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Bottom-Up Approaches Towards Functional Fullerene-Containing Nanostructured Materials

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Abstract. Fullerenes can play an important role in functional materials, the most common being that of an electron acceptor and electron transport material. Functional feasibility of fullerene derivatives has been shown in photovoltaic, photo detection, and image scanning devices, for example. In these applications, the fullerene acts together with a donor component. An efficient photovoltaic active layer made of molecular electron donor and acceptor moieties is especially demanding with respect to the morphology formed by the two electronic counterparts. An overview is given on the synthetic strategies towards molecular donor-fullerene architectures that have been used up to now in trying to obtain desired morphologies of fullerene-containing functional materials.

INTRODUCTION

The discovery of the ultra-fast photoinduced electron transfer between molecular donor materials like certain conjugated polymers and fullerene C₆₀ in 1992 by Sariciftci and Heeger has led to substantial number of publications on the working principles, the underlying physics, and the potential applications.[1] The applications that have been most actively pursued until now are in molecular photovoltaics (PV), photo-detectors, and scanning devices, and to a lesser extent in optical limiting and photorefractive materials. The first three applications demand not only for efficient photo-induced electron transfer and a substantial lifetime of the charge-separated state, but also for efficient charge transport through the molecular photoactive layer to the electrode materials of the device. The need for both efficient charge generation and transport in a PV device puts a number of constraints on the architecture of the active layer and the device as a whole. First, in order to obtain efficient photo-induced electron transfer throughout the active layer, the distance between any donor molecule and an acceptor molecule, and vice versa in the case that both materials absorb the incoming light to a certain extent, has to be less than the exciton diffusion length in the donor or the acceptor material, respectively. Since the exciton diffusion length in organic materials is far less than the absorption depth, a classic two layer p/n junction is not a feasible configuration for an efficient device. The concept of mixing donor and acceptor molecular materials in order to form a blend with a morphology of interpenetrating networks, leading to a bulk-heterojunction functionality, introduced in 1995, solves this problem.[2,3] However, independent of the way the donor-acceptor material is constructed (e.g. covalent, supramolecular / self-organizing, random

mixture, or combinations thereof, low and/or high molecular weight components, etc.), the donor-acceptor layer has to contain (or consist of) continuous domains of both electron and hole conducting materials for efficient collection of the photogenerated charges. In the simple form, all the necessary functional tasks in the bulk-heterojunction can be performed by a donor component (light absorption, electron transfer donor, hole transport) and an acceptor component (light absorption, electron transfer acceptor, electron transport). Light absorption in the donor leads to LUMO-to-LUMO electron transfer, while light absorption in the acceptor leads to HOMO-to-HOMO electron transfer. The latter process can be considered as the molecular analogue of the process called ‘hole transfer’ in classical semiconductor physics. Both types of electron transfer may happen concurrently, depending on the match between the UV-vis absorption spectra of the donor and acceptor chromophores and the spectral distribution of the incoming light.

Based on these considerations, we can define certain limits with respect to the morphology of a simple donor-acceptor active layer. In Figure 1, a highly schematic side view on a bulk-heterojunction PV cell is shown: a donor-acceptor layer between two electrodes.

FIGURE 1. Schematic view on a bulk-heterojunction device. Light and dark regions are donor and acceptor material domains, respectively.

Independent of the real architecture of the donor-acceptor material (only for simplicity a highly ordered structure with a kind of alternating standing plates of donor and acceptor materials is shown here), it is clear that the optimal thickness of the layer is at the point of balance between light absorption and serial resistance. The upper limit for the width (or diameter, depending on the morphology) of the domains is determined by the exciton diffusion length in each phase (or, in an alternative view, by the width of the depletion layer in each phase). The thread of charge recombination may set a lower limit for the width of the domains, but no experimental evidence for such a limit was found until now.

Up to now, the most efficient PV cells, based on a donor-fullerene bulk-heterojunction, are made with an active layer of a blend of MDMO-PPV and PCBM, sandwiched between a positive electrode of PEDOT-PSS on ITO coated glass and a negative electrode made of a sub-nanometer LiF layer and aluminum ($\eta = 2.5\%$).[4]

In collaboration with the groups of Janssen, Meijer (Technical Univ. of Eindhoven), and Sariciftci (J. Kepler Univ. Linz), we have simultaneously investigated various bottom-up approaches towards more structured donor-fullerene active layers for photovoltaic application. Below, we will give an overview of a part of this work.

OLIGOMER-FULLERENE DYADS AND TRIADS

One way to obtain mesoscopic order in organic materials is by constructing block copolymers. Using donor-acceptor block copolymers, spontaneous formation of donor and acceptor domains may be expected. In principle, by varying the size of the blocks, the morphology of the material can be controlled. This opens the possibility to fine-tune the material towards optimal functionality in the sense mentioned above. In order to learn about the basic functionalities in such materials, two series of model compounds were synthesized. Both series are conjugated oligomer - fullerene donor-acceptor compounds. The first is a series of three fullerene-oligothiophene-fullerene (C_{60} - T_x - C_{60}) triads with different donor size, and the second is a series of four oligo(p-phenylene vinylene)-fullerene (OPV_x - C_{60}) dyads with increasing donor length.[5,6,7,8] The chemical structures of the compounds are shown in Figure 2.

FIGURE 2. A series of oligothiophene-fullerene triads (left; C_{60} - T_{3n} - C_{60} , with $n = 1, 2, 3$), and a series of oligo (p-phenylene vinylene)-fullerene dyads (right; OPV_x - C_{60} ; $x = 1$ to 4, with $n = 0, 1, 2, 3$).

The photophysical properties of these triads and dyads have been thoroughly investigated by the Janssen group. The data obtained using UV-vis, photoinduced absorption, and fluorescence spectroscopy are consistent with the following picture. In solution, independent of the polarity of the solvent, the first photophysical process is light absorption by either the donor or the acceptor leading to the respective singlet excited states. In case the donor part is excited, a fast (~ 1 ps on average) singlet energy transfer to the fulleropyrrolidine moiety occurs. The nature of the *next* step depends (a) on the polarity of the solvent, and (b) on the conjugation length (or better: ionization potential) of the donor moiety: in apolar solvents, all compounds show intersystem crossing to the fullerene triplet excited state, either after the initial singlet energy transfer or directly from the fullerene singlet excited state. Charge transfer does not occur in apolar solvents. In polar solvents, like 1,2-dichlorobenzene (ODCB) and

benzonitrile, the dyads and triads with the longer donor moieties all show charge transfer. Since this happens in the (singlet) excited acceptor state, it is of the HOMO-HOMO electron transfer type. The electron transfer occurs within 60 and 30 ps in ODCB for OPV3-C₆₀ and OPV4-C₆₀, respectively. In solution, the lifetime of the *intramolecular* charge separated state is very short (~ submicrosecond). In contrast, in solid films of OPV3-C₆₀ and OPV 4-C₆₀, a long-lived charge-separated state is formed after photoexcitation. The long lifetime in the film is attributed to the migration of charges to different molecules.

Interestingly, an *intramolecular* two-step mechanism, shown by the dyads and triads in solution, contrasts with the observation of a single step *intermolecular* subpicosecond (~ 45 fs!) electron transfer in conjugated polymer - (methano) fullerene blend thin films.⁹ Ultra-fast spectroscopic methods are now being used to study the processes in thin films of the dyads and triads, since it is possible that a similar direct one-step (*intermolecular*?) process may occur in these compounds in the solid state.¹⁰

A photovoltaic cell, using OPV4-C₆₀ as the sole active layer material, showed a remarkable efficiency, taking into account the fact that any donor-acceptor phase separation is highly restricted by the nature of this dyad material.[6]

COVALENT CONJUGATED POLYMER - FULLERENE COMPOUNDS

Recently, two types of regular covalent conjugated polymer-fullerene compounds have been synthesized. The first type consists of a conjugated polymer backbone, densely substituted with pending fullerene units in a regular and chemically well-defined fashion. This type of compound was dubbed a 'double cable' since it should

FIGURE 3. 'Double cable' compounds. Left: an electropolymerized 2,2'-dithienyl by Cravino et al.[13]; Right: the hybrid poly (p-phenylene ethynylene)-(p-phenylene vinylene) polymer by Marcos R. et al.[12]

conduct holes through the main chain and electrons through the array of pending fullerene moieties.[11,12] Other conjugated polymer-fullerene are known, but they have not been incorporated in PV devices.[13,14] A PV cell, using the polymer depicted at the right in Figure 3 as the sole active material, showed a V_{oc} of 0.83 V, a I_{sc} of 0.42 mA/cm² and a fill factor of 0.29 under 100 mW/cm² AM1.5 light.[12]

The second type is a two-block copolymer consisting of a PPV type donor block and a polystyrene block, grafted with fullerenes through a radical addition reaction.[15]

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