

DAMASCO-Preparation and Application of new n-type, Electron Acceptor Materials in Organic Solar Cells FP7-PEOPLE-2010-RG-268229

The solar energy represents the foremost renewable source, that holds the highest potential to respond to the world's growing energy needs in the context of a sustainable growth, taking into account also ecological concerns. There are many possibilities to convert the solar energy to electricity, but there is a broad consensus that the most promising alternative towards low cost, highly versatile cells involves devices based on organic active layers, also in combination with inorganic materials.

The organic photovoltaic cells are made with conjugated polymers or small organic molecules. These organic materials have important advantages compared to traditional inorganic semiconductors, due to their moderate production costs and easy processability and eco-friendly disposal.

Among organic solar cells, the so-called bulk-heterojunction (BHJ) is the most common device technology, in which the active organic layer is composed by blends of electron-donating and electron-accepting materials. Although various conjugated polymers have been explored as electron donor and hole transporter (p-type transport) in bulk-heterojunction, not so many polymers have been used as acceptor and electron transporter (n-type transport).

The fullerene derivatives are the main acceptors for BHJ, as they have outstanding electron affinity and ability to transport charge effectively, but they are non-ideal materials due to their weak absorption and high commercial value, which is a significant drawback in industrial applications. Perylene-3,4,9,10-perylene tetracarboxylic acid diimides (PDIs) are one of the most significant n-type organic semiconductors proposed as substituted of fullerenes. Because of their good thermal and photochemical stability, high electron affinity, high absorption and fluorescence quantum yield, perylene bisimide derivatives have been extensively studied as one of the most interesting functional materials. They were also used in bulk-heterojunction solar cell as acceptor components because of their electronic properties and their good harvesting of the solar light, but the devices have shown low efficiencies, most likely due to the poor morphology of the photo-active blends. PDI photophysical and redox properties can be easily modified by introducing substituent groups in the diimide positions or in bay positions, this demonstrating the chemical versatility of this dye molecule. However, the number of perylene-based materials with electron transport properties that have been synthesized and used as photoactive component in solar cells is small. The aim of DAMASCO was the development of novel perylene based molecules and polymers with n-type, acceptor properties, good harvesting of the solar light and solution-processable.

The main objectives of DAMASCO:

1. Design and synthesis of novel electron acceptor perylene based systems for BHJ solar cells.
2. Preparation of donor/acceptor photoactive blends.
3. Preparation of BHJ solar cells and photovoltaic performance evaluation.

The development of novel perylene based materials was strongly oriented to create structures with interesting features and most importantly, with low aggregation.

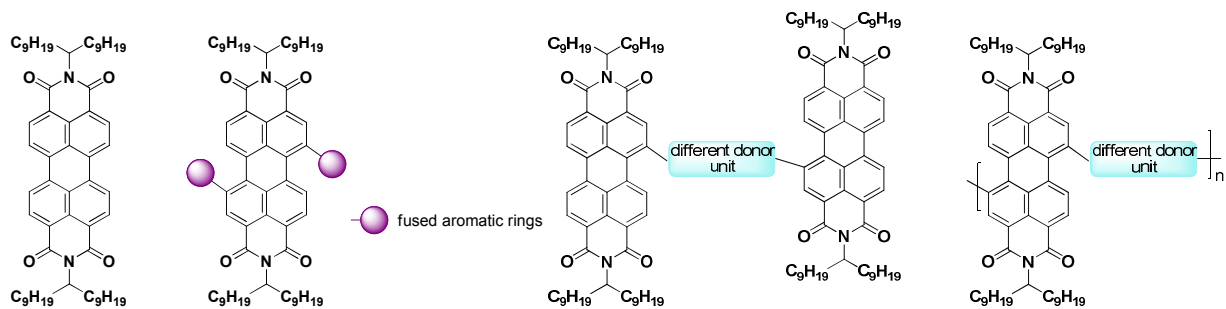


Figure 1. Molecular representation of the PDI based molecules, dimmers and polymers

A series of PDI based molecules with different fused aromatic rings (PDI-FAR, FAR: dibenzofuran, acenaphthene, naphthalene, spirofluorene, di-octyl-fluorene) in the bay positions have been design and studied (figure 1). This kind of substitution leads to twisted perylene planes and creates a strong steric hindrance. This decreases the π - π stacking and leads almost to an isolation of the π systems in the solid state, which was observed only for core tetrasubstituted perylenes. According to the spectroscopical data, the aggregation is practically inexistent, since the absorption properties in solution and thin film are identical.

The theoretical calculations show that in the case of an unsubstituted PDI, the perylene core is nearly planar, while the substitution with fused aromatic rings show low energy molecular conformations characterised by a twisted perylene core with high dihedral angles, clearly preventing a close contact of neighbouring PDI planes. The DSC measurements give additional proofs, where a poor organization in the solid state was observed.

The new PDI based materials were fully characterized (chemical, optical, electrochemical properties). Their HOMO-LUMO energy levels are suitable to use them as acceptors in blends with poly-3-hexylthiophene (P3HT). Moreover, the photoluminescence quenching in P3HT/PDIs blends provide an indication that photoinduced charge transfer takes place between the donor polymer and the acceptor PDI.

The P3HT blends with PDI-FAR showed good filming properties, as observed by optical microscopy. The photovoltaic properties were investigated by fabricating solar cells with an ITO/PEDOT:PSS/P3HT:PDI-FAR/Ca/Al structure. Using this architecture, ten fold improvement in solar cell efficiency was obtained in comparison with a device containing the unsubstituted PDI. Efficiencies around 1% have been obtained, which represents one of the best results for the bulk heterojunction solar cells containing PDI/P3HT as active layer.

All the results mentioned above are fully described in four peer reviewed publications (including a review article on the perylene diimide based materials for organic solar cells).

The development of other n-type materials is an ongoing process within the Regional Italian Project N° 17348 "Technologies and Materials for the efficient use of the solar energy". Perylene diimide dimers and polymers based acceptors using different donor units (benzodithiophene, alkyl substituted thiophenes) have been synthesized and their photovoltaic properties with suitable donor components is in progress.