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Synthetic strategies for modifying dielectric properties and the electron mobility of fullerene derivatives

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Summary

In the 1985, a new class of all-carbon molecules known as fullerenes was discovered, which shortly caught the interest of many scientists due to their interesting features. From a structural point of view, fullerenes are (close to) spherical molecules consisting of pentagonal and hexagonal rings. All the rings are fused in such a way that no two pentagon rings are next to each other and all the double bonds are conjugated.

From a functional point of view, fullerenes provide abundant research opportunities in pure chemistry, materials science, medical sciences and many other disciplines due to their unique properties. However, great electron accepting and conducting capability of fullerenes have made them a suitable candidate in organic electronics and specially solar cell applications.

Organic solar cells (OPV) usually consist of two main components. The first one is a light absorbing material (often a conjugated polymer), which conducts positive charges (donor) and the latter one is an electron accepting material (in our case a fullerene derivative), which conducts negative charges (acceptor). The working principle of an organic solar cell is as follows: when light with suitable energy is absorbed by polymer, an electron is excited to a higher energy orbital and leaves behind a positive charge called "hole", thereby forming a tightly bound electron-hole pair, called exciton. If this happens in the vicinity of an electron accepting material (i.e. fullerene), this exciton can diffuse to the interface between polymer and fullerene and then the electron can be transferred to the fullerene. The fullerene molecule has now a negative charge, while the polymer molecule is left with the positive charge (hole). Once the charge transfer exciton is successfully separated into free charges the electron and the hole travel through the fullerene and polymer domains and finally towards the electrodes, where they are injected (Fig. 1).

As it was explained, the working principle of OPV devices is based on the dissociation of exciton (electron-hole pair) upon light absorption. It is known that these electron-hole pairs are Coulombically bound in organic materials. Therefore, it stands to reason that if the Coulomb interaction between the electron and hole were decreased, the charge separation would be easier and consequently the efficiency of the OPV devices would increase. Since Coulomb interaction is inversely related to the relative dielectric constant of the medium, ϵ_r , a major bottleneck for using organic materials in high efficiency OPV applications is their low dielectric constant and

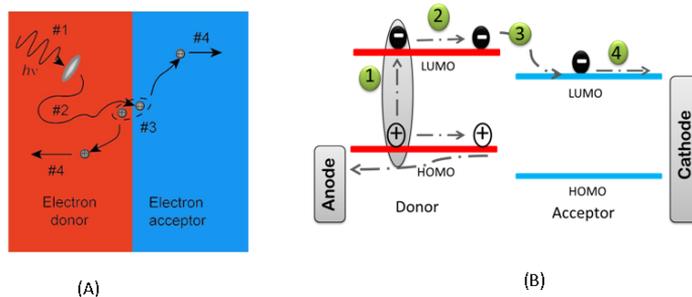


Figure 1: the mechanism of charge extraction in a donor/acceptor solar cell.

consequently high exciton binding energy. It should be noted that the low dielectric constant in organic materials not only increases the exciton binding energy but also favors charge recombination. Recombination can occur between electrons and holes that stem from the same excitation (i.e. geminate recombination) or from different excitations (non-geminate recombination). The recombination of electron-hole pairs has been found to be one of the major loss mechanisms in OPVs. Therefore, one of the apparent mechanisms to increase the efficiency of the solar cells is increasing the ϵ_r of organic materials, which is the main subject of this thesis. Altogether, in order to push the limits of organic photovoltaics, developing novel methods to increase the dielectric constant of organic semiconductors seems crucial. Despite its importance, to date, only very few attempts at increasing the dielectric constant of organic semiconductors have been published. In this thesis, we mainly focus on fullerene derivatives as a potential candidate for solar cell applications. The aim of the work described in this thesis is to develop fullerene derivatives with higher dielectric constant and electron mobility, through synthetic approach, while keeping all other electrochemical properties unchanged. This thesis is organized as follows:

In chapter 2, the effect of installing strong permanent dipole groups on polarizability and the dielectric constant of fullerene derivatives is studied. In this respect, synthesis, characterization and electrochemical properties of fullerene derivatives with push-pull (electron pushing and electron pulling) group in the side chain (PCBDN and PPP) and their reference analogues without a push-pull group (PCBBz and PP) are described. Experimental measurements on the synthesized compounds suggest that the incorporation of these dipole groups does not have a considerable effect on the dielectric constant of the compounds. However, theoretical analyses show an enhanced charge separation in these compounds due to the reorientation of the

dipoles, which can lead to improved OPV devices.

A synthetic way to increase the dielectric constant of fullerene derivatives by incorporation of flexible polarizable side groups into the chemical structure of fullerene derivatives is proposed in chapter 3. It is demonstrated that introducing triethylene glycol monoethyl ether (TEG) side chains to fulleropyrrolidines increases the dielectric constant by ~ 46 percent without devaluation of optical properties, electron mobility, and orbital energy levels of the compound.

In chapter 4, the effect of several parameters on the dielectric constant of fullerene derivatives is systematically studied. First, we investigated the effect of changing the length of ethylene glycol-type side chains. The results show that dependency of the dielectric constant on the length of the TEG chain is not significant. Next, we studied the effect of installing high dielectric constant side chains and highly polarizable groups into the chemical structure of the fullerene. However, we do not have enough measurement data on these compounds at this point to draw any conclusion.

Our quest for conjugated organic materials that exhibit high electron mobility is described in chapter 5. First, three fullerene derivatives with different numbers of acetylene groups in the side chains were designed, synthesized, and characterized. Next, their electron mobility was investigated using the space-charge limited current (SCLC) method. Our results first suggested dramatically improved electron mobility in thin films of fullerene derivatives with one acetylene moieties in each alkyl side chain (F2M) and even in a film of a similar fullerene derivative with simply saturated alkyl side chains (F2A), after mild thermal annealing. This annealing also resulted in highly ordered layers, as visualized by TEM. However, these spectacular mobility values showed a strong dependence on the contact material used for charge injection into the organic layer. Changing the contact material resulted in standard charge carrier mobilities. From these investigations, we conclude that some kind of doping of the organic semiconductor layer must occur, when a LiF contact layer is applied.