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Doped-carbazolocarbazoles as hole transporting materials in small molecule solar cells with different architectures

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ABSTRACT

The adaptation of interfacial layers to the stacked architecture of organic solar cells represents a very useful strategy for improved device operation. In this context, heteroacenic structures such as carbazolocarbazoles have been doped and evaluated as hole transporting materials in small molecule solar cell with either inverted or conventional architecture. S-kinks in the IV-curve detected for the inverted solar cells could be remarkably corrected by reversing the deposition sequence, highlighting the importance of buffer layer adjustment. Some of the studied carbazolocarbazoles proved to be a suitable molecule to be used as hole transporting materials.

1. Introduction

The intensive research on the understanding and the optimisation of the performance of organic solar cells has rendered excellent results [1–9] which have made organic photovoltaics into a potential alternative within the area of solar energy. Nevertheless, the critical aspect limiting a faster progress in organic solar cells is due to the inherent difficulty of the charge carrier generation and transport in conjugated organic materials [10,11]. This topic becomes even more relevant when considering the typical multi-layer architecture where several materials are combined for the fabrication of an organic solar cell. The multilayer design covers from the simple two component device, with either a flat or a bulk heterojunction [12,13], going through the incorporation of anode and cathode buffer layers [14], to eventually arrive at the more sophisticated tandem solar cells [15]. Going back to the problem of charge transport, the stacked structure of organic photovoltaic devices involves not only the charge transport within a certain material, but even more challenging, the charge transfer at the interface between different materials, namely electrode/organic [16–18], inorganic/organic [19,20] or organic/organic heterojunctions [21,22]. In this regard, the incorporation of interfacial hole and electron transporting layers has been proven to enhance organic solar cell operation owing to several reasons such as smoothing the electrode surface, protecting the active layer from the electrode, favouring the energy gradient for charge transport, blocking excitons and wrongly directed charge carriers, or acting as optical spacers [23–26].

The important role of these interfacial layers has led us to explore the use of recently described carbazolocarbazoles **1** and **2** (Fig. 1) [27–29], as hole transporting materials (HTM) in small molecule organic solar cells. The electronic structure of carbazolocarbazoles, with appropriate HOMO and LUMO energies (Fig. 2) and transparency to the visible radiation, makes them good candidates to be used as organic buffer layers. Besides, the two different *N*-substituents on the

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carbazolocarbazole system will further enable the study of the correlation between the structure of the molecule and its adequacy to operate as HTM. Additionally, we also examined the effect of the solar cell architecture on the *J–V* characteristics by preparing devices with inverted and conventional structure.

2. Materials and methods

Device fabrication was carried out in custom-made high-vacuum chambers at a base pressure of 10^{-6} to 10^{-7} mbar. The organic materials and the metal electrodes were thermally evaporated through different shadow masks which were exchanged without breaking the vacuum. Indium-tin oxide (ITO) coated glass with a sheet resistance of 30 Ω/sq. was used as transparent substrate. These substrates were cleaned by washing with acetone, ethanol, and then treating with oxygen plasma.

Both the inverted and the conventional solar cells were made by evaporating the following materials: carbazolocarbazoles **1** and **2** were used as hole transporting materials and were doped with 20 wt%. NDP9 (p-dopant produced by Novaled GmbH) [30] using a coevaporation protocol; indenoperylene derivative **3** was used as donor material and fullerene was used as acceptor material to build up a flat heterojunction active layer; in the solar cells with conventional architecture 4,7-diphenyl-1,10-phenanthroline (BPhen) **5** was used as cathode buffer; the devices were completed by thermally evaporating aluminium as top electrode.

The solar cells were protected by an encapsulating glass glued and UV-cured under inert atmosphere. The overlapping region between the ITO and the top electrode defined a device active area of 6.4 mm^2.

Current–voltage (*J–V*) characteristics were scanned using a source measurement unit (Keithley) and a sun simulator (SC 1200, KHS Technical Lighting, Germany) to reproduce the standard terrestrial solar spectra at AM 1.5G. Measurements were monitored by a Hamamatsu S1337 silicon photodiode (calibrated by Fraunhofer ISE) used as reference for the intensity values. The reported efficiency values are corrected for spectral mismatch.

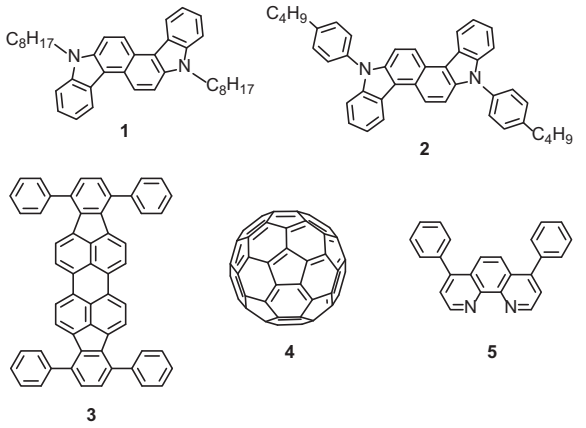

Fig. 1. Chemical structure of the used molecules.

3. Results and discussion

Due to the benefits of molecular doping for the charge carrier transport in organic semiconductors [31,32], preliminary lateral conductivity experiments were carried out by coevaporating the studied carbazolocarbazoles with NDP9. The gradual increase of the p-dopant/HTM ratio led to a noticeable improvement in the conductivity of the evaporated thin film as a result of the increased charge carrier concentration induced by the electron transfer process between the carbazolocarbazole and the p-dopant. Conductivity values of $2{\cdot}10^{-6}$ S/cm for carbazolocarbazole **1** and $1{\cdot}10^{-8}$ S/cm for compound **2** were measured for a dopant concentration of 10% w/w. According to the very similar HOMO energies of these two materials, the difference in the observed conductivities should be related to the structure of the organic molecule. The different solid state packing of compounds **1** and **2** has been demonstrated to influence their charge mobility [27]. Additionally, it is likely that the 4-butylphenyl substituents in compound **2** cause steric hindrance which also makes more difficult the intermolecular close contact with the dopant and consequently affects the doping process.

Once it had been proven that carbazolocarbazoles could be doped with conductivities suitable to be used as hole transporting materials, they were integrated into the multilayer structure of small molecule solar cells. The flat heterojunction device with an inverted architecture (Fig. 2)

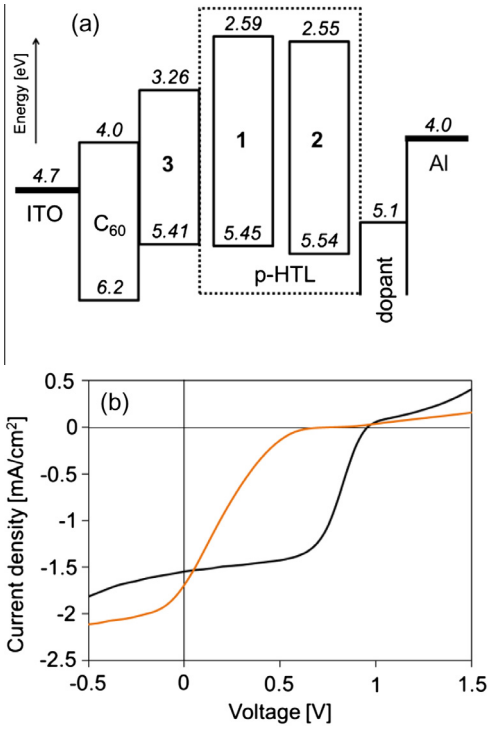

Fig. 2. (a) Sketch of the organic solar cell with inverted architecture and (b) *J–V* characteristics under illumination, 1.5 AM, 100 mW/cm^2. (black: p-HTM **1**; orange: p-HTM **2**). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)