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Photo-induced charge transfer in fullerene–oligothiophene dyads – A quantum-chemical study

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ABSTRACT

The excited states of fullerene–oligothiophene dyads were studied by quantum-chemical methods in respect of their theoretical suitability as solar-cell materials. Compared to the constituents a significant extension of the absorption spectra to the red has been found caused by optically excitable charge transfer states. These states seem to be responsible for the low energy conversion efficiency of fullerene–oligothiophene dyads in photovoltaic devices.

1. Introduction

The photo-induced electron-transfer from a conjugated polymers, e.g. poly 3-hexylthiophene (P3HT), to a fullerene, e.g. [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), is the key-process for polymer-based organic solar cells [1]. To optimize this process the contact between electron donor and acceptor has to be very close. Thus on may assume that fullerenes covalently bound to the polymer are optimum materials for organic solar cells. In principle there exist two possibilities to link the fullerene and the conjugated polymer: either attaching the fullerene by a non-conjugated bridge-group to the polymer or building a dyad in such a way that a conjugated oligomer and a fullerene form a common conjugated system [2–6]. The performances yielded by the first approach were rather disappointing for energy conversion efficiencies <0.4% [4,7–9], whereas non-linked blends of P3HT and PCBM yield up to 5.1% energy conversion [10]. For finding more efficient dyads, a large number of possible combinations of oligomers and fullerenes has to be screened. Thus it makes sense, before starting costly chemical synthesis, first to check the candidates by quantum-chemical methods theoretically.

Sun et al. [11] for example have studied the photo-induced charge transfer in the quater-thiophene-$C_{62}N$ dyad, where oligothiophene and fullerene are linked via an indiol-bridge [3,6,12], by time-dependent density functional theory (TD-DFT). They calculated the first 40 excited states, and really found that the lowest of them at 1.788 eV represents an internal charge transfer state, i.e. the electron is located on the C_{60} and the hole on the quarter-thiophene, as expected. However, the 25 excited states below 3.28 eV turn out to have none or only weak oscillator strengths, independently, whether they are of charge transfer character or not. The lowest optically allowed transition appears at 3.286 eV with 1.7975 oscillator strength. This transition is clearly related to the $\pi \rightarrow \pi^*$ transition of the quarter-thiophene. Due to the large energy difference between optically excited and charge transfer state, with many intermediate states between them, would not be a really promising candidate for a solar-cell. The excitation energy is quite high compared to the AM1.5 solar spectrum and the intermediate states may force geminated recombination, quenching the internal quantum efficiency.

To our mind two properties of the studied dyad are responsible for the failure of this specific dyad as solar-cell material: (i) the quarter-thiophene is definitely too short for providing a sufficient low optical absorption, and (ii) the indiol-group causes some of the nasty additional excited states (see CDDs of the states 5, 24, and 25 in Table 5 of Ref. [11]). Nitrogen-containing groups build into polythiophenes or polyphenylenes are known to act as electron acceptors [13]. To a great deal the first problem should have been solvable by extending the attached oligothiophene up to a

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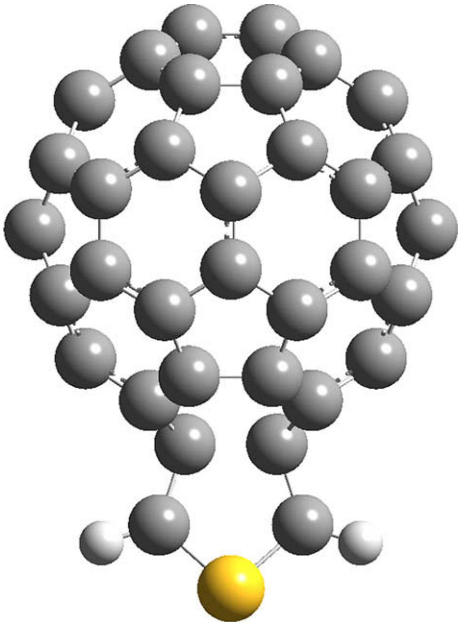

Fig. 1. Structure of the $C_{62}SH_2$ molecule.

sedeci-thiophene, but the best power-efficiency was still only ~0.4% [7]. Thus in the present work we will concentrate on the second problem. For this purpose we will study systems where the C_{60} is directly connected to oligothiophenes of different length by sharing the two carbons in the 3 and 4 position of the respective thiophene ring, which belong also to the double-bond separating two hexagons of the C_{60}. For the simplest representative of this fullerene–thiophene, $C_{62}H_2S$ see Fig. 1. By adding a certain number of thiophene rings at the (ortho-)positions next to the sulfur, one obtains several fullerene–oligothiophene dyads of this kind.

2. Methods

There is a great deal of arguing going on, which quantum-chemical method is adequate to describe extended π-systems properly [14,15]. We found that DFT for the ground and TD-DFT for the excited states, both using the Becke's hybrid-functional B3-LYP and the 6-311G basis set, provide good results for short conjugated oligomers [16,17]. The usage of a hybrid-functional instead of those with local density approximation (LDA) or generalized gradient approximation (GGA) is recommended, especially, to study charge transfer between neighbored molecular groups where exchange interaction may be important [18].

For longer conjugated oligomers and polymers even the B3-LYP functional may be less accurate [15]. In these cases we found that

Table 1
Structures of the studied $C_{62}S$ – thiophene_{10} isomers (a1, a2, a3, b1, c1) and their constituent undeci-thiophenes conformers (a0, b0, c0). Ground state energies given relatively to the structures a0 and a1, respectively.