Simple donor-acceptor molecule with long exciton diffusion length for organic photovoltaics

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ABSTRACT

To succeed in commercial applications, donor materials for organic solar cells should combine high stability and simple synthesis with high performance in devices. Here, we present a new small π-conjugated molecule, TPA-T-DCV-Ph, which meets those requirements. Simple and efficient three-step synthesis produces a push-pull molecule with triphenylamine donor and phenyldicyanovinyl acceptor groups, which is suitable for both solution processing and vacuum deposition. The unique property of TPA-T-DCV-Ph is an unusually long exciton diffusion length of > 25 nm due to the combined effect of long exciton lifetime and surprisingly low energy disorder. This, together with a device engineering, resulted in > 5% efficiency for TPA-T-DCV-Ph:C_{70} vacuum-processed solar cells. The results obtained are envisioned to be further improved by optimizing the absorption of the molecule and light management in the device which can push the efficiency even further.

1. Introduction

Organic solar cells (OSCs) based on push-pull small molecules (SMs) complement advantages of polymer-based OSCs and well-established benefits of small molecules like excellent batch-to-batch reproducibility and vacuum processability [1–9]. The efficiency of SM-based OSCs keeps on increasing over the years, with record values over 10% in single-junction [10,11] and over 13% in multi-junction vacuum-deposited [12] devices. Achieving the highest efficiencies often requires complicated multistep synthesis [10,11] in combination with laborious device optimization [3,5,13–15] which essentially limits the boundaries for large-scale production of SM-based OSCs [16,17].

Simple synthetic procedure is one of the key requirements for the organic materials to become successful in industrial mass production [16,17]. However, SMs which show the best performance in OSCs are typically hard to synthesize (8–14 synthetic steps), which lowers the overall yield to 3–15% [11,16–19]. The approach to simplifying the synthetic process was thoroughly explored by Roncali and coworkers [9,16,20–28] who designed a number of easy-to-synthetize SMs based on triphenylamine (TPA) as donor and dicyanovinyl (DCV) as acceptor blocks. Unfortunately, the efficiencies of OSCs based on easy-to-synthesize molecules typically are in the range of 3–4%, even after rigorous optimization [9,21–23].

Next to simplifying the synthetic procedure, the major challenge lies in the optimization of the active layer [29,30]. To maximize the quantum efficiency, one needs to match the exciton diffusion length in the active materials with the characteristic spatial scale of donor-acceptor separation [31–34]. In typical organic materials, the exciton diffusion length does not exceed 10 nm [35–37] which enforces application of the bulk heterojunction (BHJ) concept [38]. The laborious optimization of the BHJ morphology aims at achieving a multi-parameter compromise between the short exciton diffusion length, non-geminate recombination of charges and charge transport to the electrodes [39–44]. Had the exciton diffusion length been significantly larger, the very design of the OSCs would have been substantially simpler.

In this paper, we report a new molecule, TPA-T-DCV-Ph, that combines simple and efficient synthesis with long exciton diffusion length. Due to its push-pull nature, TPA-T-DCV-Ph exhibits strong absorption in the blue to red region, while a simple chemical structure and low molecular weight make it suitable for vacuum deposition. TPA-T-DCV-Ph demonstrates extremely long exciton diffusion length exceeding 25 nm in vacuum-deposited films, which is highly beneficial for simplified device optimization. Vacuum-deposited TPA-T-DCV-Ph:C_{70} 1:1 OSCs demonstrate up to 5.1% efficiency. All these suggest high potential of TPA-T-DCV-Ph for easy-to-make mass-scale manufactured OSCs.

2. Experimental

2.1. Materials and synthesis

[1,1′-*Bis*(diphenylphosphino)ferrocene]dichloropalladium(II) Pd (dppf)Cl_2, (4-bromophenyl)diphenylamine, 2-bromothiophene, *n*-butyllithium (2.5 M solution in hexane), magnesium, benzoyl chloride, malononitrile were obtained from Sigma-Aldrich Co. and used without any further purification. Pyridine, THF, dichloromethane and hexane were dried, purified according to the known techniques and then used as the solvents. All reactions, unless stated otherwise, were carried out under an inert atmosphere. Details of the synthesis and characterization are available in Supplementary Information (SI).

2.2. Sample preparation

Prior to deposition the substrates were cleaned with 1:10 RBS 25 concentrate (Chemical products R. Borghgraef S.A.): Di-ionized (DI) water, then rinsed with tap water and DI water and dried with N_2. 10 min exposure to O_2 plasma using a Plasma Cleaner (Harrick Plasma) helps to improve the adhesion of the first barrier layer on the anodic substrate. The layers composing the photovoltaic stack were deposited by thermal sublimation (see below for technical specifications).

The photovoltaic devices consisted of a ITO/glass substrate on which a 25 nm-thick MoO_3 barrier layer, a 100 nm-thick 1:1 (wt%) TPA-T-DCV-Ph:C_{70} photoactive layer, 10 nm of BCP (bathocuproine as exciton-blocking layer) and a 100 nm-thick Al cathode were successively deposited. When necessary, a post-fabrication annealing treatment of the devices was performed in a N_2-filled glovebox (O_2 and H_2O within few ppm) on a Stuart SD 300 (600 W) hot plate. The ITO patterned glass substrate was purchased from Naranjo BV (thickness: ~100 nm, $R_\square$ ~15 $\Omega_\square$). The materials (oxides, organic compounds, metals) were deposited by thermal sublimation in high vacuum ($< 5 \cdot 10^{-6}$ mBar) within a K.J. Lesker Spectros evaporating chamber. Al, MoO_3 and BCP were purchased from Sigma Aldrich and C_{70} from Lumtec (> 99% grade). No additional purification was carried out. For each sample, three devices were obtained with a 0.18, 0.20 and 0.45 cm^2 photoactive area, respectively; no apparent influence of the device area on the device performance was observed.

The stack architecture for the determination of the carrier mobility consisted of a 10 nm-thick layer of MoO_3 deposited on ITO, onto which a 150 nm-thick layer of TPA-T-DCV-Ph was deposited, then covered with a 10 nm-thick Yb layer to improve the charge collection [45,46] and 100 nm-thick Al cathode. Likewise, all layers were thermally

sublimated.

The stacks for PL measurements consist of a glass substrate on which layers of TPA-T-DCV (thickness: 6, 12, 24, 48 and 96 nm) are sandwiched between two 10 nm layers of C_{60}. The stacks were also thermally sublimated.

2.3. Optical

Absorption spectra were recorded with a Perkin Elmer Lambda-35 (ODCB solution) or Lambda-900 (films) spectrometers. Time-resolved PL was measured with a Hamamatsu C5680 streak-camera. The excitation (550 nm) was generated in a Newport SHG-800 hollow fiber pumped by a Mira Ti:sapphire laser.

2.4. Efficiency and mobility measurements

The photovoltaic performances of the devices were determined in the glovebox from *J-V* profiles obtained with a Keithley 2400 source meter. The devices were exposed to AM 1.5 irradiation provided by a Sun 2000 solar simulator (ABET Tech.). 1 sun (100 mW cm^{-2}) irradiation was calibrated using a reference Si solar cell (Rera System).

The carrier mobility was also determined from *J-V* profiles. At high forward bias, space charge-limited current is shown to govern charge transport in the active layer. Quadratic variation of the current with the applied bias is observed and the analytical expression of the Mott-Gurney law (See SI) in the infinite plate approximation can be used to determine the carrier mobility in the material [47].

2.5. External quantum efficiency measurements

External quantum efficiency was measured under short-circuit conditions; the device area of 0.245 cm^{-2} was selected by a shadow mask. The monochromatic light was produced by selecting 10 nm portions of white light (produced by an Osram 64655 HLX halogen lamp) at the given wavelengths by a set of band pass filters. The measurements were calibrated using a Si photodiode.

3. Results and discussion

Fig. 1 shows the synthetic route towards TPA-T-DCV-Ph (see SI for the detailed synthetic procedures). Synthesis of TPA-T-DCV-Ph consists of three steps (Fig. 1): First, diphenyl[4-(2-thienyl)phenyl]amine (**1**) was prepared in 77% isolated yield from commercial available (4-bromophenyl)diphenylamine and 5-bromothiophene via Kumada cross-coupling using freshly prepared Grignard reagent of the latter. Second, {5-[4-(diphenylamino)phenyl]-2-thienyl}(phenyl) (**2**) was prepared by reaction of the lithium derivative of **1** and benzoyl chloride in 70% isolated yield. Finally, TPA-T-DCV-Ph, was obtained in an 81% isolated yield by Knövenagel condensation between ketone (**2**) and malononitrile in pyridine using a microwave heating.

Simplicity and the high overall yield (44%) make the synthesis of TPA-T-DCV-Ph one of the most efficient among the known push-pull molecules developed for organic photovoltaics. The compound demonstrates good solubility in tetrahydrofuran, chloroform, and 1,2-dichlorobenzene (ODCB); the measured solubility of TPA-T-DCV-Ph in ODCB was found to be 25 g/L. The molecule demonstrates high thermal
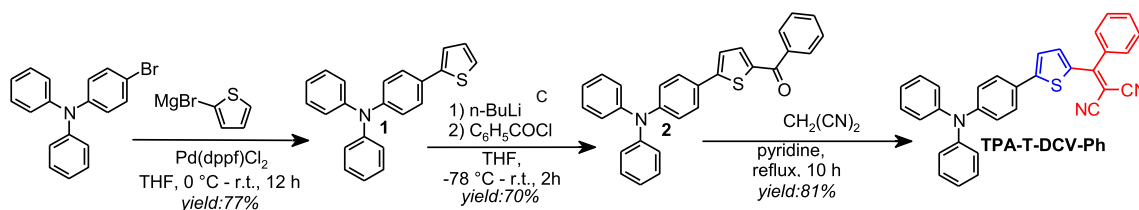

Fig. 1. Synthesis of TPA-T-DCV-Ph.