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Superabsorbing Fullerenes: Spectral and Kinetic Characterization of Photoinduced Interactions in Perylenediimide−Fullerene-C_{60} Dyads

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Two n-type molecular materials are covalently combined into a new photovoltaic component for polymer solar cells. Light harvesting by the perylenediimide results in very fast energy transfer to the fullerene unit, as shown with femtosecond transient absorption spectroscopy in toluene solution. Two energy transfer rates are observed of 2.5×10^{12} s^{-1} (53%) and 2×10^{11} s^{-1} (47%), attributed to two conformations. The final excited state that is populated is a perylenediimide-based triplet state that is formed on the nanosecond time scale with a high yield.

Fullerene-C_{60}[1] still represents one of the most promising n-type material components in polymer solar cells,[2,3] and the reported power conversion efficiencies of polymer-C_{60} cells are steadily increasing[4] by manipulating the polymer/fullerene heterojunction morphology.[5] However, it is expected that the low molar absorption coefficient in the visible light region of C_{60} and its derivatives impedes attaining very high efficiencies of solar energy conversion. Thus, C_{70} and its derivatives, due to their lower symmetry and concomitant higher absorption perform better in this respect.[6] In the first two-layer organic solar cell, as reported by Tang[7] in 1986, a perylene dye (3,4:9,10-perylene tetracarboxylic bis(benzimidazole)) was used as the n-type material. These types of dyes[8] that have very high absorption coefficients are also used in car paints, photoactive layers in copy machines, as laser dyes and are very popular in photonic research.[9,10]

The covalent combination of perylene dyes and fullerenes attempts to combine the beneficial absorption characteristics of perylenediimides with the special structural, organizational and electron-transfer properties of fullerenes, and attained much attention in the last 2 years. Whereas the synthesis of many systems[11−17] has now been reported, the spectral and kinetic characterization of the photoinduced processes that are inherent to their combination and will partly determine their efficiency in solar cells, has eluded.

Here we report on the photoinduced processes occurring in a fullerene C_{60}−perylenediimide (C_{60}−PDI) dyad as studied with time-resolved (transient) absorption spectroscopy[18] in toluene solution. We observe that the light energy that is harvested by the perylenediimide antenna is transferred very efficiently to the fullerene moiety on a (sub)picosecond time scale and that a perylenediimide-based triplet is the final state populated.

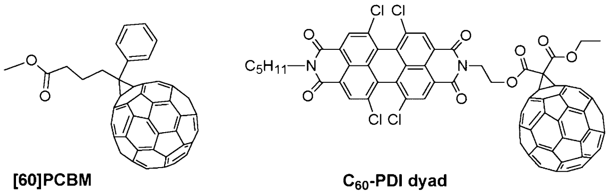

Figure 1. Representation of [60]PCBM ([6,6]-phenyl C61−butyric acid methyl ester) known until now as the most efficient C_{60} derivative acceptor for plastic solar cells and the fullerene−perylenediimide dyad used in this study.

The synthesis and steady-state spectroscopy of C_{60}−PDI (Figure 1) were previously reported.[15] The raw spectral data obtained using pump−probe spectroscopy of C_{60}−PDI in toluene is shown in Figures 2 and 3. At early times the ground state bleaching (500−550 nm) (depopulation of the ground state molecules in the probe area) and the emission (550−600 nm) of the perylenediimide is observed, together with its singlet−singlet absorption at 700−800 nm.

Figure 4a exemplifies the complementarity of the fast decay of the emission (600 nm) inherent to the perylenediimide singlet excited state and its absorption (725 nm). The characteristic fullerene singlet−singlet absorption[20] that is thus evolving indicates that the fullerene-based excited state is formed on a 5 ps (47%) time scale after perylene excitation. An important shorter 0.4 ps (53%) component, close to the fwhm of the pulse is also present. Due to the large difference in absorption coefficients at 530 nm (ratio of ∼20) the perylenediimide excitation is virtually selective. The formation of the first excited

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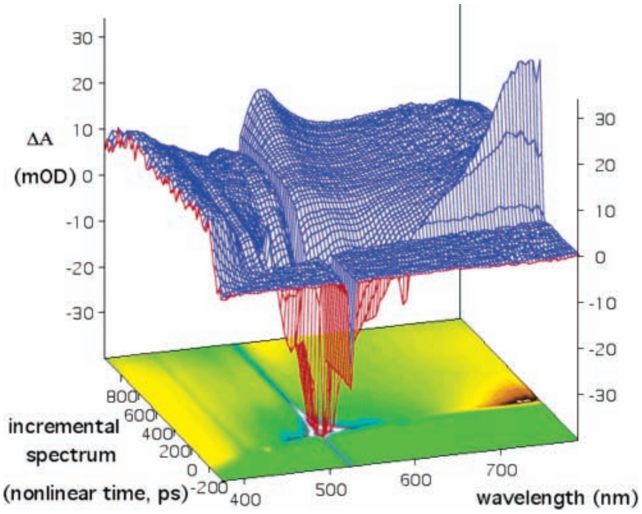

Figure 2. 3D surface plot of the femtosecond transient absorption data of the dyad C_{60}−PDI in toluene (2 mm cell path, 5 μJ per pulse, 530 nm, 120 fs fwhm). Signal intensity is also projected on the *xy* plane. The incremental time delay between the spectra is short (0.02 ps) at the start and longer (15 ps) at later times (total time scale: −10 to +1000 ps). At the earliest times, the scattered laser pulse, the chirp and the Raman scatter peaks are observed.

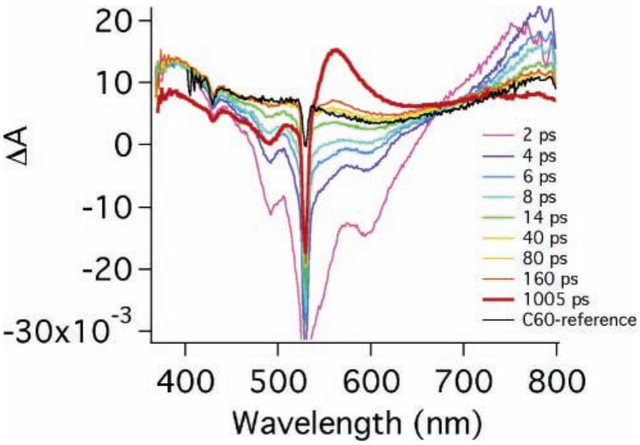

Figure 3. Representation of selected transient absorption spectra of C_{60}−PDI at different incremental time delays (530 nm excitation) taken from the data of Figure 2. Also shown is the transient absorption spectrum at 80 ps of the diethylmalonyl−C_{60} reference compound (black line).

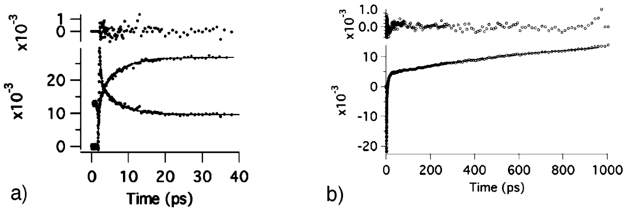

Figure 4. (a) Complementarity of the decay (with fit) of the emission (600 nm) and the excited-state absorption of the perylenediimide (singlet excited-state at 725 nm) of C_{60}−PDI in toluene. (b**)** Kinetic trace at 560 nm (together with a triexponential fit) of C_{60}−PDI in toluene.

singlet state of the fullerene was also confirmed (see Figure 3) by using the appropriate model Bingel-type[19] adduct diethylmalonyl-C_{60} as the C_{60} reference.

Whereas this primary process, i.e., the energy transfer from the perylenediimide to the fullerene may be anticipated, after this event an absorption band around 560 nm is evolving on an ∼800 ps time scale (Figure 4b) that is not attributable to the fullerene triplet[21] state. The increase in intensity of the perylenediimide ground state bleaching at 500 nm can also be observed (compare trace at 160 vs 1005 ps). These observations indicate the formation of a long-lived state that is localized on the perylenediimide unit.

The triplet state of the perylenediimide, normally quite elusive, was reported in 1987 by Ford and Kamat[22a] obtained by using a triplet sensitizer. The spectral agreement with the 1005 ps spectrum reported here is clear and demonstrates the population of the perylenediimide triplet state in our dyad.[23] More recent reports where the triplet state of the perylenediimide is observed are also available.[22b−e] Whereas the fullerene triplet should be an intermediate, it is not observed, most likely because its population does not build up. A kinetic trace displaying the two consecutive processes is depicted in Figure 4b.

Our results display direct proof of the interactions of the two chromophores and also indicate that the final excited state is a low-energy (1.2 eV)[22a] triplet state localized on the perylenediimide, normally rarely formed in perylene dyes.[18] The combination of two molecular n-type materials, fullerene and perylenediimide, effectively results in a much more intense visible light absorption, and this enhancement of harvested photon energy is efficiently transferred to the fullerene moiety on a subpicosecond time scale.

Global analysis[26] of the femtosecond data shows five components (see Supporting Information). A pulse related phenomenon is observed at ultrashort time scale. Two perylenediimide excited states are observed, one that decays in 0.4 ps and one that decays in 5 ps, attributed to a folded and an extended conformation. From both states the singlet excited state of the fullerene is formed. The final species formed is the triplet state of the perylenediimide, with a yield of at least 40%.

These results have many implications with respect to the application of these types of dyads in solar energy conversion. In our closely linked dyad system, the intramolecular energy transfer rate (0.4−5 ps) is competitive, as compared to the ultrafast photoinduced electron transfer interactions occurring between C_{60} and the conducting polymer.[2,3] However, the linkage between the two chromophores could be even shorter if electron transfer is designed to arise exclusively from the fullerene, as this will increase the energy transfer rate.[24] All excited states observed here can be considered very good electron acceptors (n-type materials). The low-energy perylene triplet state could reduce the open circuit voltage of a solar cell, however its population should be negligible in a solar cell due to the fast competitive processes on the subnanosecond time scale. The efficient population of this triplet state however, could be very suitable for singlet oxygen production for photodynamic therapy applications, especially because the compound absorbs strongly in the 500−700 nm region.

Now that the ultrafast energy transfer in perylenediimide functionalized fullerenes are established, the charge localization and charge hopping in the solid state are important issues to consider. These aspects can be influenced by tuning the redox properties of the imide part.

The morphology of the nanoscopic interpenetrating networks[25] is the key to more efficient polymer solar cells, and this property appears to be intrinsic to the fullerene adduct (e.g., 60[PCBM] see Figure 1) packing properties. Maintaining this specific fullerene property while enhancing its molar absorption coefficient by perylenediimide functionalization will be highly beneficial.

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Supporting Information Available: Transient absorption spectra of the two separate chromophores and outcome of global and target analysis[26] of the femtosecond data of C_{60}−PDI. This material is available free of charge via the Internet at http://pubs.acs.org.

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