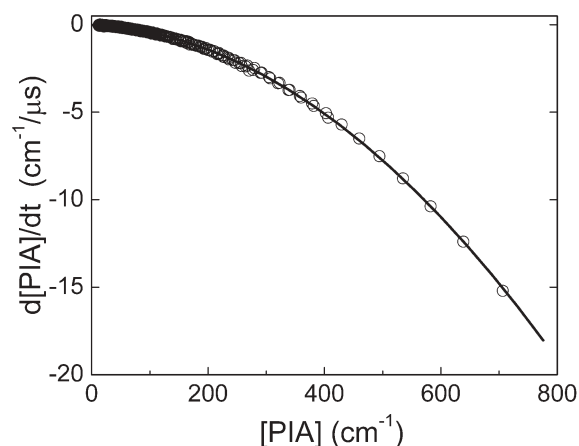
to first order at low concentration ($t > 500$ μs), and at high concentration it is significantly affected by *inter*molecular BET. The decay behavior follows:

$$\frac{d[CS]}{dt} = -k_{1st}[CS] - k_{2nd}[CS][CS]$$

where k_{1st} ($= 1/\tau_{\text{lifetime}}$) and k_{2nd} are *intra-* and *inter*molecular decay rate constants respectively. The dependence of the charge separation (CS) state decay rate on [CS] was examined by employing different laser powers over a wide range and it exhibits a good second order polynomial fit (see Fig. 2). This fitting process gives us values for both first and second order rate constants, so we can calculate the lifetimes expected for the first order process alone. The first order lifetimes of D1 and D2 were determined to be 1.1 and 0.7 ms, respectively. These values are approximately two times larger than what we get from single exponential fitting at low concentrations and long times, since the *inter*molecular BET contribution is still present at the lowest concentrations used.

To our knowledge, the millisecond lifetime is the longest CS lifetime in solution ever reported for *intra*molecular charge recombination at room temperature. Evolution of the 8800 cm^{-1} CS band shape over a 300 ns timescale suggests conformational changes resulting in some solvent separation of the linked DPAP$^+$ and $C_{60}{}^-$. This may lead to a new synthetic strategy to attain long lifetime charge separation donor–acceptor dyads by using flexible linkages and controlling the folding. Further research is under way to probe this point.

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