OLIGOMER-FULLERENE DYADS: PHOTOPHYSICS AND PERFORMANCE AS ACTIVE LAYER MATERIAL IN PHOTOVOLTAIC CELLS

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Abstract:

The photophysics of a homologous series of oligo(p-phenylene vinylene)-fulleropyrrolidine (OPVn-C_{60}, n = 1 to 4, with n the number of phenyl rings) donor-acceptor dyads and the corresponding single moiety model compounds were studied. Fast intramolecular singlet-energy transfer occurs after photoexcitation of the OPVn moiety in an apolar solvent. Photoexcitation in a polar solvent results in electron transfer for OPV3-C_{60}, OPV4-C_{60}, and to some extent for OPV2-C_{60}, but not for OPV1-C_{60}. These results are compared to the results obtained for mixtures of the single moiety model compounds in the same solvents. In these dyads electron transfer is likely to occur via a two-step process, *i.e.* a very fast singlet-energy transfer prior to charge separation. In thin films of OPV3-C_{60} and OPV4-C_{60}, a long-lived charge-separated state is formed after photoexcitation. This long lifetime is attributed to the migration of charges to different molecules. A flexible photovoltaic device, prepared from OPV4-C_{60}, is presented.

INTRODUCTION

Photoinduced charge transfer between π-conjugated polymers and derivatives of [60]fullerene (C_{60}) is of considerable interest for photovoltaic energy conversion. The highly efficient process occurs in the femtosecond time domain.[1-3] The charge separation in these blends is assisted by the large interfacial area between donor and acceptor phases, which is formed spontaneously during spin coating.[4] The charge-separated state can persist even in the microsecond and millisecond time domains.[1,5] At present, the energy conversion efficiency of these photovoltaic cells is restricted by the carrier collection efficiency and the limited charge carrier mobility in the disordered blends.[6,7] Therefore, studying photovoltaic efficiency in relation to morphology and mesoscopic ordering in the active layer is of profound interest.[8]

Many C_{60}-based donor-acceptor dyads have been investigated to gain insight in the *intra*molecular photophysical processes, such as energy and electron transfer.[9] Only a few examples have been reported where π-conjugated oligomers are covalently attached

to C_{60}.[10-14] Apart from being well-defined model systems for photophysical characterization, the covalent linkage between donor and acceptor in these molecular dyads provides a simple method to achieve dimensional control over the phase separation in D-A blends.

Here, the photophysical properties of a series of well-defined donor-C_{60} dyad molecules with a π-conjugated oligo(p-phenylene vinylene) as the donor moiety (OPVn-C_{60}; n = 1 to 4, with n the number of phenyl rings[15]) are described. The results are compared to those of mixtures of N-methylfulleropyrrolidine (MP-C_{60}) and to those of a series of α,ω-dimethyl-oligo(p-phenylene vinylene)s (OPVns). A flexible photovoltaic device, prepared from OPV4-C_{60}, is presented.

RESULTS AND DISCUSS₁ON

Materials: The structures of the materials used in this study are shown in Figure 1. Details of the synthetic procedures for these compounds are given elsewhere.[16]
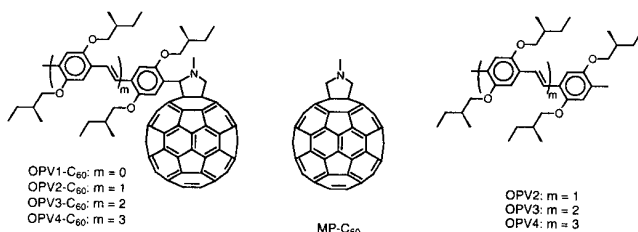

OPV1-C_{60}: m = 0
OPV2-C_{60}: m = 1
OPV3-C_{60}: m = 2
OPV4-C_{60}: m = 3

MP-C_{60}

OPV2: m = 1
OPV3: m = 2
OPV4: m = 3

Figure 1. *Structures of the materials used in this study.*

Ground-state absorption spectra: The absorption spectra of the OPVn-C_{60} dyads in toluene or o-dichlorobenzene (ODCB) closely correspond to a superposition of the spectra of the donor and acceptor chromophores. It is possible to excite the fullerene moiety selectively at 528 nm (one of the lines available from the Ar-ion laser). The OPV4 moiety, and to some extent the OPV3 moiety, can be excited selectively at 458 nm. It is not possible to selectively excite either the OPV2 or OPV1 segments.

Photoexcitation of OPVn in solution: Recently, we have reported on the singlet and triplet photoexcitations of oligo(p-phenylene vinylene)s (OPVns, n = 2 to 7).[17] The singlet excited state, OPVn(S$_1$), decays radiatively or non-radiatively to the ground state and via intersystem crossing to the OPVn(T$_1$) triplet state. The S$_1$ lifetimes (t) have been determined for OPV3 (t = 1.70 ns) and OPV4 (t = 1.32 ns) in toluene solution at room temperature and there is no significant dependence of t on the nature of the solvent.[17] The CW-modulated photoinduced absorption (PIA) spectra of OPV3 and OPV4 under matrix-isolated conditions in 2-methyltetrahydrofuran at 100 K exhibit a monomolecularly decaying T$_1$→T$_n$ transition at 2.00 and 2.27 eV for OPV3 and at 1.80 eV for OPV4 with lifetimes of 7.9 and 3.6 ms, respectively.[17]

Photoexcitation of MP-C_{60} in solution: Photoexcitation of MP-C_{60} in toluene or ODCB results in weak fluorescence at 1.74 eV and a long-lived triplet excited state. The fluorescence quantum yield in toluene is known to be 6×10^{-4}.[18] S$_1$ lifetimes of 1.45 ns[14]

and 1.28 ns[18] have been reported for toluene solutions. The quantum yield for intersystem crossing from MP-C_{60}(S_1) to MP-C_{60}(T_1) is near unity,[18] and the T_1 lifetime is about 200 μs.[14] The triplet state PIA spectrum of MP-C_{60} exhibits a $T_1 \rightarrow T_n$ absorption at 1.78 eV with a characteristic shoulder at 1.54 eV.[14] The T_1 energy level has been determined from phosphorescence to be at 1.50 eV above the ground state level.[18]

Intramolecular singlet-energy transfer in OPVn-C_{60} dyads in toluene: The fluorescence from the OPVn moieties of the dyads is quenched by more than three orders of magnitude compared to that of the pristine OPVn oligomers (λ_{ex} = 330, 366, 415, 443 nm for n = 1-4, respectively). The spectra also show a weak fluorescence of MP-C_{60}(S_1) at 715 nm. The excitation spectra of the fullerene fluorescence coincide with the absorption spectra of the OPVn-C_{60} dyads. Surprisingly, the fullerene fluorescence quantum yield in toluene is equal for all four dyads, nearly identical to that of MP-C_{60}, and does not alter with the excitation wavelength. Hence, the fluorescence spectra of OPVn-C_{60} provide clear evidence for an efficient *intra*molecular singlet-energy transfer from the OPVn(S_1) state to the fullerene moiety for n > 1.[19] From the extent of quenching of the OPVn fluorescence in the dyads, it can be calculated that extremely fast (~1 ps) singlet-energy transfer occurs in OPV3-C_{60} and OPV4-C_{60}. The PIA spectrum recorded for all four dyads in toluene solution shows the characteristic MP-C_{60} $T_1 \rightarrow T_n$ absorption at 1.78 eV with a shoulder at 1.54 eV. The observations from fluorescence and PIA spectra provide strong evidence that in toluene the OPVn moieties of the OPVn-C_{60} dyads with n > 1, serve as an antenna system to funnel the excitation energy to the fullerene moiety. [19]

Intermolecular triplet-energy transfer in OPVn/MP-C_{60} mixtures in toluene:. The PIA spectrum of MP-C_{60} and OPV4 (1:1 molar ratio) in toluene, recorded upon selective excitation of OPV4 at 458 nm, exhibits a monomolecularly decaying (~200 μs) band at 1.80 eV with a weak shoulder at 1.52 eV, characteristic for the MP-C_{60}(T_1) state. This observation indicates that, after intersystem crossing, an efficient *inter*molecular triplet energy-transfer occurs from the OPV4(T_1) state to MP-C_{60}. Because the photogenerated OPV4(T_1) state is quenched by the presence of MP-C_{60}, the triplet state energy of MP-C_{60} must correspond to the lowest excited state in toluene. Consistently, the PIA spectra of MP-C_{60} and OPVn (n =2, 3 or 4) in toluene (1:1 molar ratio), recorded using selective photoexcitation of MP-C_{60} at 528 nm, all exhibit the absorption of MP-C_{60}(T_1).[14] Weak fullerene fluorescence at 1.73 eV was observed for all three mixtures. PIA bands of OPV$n^{+\bullet}$ radical cations or MP-$C_{60}^{-\bullet}$ radical anions were absent. Hence, electron transfer does not occur in toluene solution.

Intermolecular electron transfer in OPVn/MP-C_{60} mixtures in *o*-dichlorobenzene: The PIA spectra of 1:1 molar mixtures of MP-C_{60} and OPV4 or OPV3 in ODCB give direct spectral evidence for *inter*molecular photoinduced electron transfer. For both mixtures an intense PIA spectrum of the charge-separated state was observed after selective excitation of MP-C_{60} at 528 nm. Strong absorptions for the OPV4$^{+\bullet}$ (0.66, 1.52, and 1.73 eV) and OPV3$^{+\bullet}$ (0.77, 1.70 and 1.97 eV) radical cations were observed, together with the characteristic absorption band of the MP-$C_{60}^{-\bullet}$ radical anion at 1.24 eV. The charge-separated state lifetimes were 2.5-3.1 ms for OPV4$^{+\bullet}$/MP-$C_{60}^{-\bullet}$ and 4.1-4.7 ms for OPV3$^{+\bullet}$/MP-$C_{60}^{-\bullet}$. Pump beam intensity dependency measurements clearly indicated an intermolecular recombination mechanism. We attribute the formation of radical ions to an *inter*molecular electron transfer between ground state OPV3 or OPV4 as a donor and the triplet state of MP-C_{60} as an acceptor.[20] *Inter*molecular charge transfer between OPV2 and MP-C_{60} does not occur in ODCB.[21]

Intramolecular electron transfer in OPVn-C$_{60}$ dyads in o-dichlorobenzene:
The fluorescence of the OPVn moiety of the dyads in ODCB is again strongly quenched (λ_{ex} = 330, 366, 415, 443 nm for n = 1-4, respectively). The most dramatic difference in ODCB is the strong quenching of the fullerene emission at 715 nm by a factor 5 for OPV2-C$_{60}$, via 26 for OPV3-C$_{60}$, to more than 50 for OPV4-C$_{60}$ (but not for OPV1-C$_{60}$). The quenching of the fullerene emission in the dyads may either result from an ultra-fast process that quenches the initially formed OPVn(S$_1$) state or from a rapid relaxation of the MP-C$_{60}$(S$_1$) state, once this is formed via energy transfer. The experimental observation that the residual OPVn fluorescence of the OPVn-C$_{60}$ dyads in ODCB is comparable to that in toluene, gives support to the latter explanation.

Although the intensities of the OPV$n^{+\bullet}$ radical cation and MP-C$_{60}$$^{-\bullet}$ radical anion absorptions are significantly lower in comparison with the PIA signals observed for mixtures of OPVn and MP-C$_{60}$ in ODCB, the characteristic features are evident. Remarkably, lifetimes up to 20 ms can be observed for these charge-separated states. In view of the expected (sub)nanosecond lifetime,[9] we consider this extremely long lifetime to be incompatible with an *intra*molecular charge-separated state, and attribute the signals to an *inter*molecular charge-separated state. This intermolecular charge-separated state is formed either by direct charge transfer between singlet excited OPVn-C$_{60}$(S$_1$) and a second dyad in the ground state or by charge transfer from the short-lived *intra*molecular charge-separated OPV$n^{+\bullet}$-C$_{60}$$^{\bullet}$ state to a neutral OPVn-C$_{60}$ dyad resulting in separate OPV$n^{+\bullet}$-C$_{60}$ and OPVn-C$_{60}$$^{-\bullet}$ radical ions. The longer lifetime as compared to OPVn/MP-C$_{60}$ (n = 3,4) mixtures is due to the lower concentration of the OPV$n^{+\bullet}$-C$_{60}$ and OPVn-C$_{60}$$^{-\bullet}$ radical ions and, hence, the reduced bimolecular decay rate.

Photoexcitation of OPV2-C$_{60}$ in ODCB leads to partial quenching of fullerene emission, while the MP-C$_{60}$(T$_1$) state is observed in the PIA spectrum, indicating simultaneous energy and electron transfer. The PIA spectrum of OPV1-C$_{60}$ in ODCB shows the MP-C$_{60}$(T$_1$) absorption, while no significant quenching of the fullerene emission is observed. Both observations are consistent with the absence of photoinduced electron transfer for OPV1-C$_{60}$ in ODCB.

Photoinduced electron transfer of OPVn-C$_{60}$ in thin films: The PIA spectra of thin films of OPV3-C$_{60}$ and OPV4-C$_{60}$ recorded with excitation at 458 nm differ dramatically from those of OPV1-C$_{60}$ and OPV2-C$_{60}$. For OPV3-C$_{60}$ and OPV4-C$_{60}$ the characteristic absorption band of the MP-C$_{60}$$^{-\bullet}$ radical anion is observed at 1.25 eV. Furthermore, the spectra show bimolecularly decaying absorptions for the OPV3$^{+\bullet}$ and OPV4$^{+\bullet}$ radical cations at 0.82 and 1.66 eV (OPV3$^{+\bullet}$) and at 0.64, 1.44 and 1.70 eV (OPV4$^{+\bullet}$). These observations are fully consistent with photoinduced electron transfer. The average lifetime of the charge-separated states is in the order of 0.5-1.5 ms. This lifetime is in strong contrast with the one of the *intra*molecular charge-separated state in ODCB. We propose that the long lifetimes in the film result from migration of the photogenerated hole and/or the electron to other molecules in the film, deminishing the the fast geminate *intra*molecular back electron transfer.

Energetic considerations for energy and electron transfer: The free energies of the *intra*molecular (G_{cs}) and *inter*molecular (G_{cs}^{∞}) charge-separated states were calculated with some approximations, using the Weller equation. The *intra*molecular charge-separated state is energetically located below the OPVn(S$_1$) state in toluene and ODCB for each n. However, in toluene all charge-separated states are higher in energy than the MP-C$_{60}$(S$_1$) and MP-C$_{60}$(T$_1$) states. In ODCB the situation changes dramatically; the energy of the *intra*molecular charge-separated state drops below that of the MP-C$_{60}$(S$_1$) state for each n, and even below that of the corresponding MP-C$_{60}$(T$_1$) state

except for $n = 1$, indicating that electron transfer will result in gain of free energy for $n > 1$. This is in excellent agreement with the quenching of the MP-$C_{60}(S_1)$ fluorescence, which occurs for $n > 1$. For the *inter*molecular charge-separated states the relevant state for comparison is the MP-$C_{60}(T_1)$ state only, since these charge-separated states are formed via the triplet manifold. *Inter*molecular electron transfer was calculated to be energetically favored in ODCB for OPV3 and OPV4 but not for OPV2, again in full agreement with the experimental results. These results show the strength of this approach in explaining the discrimination between photoinduced energy and charge transfer in conjugated oligomer - fullerene dyads.

Kinetics of energy and electron transfer: From the quenching ratios, the rate constants for energy transfer in toluene were estimated to be 1.1×10^{12} - 2.1×10^{12} s^{-1} for OPV3-C_{60} and OPV4-C_{60}. We assume similar values in ODCB. In principle, *intra*molecular photoinduced electron transfer, as observed for OPV2-C_{60}, OPV3-C_{60}, and OPV4-C_{60} in ODCB, can either take place directly from the initially formed OPV$n(S_1)$ state or indirectly, in a two-step process, via the MP-$C_{60}(S_1)$ state. The rate of *indirect* electron transfer can be calculated from the quenching ratio of the fullerene emission of the OPVn-C_{60} dyads in ODCB in comparison with MP-C_{60} and the lifetime of MP-$C_{60}(S_1)$ to be ~60 ps for OPV3 and ~30 ps for OPV4. In case of *direct* electron transfer from OPV$n(S_1)$, the decrease in fullerene emission has to result from quenching of the OPV$n(S_1)$ state, since it has to be faster than the energy transfer reaction. Such direct *intra*molecular electron transfer has to be extremely fast (14-16 fs, as calculated from the quenching ratios) and additional quenching of the residual OPVn emission must occur. This effect was not observed. Hence, the results strongly suggest that photoinduced electron transfer in the OPVn-C_{60} dyads in ODCB solution is a two-step process, involving singlet-energy transfer prior to charge separation.

The activation barrier for charge separation: The Marcus equation provides an estimate for the barrier for photoinduced electron transfer from the change in free energy for charge separation (ΔG_{cs}) and the reorganization energy (l).[22] The reorganization energy consists of internal (l_i) and solvent (l_s) contributions. The former can be calculated in the Born-Hush approach.[18,23] The calculated free energy change (ΔG_{cs}) and barrier ($\Delta G^{\ddagger}_{cs}$) for *intra*molecular electron transfer in the OPVn-C_{60} dyads relative to the OPV$n(S_1)$ and MP-$C_{60}(S_1)$ excited states show that the indirect photoinduced electron transfer is in the "normal" Marcus region ($l > -\Delta G_{cs}$), with an activation barrier of less than ~0.1 eV for $n > 1$. Direct forward photoinduced charge separation would occur in the Marcus "inverted" region ($l < -\Delta G_{cs}$), irrespective of the solvent or conjugation length of the OPVn donor. Using the values for l and for k_{cs} and $\Delta G^{\ddagger}_{cs}$ for the direct and indirect charge transfer mechanisms, the electronic coupling V between the donor and acceptor in the excited state can be calculated.[24] For the indirect mechanism, the values calculated for V are 30 ± 3 cm^{-1} for OPV3-C_{60} and OPV4-C_{60} in ODCB. For the direct mechanism, V has to be 1300-2600 cm^{-1}. Such a coupling would probably cause differences in the absorption spectrum of the OPVn-C_{60} dyads, which is not observed. Moreover, such coupling is much larger than the interaction expected between two chromophores separated by a bridge of three sigma bonds.[25] The kinetic analysis supports the conclusion inferred from the residual OPVn fluorescence of the OPVn-C_{60} dyads in ODCB, that charge separation in these systems is preceded by energy transfer.

Photovoltaic devices of OPV4-C_{60}: Photovoltaic devices in which OPV4-C_{60} is sandwiched between aluminum and PEDOT/PSS-covered ITO electrodes were fabricated. The *I/V* curves were completely reversible and the devices showed diode

behavior with a rectification ratio between -2 and +2 V of approximately 100, which shows that the devices have little or no shunts. Under ~65 mW cm^{-2} white-light illumination a short-circuit current (I_{sc}) of 235 μA cm^{-2} and an open-circuit voltage (V_{oc}) of 650 mV were observed. The filling factor (FF) was 0.25. The relatively low FF may be explained by the recombination of the charges at the ITO electrode. The values of I_{sc} and V_{oc} are quite similar to the ones found for π-conjugated polymer/fullerene solar cells in early reports,[26] although there has been considerable progress in energy conversion efficiencies of these devices recently.[27] The covalent linkage in the molecular dyad limits the domain size of a biconituous donor-acceptor 'network' in a film of OPV4-C$_{60}$ to the nanometer scale. Our results indicate that concurrent electron and hole transport through such a finest scale network does not necessarily suffer from a massive charge recombination problem.

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