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Oligomer-fullerene dyads and triads as model compounds for bulk-heterojunction PV cells

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Abstract. Covalent oligomer-fullerene donor-acceptor structures can serve as important model systems for plastic PV cells, based on interpenetrating networks of conjugated polymers and fullerene derivatives. Several series of [60]fullerene-oligomer dyads and triads were prepared. Photoinduced electron transfer phenomena were studied using photoinduced absorption spectroscopy. Measurements in solution and in the solid state reveal that the environment plays a crucial role in the formation and lifetime of the photoinduced charged states in these molecules.

INTRODUCTION

Photovoltaic cells, based on composites of conjugated polymers and fullerene derivatives (1,2), are considered as promising devices for solar energy production. At present, the efficiency of such 'plastic' PV cells is limited because the devices only produce current when a relatively thin active layer is used. As a consequence, only a small fraction of the incoming light is absorbed (3). The ruling paradigm is that the plastic PV devices suffer from low charge carrier mobility because of the random nature of the interpenetrating networks, formed spontaneously upon spin coating of a co-solution of the two constituents of the active layer. It is expected that structural ordering of the constituents will lead to a substantial increase in charge carrier mobility: the concept of a 'molecular electronic highway'. At present, little or nothing is known about the relation between the architecture of molecular (multi-)donor-(multi-) acceptor structures on one side and their material properties such as the efficiency of formation, the mobility, and lifetime of the photo-generated charge carriers on the other. A remarkable feature of conjugated polymer/fullerene blends is the fact that an ultra-fast forward electron transfer reaction occurs (< 1 ps), whereas the recombination of photogenerated charges is slow (> ms). The large difference in electron transfer rates can, in principle, be either an intrinsic property of the structures involved or a material property. In order to gain some insight in these matters, we are investigating model systems for such architectures. We use conjugated oligomers as

model compounds for the polymer. These oligomers have been synthesized, functionalized, and coupled to C_{60} in such a way that well-defined donor-acceptor dyad or triad molecules are obtained that can be studied both as individual molecules in solution and as (ordered) assemblies in the solid state. Plastic PV cells are usually made using either polythiophenes or poly[p-phenylenevinylene]s. Therefore, model systems were constructed that contain oligomer parts of these two types of polymers.

RESULTS AND DISCUSSION

Two types of oligothiophene-fullerene compounds were synthesized using the well-established Prato reaction (4). First, a simple dyad containing a terthiophene donor moiety and one fullerene acceptor moiety was prepared. Terthiophene monoaldehyde (**1b**), N-methyl glycine, and C_{60} were heated in toluene at reflux temperature during 16 hrs to yield a mixture of C_{60} , the desired mono-fulleropyrrolidine **2** and some higher adducts (Figure 1, left). The monoadduct was isolated in 47% yield using standard column chromatography. Dyad **2** was soluble enough in the standard organic solvents to allow for full characterization.

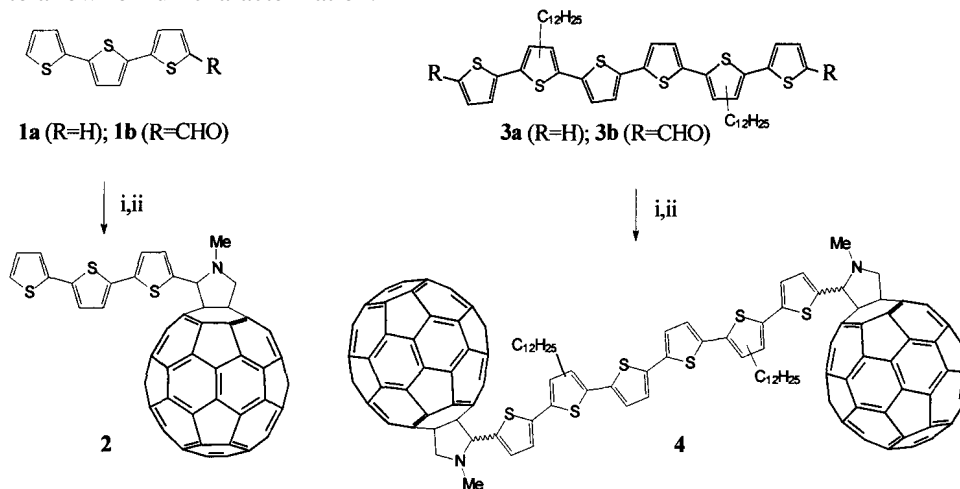


FIGURE 1. Synthesis of oligothiophene-fullerene dyads. Step i: DMF, POCl_3 ; step ii: N-methylglycine, C_{60} , toluene, Δ .

Similarly, triad **4** was prepared by refluxing a chlorobenzene solution of the highly soluble sexithiophene α,ω -bisaldehyde **3b**, N-methyl glycine, and C_{60} during 16 hrs (Figure 1, right). Since the starting oligomer material consisted of a mixture of three isomers and because the Prato reaction yields chiral products in the case of aldehyde starting material, triad **4** is a mixture of (maximally) 10 regio- and stereoisomers. Nevertheless, molecular models indicate that in all of these isomers the donor-acceptor configuration is very similar. $^1\text{H-NMR}$ spectroscopy indicates the

presence of (at least) 2 isomers. In HPLC analysis, 3 peaks (~ 1:2:1) were observed. These peaks most likely represent the three groups of isomers with different types of arrangements of the solubilizing chains on the sexithiophene unit. Triad **4**, was further characterized by MALDI-TOF MS and UV-vis spectroscopy.

Second, a series of oligo[p-phenylenevinylene] containing donor-acceptor dyads was prepared. The homologous series of compounds **6-9** was prepared in 44, 47, 48 and 40 % yield, respectively, from the corresponding oligomer ω -aldehydes, again using the above mentioned Prato method (Figure 2). The monoadducts **6-9** (each as a mixture of 2 diastereoisomers) are all highly soluble compounds that were fully characterized by MALDI-TOF MS, ^1H - and ^{13}C -NMR, UV-vis and IR spectroscopy.

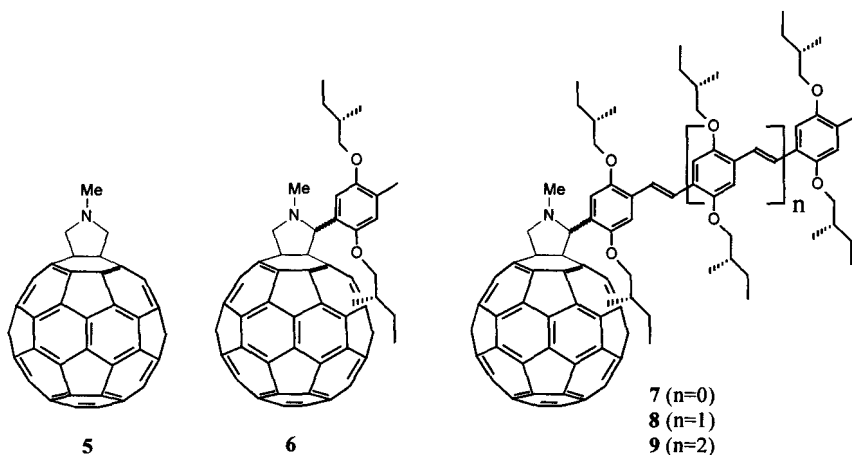


FIGURE 2. Homologous series oligo[p-phenylenevinylene]-fullerene dyads

We now turn to the photoinduced absorption measurements. Bis(dodecyl)-sexithiophene **3a** (6T) and N-methylfulleropyrrolidine **5** (**4**) were used as reference compounds. Photoinduced absorption (PIA) spectra were recorded between 0.25 and 3.5 eV by exciting with a mechanically modulated Ar-ion laser (458 nm, 50 mW, 275 Hz) pump beam. The resulting change in transmission of the probe light through the sample (ΔT) was monitored with a phase sensitive lock-in amplifier after dispersion by a triple grating monochromator and detection, using Si, InGaAs, and cooled InSb detectors. Oxygen-free solutions were studied at room temperature. Thin films were held at 80 K using an Oxford Optistat continuous flow cryostat.

When benzonitrile solutions of **3a** or **5** are studied with PIA spectroscopy, long-lived photo-excitations are formed in both cases (Figure 3a and 3b). For **3a**, the triplet state exhibits a narrow triplet-triplet absorption band at 1.78 eV with a vibrational shoulder at higher energy (5). The lifetime of the 6T triplet state is 155 μs . In addition, **3** shows photoluminescence (PL) at 2.40 eV with a shoulder at 2.25 eV. For **5**, the PIA spectrum also shows the formation of a triplet state with characteristic bands at 1.78 eV and 1.52 eV. The lifetime of this triplet state is 220 μs . At 1.26 eV a small band of the radical anion of **5** can be seen. Its formation is attributed to the

presence of a small impurity of isocyanobenzene (PhNC) in benzonitrile (PhCN) which acts as a donor to the triplet state of **5**. This is a bimolecular reaction and

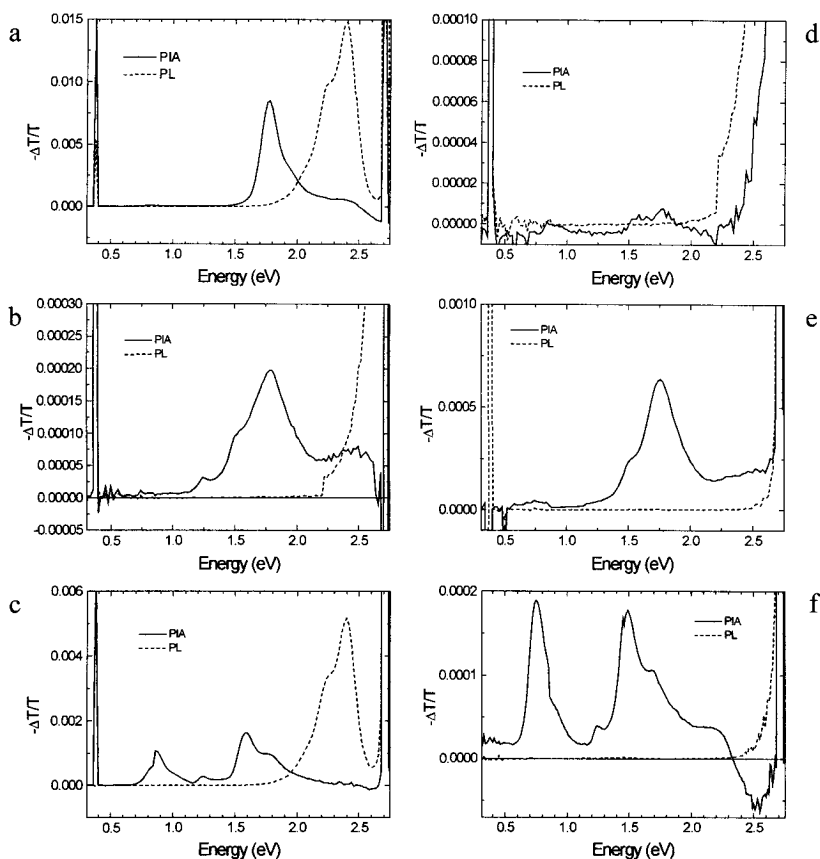


FIGURE 3. PIA and PL spectra of (a) **3a** in benzonitrile; (b) **5** in benzonitrile; (c) **3a** and **5** (1:1 molar ratio) in benzonitrile; (d) **4** in benzonitrile; (e) **4** in toluene; (f) a thin film of **4** on quartz. Spectra a-e were recorded at 295 K, spectrum f was recorded at 80 K. The PL curves shown in spectra band d-f are mainly due to scattering of the excitation laser beam

the lifetime of the anions formed is long because charge recombination is hampered by follow-up reactions of the isocyano-benzene cation radical, acting as a sacrificial electron donor. When **3a** and **5** are dissolved in benzonitrile in a 1:1 ratio, we find the clear characteristics of the $6T$ radical cation with bands at 0.87 and 1.60 eV in solution and a band of the radical anion of **5** at 1.24 eV (Figure 3c) (6). The fact that under these conditions the fluorescence of **3a** is not quenched demonstrates that electron transfer does not occur from the S_1 -state of **3a** which is formed preferentially at first. Rather electron transfer occurs from the T_1 triplet state of **3a** which is formed via intersystem crossing from S_1 . The lifetime of the $6T$ radical cation is on the order of 200-400 μ s. The determination of the lifetime of the radical anion of **5** is hampered by

the isocyanobenzene impurity which remains to act as electron donor to the triplet state of **5**. When **3a** and **5** are photoexcited in an apolar solvent such as toluene, instead of the highly polar benzonitrile, only triplet states are formed. Photoexcitation of the 1:1 mixture in toluene results in triplet energy transfer from 6T(T₁) to **5** rather than electron transfer, similar to previous observations for mixtures of 6T and C₆₀ (6). The reason for a preference for energy transfer in toluene is that the charge-separated state is less stabilized in apolar solvents.

Photoexcitation of a benzonitrile solution of triad **4** results neither in a detectable PIA signal nor in a detectable PL signal (only scattering of pump laser) (Figure 3d). Apparently, the S₁-state of the 6T moiety is completely quenched. This behavior can be rationalized by assuming that in benzonitrile a fast forward electron transfer reaction occurs resulting in an intramolecularly charge-separated state. The fact that this charge-separated state is not detected with the PIA technique is explained by assuming that the lifetime is less than about 10 μs, below the detection limit of our near-steady state PIA spectrometer.

When the solvent is changed to toluene (which is less polar) the PL is not restored but a clear PIA signal similar to the triplet state of **4** is observed with a lifetime of about 250 μs (Figure 3e). This indicates that in toluene an intramolecular energy transfer occurs in which the singlet excitation energy is transferred to the C₆₀ fragment. This singlet C₆₀ photoexcitation subsequently intersystem crosses to a C₆₀ triplet state. When triad **4** is cast from solution on quartz glass a solid film is obtained. PIA spectroscopy of this thin film at 80 K shows that a long-lived charge-separated state is formed (Figure 3f). Characteristic absorption bands of the radical cation of 6T at 0.72 and 1.49 eV and of the radical anion of C₆₀ at 1.24 eV appear in the spectrum. The PIA bands increase with the square root of the excitation intensity, indicative of bimolecular decay. The frequency dependence follows a power law: $\Delta T \propto \omega^p$, with $p = 0.12-0.17$. Such a power-law behavior is often observed for a distribution of lifetimes. We propose that such a long-lived charge-separated state can only exist when the hole and electron are localized on different molecules. The experiments of **4** in benzonitrile show that intramolecular charge recombination occurs with a time constant that must be less than 10 μs. In solution, a fast intramolecular photoinduced electron transfer reaction may occur in **4**, depending on the Coulombic stabilization of the charge-separated state by the medium. The charge transfer in solution is governed by the Weller equation (7). Intramolecular charge recombination in the photoexcited arrays occurs on short time scales (probably $\ll 10 \mu\text{s}$). This demonstrates that the long lifetime of the charge-separated states in solid blends of 6T and fullerene derivatives (8) or solid films of the C₆₀-6T-C₆₀ array is a material rather than a molecular property. In solvents where electron transfer does not occur, we invariably observe the spectral characteristics of the triplet-state of the fullerene moiety, even when the oligothiophenes are preferentially excited (6). In combination with the absence of oligothiophene fluorescence it can be concluded that in these cases an efficient energy transfer occurs from the excited oligothiophene to the fullerene. Solutions of dyad **2** in toluene and in benzonitrile show similar photoinduced absorption spectra. No signatures of charge separated states were found. Instead, the

typical absorption spectrum, corresponding to triplet C_{60} , is observed. This indicates that in both solvents either highly efficient intramolecular energy transfer occurs from the terthienyl moiety to the fullerene part of the molecule or direct excitation of the fullerene moiety takes place (at 458 nm, **5** has a higher absorption coefficient than terthienyl).

The oligo[p-phenylenevinylene]-fullerene dyads **6-9** are currently being investigated using photoinduced absorption spectroscopy in solutions and as solid films. Preliminary results show that the behavior of **8** and **9** parallels that of triad **4**. For **8** and **9** the photoluminescence is strongly quenched under all conditions. Photoexcitation of **8** and **9** in toluene gives a C_{60} triplet state, while in benzonitrile a fast forward and fast backward electron transfer reaction occurs. In thin films of **8** and **9** a long-lived charge separated state is observed with the hole localized on the oligo[p-phenylenevinylene] fragment and the electron on the fullerene moiety.

In conclusion, it has been demonstrated that compounds **4**, **8**, and **9** behave photophysically in such a way that they can serve as model compounds for conjugated polymer / fullerene blends. The formation and the lifetimes of photoinduced charge separated states in oligomer-fullerene compounds **4**, **8**, and **9** depend fully on the chemical environment of the molecules. Long lifetimes of charge separated states are only observed in the solid state. Hence, stabilization of the charge-separated state is a material property of these compounds. Based on our experiments, we propose that a rapid diffusion mechanism for a substantial fraction of the photo-generated charges to the corresponding units of neighboring molecules is operating in the solid state.

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