Structural and electronic properties of 2,2′,6,6′-tetrphenyl-dipyranylidene and its use as a hole-collecting interfacial layer in organic solar cells

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ABSTRACT

The accumulation of positive charges at the anodic interface considerably limits the efficiency of photovoltaic solar cells based on polymer/fullerene bulk heterojunctions (BHJs). Interfacial layers (IFLs) such as PEDOT:PSS improve charge injection but have no effect on the unbalanced electron/hole transport across the BHJ. We report here the use of 2,2′,6,6′-tetrphenyl-dipyranylidene (DIPO-Ph4), a planar quinoïd compound, as an efficient anodic IFL in organic solar cells based on BHJs made of poly(3-hexylthiophene)/[6,6]-phenyl-C61-butyric-acid-methyl-ester (P3HT:PCBM). When deposited under vacuum onto a glass substrate, DIPO-Ph4 thin films are constituted of densely packed and vertically aligned crystalline needles. Current-sensing atomic force microscopy (CS-AFM) reveals a considerable increase of the hole-carrying pathways in DIPO-Ph4 thin films as compare to PEDOT:PSS, thus revealing their hole transporting/electron blocking properties. Inserting a 10 nm thick IFL of DIPO-Ph4 in combination with a 5 nm thick PEDOT:PSS between the ITO electrode and the P3HT:PCBM film leads to photocurrent densities up to 11.5 mA/cm² under AM 1.5G and conversion efficiencies up to 4.6%, that is substantially higher than PEDOT:PSS-only devices.

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1. Introduction

A strategy to improve the performance of organic solar cells (OSCs) consists of tailoring the interfaces between the organic active materials and the metallic electrodes. To this end interfacial layers (IFLs) are inserted between the active layer and the respective electrodes in order to reduce the energy barriers which promote charge carrier diffusion [1–8]. IFLs operate as selective charge extraction materials for either holes or electrons, while blocking the opposite charge carriers. Conducting polymer-based IFLs are commonly used to modify the ITO surface because they ensure an electrical ohmic contact and minimize the roughness. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is the ubiquitous hole transporting layer that is used in OSCs [9]. A thin PEDOT:PSS IFL increases the open-circuit voltage (Voc) and improves hole collection at the anodic interface between ITO and the photoactive material.

However, it is well-known that PEDOT:PSS suffers from several drawbacks. Its acidic character (pH = 1–2) etches the ITO electrode and considerably shortens the long-term stability of the devices. Furthermore, PEDOT:PSS films are hygroscopic and exhibit weak electron blocking properties [10–12]. Another drawback is the weak visible light absorption of PEDOT:PSS that does not contribute to light harvesting in the devices [13]. Finally, PEDOT:PSS thin films often possess important structural and electrical inhomogeneities that are not compatible with reproducible device performances.

Therefore, alternative IFL materials have been investigated to substitute PEDOT:PSS in OSCs and other organic devices. Various organic materials have been explored as IFLs with the aim to improve charge collection, such as for example self-assembled monolayers of 4-nitrophenylthiolate [14] or halogenated propylsilanes [15], and graphene oxide [16–18]. In a previous work, we reported that 2,2′,6,6′-tetraphenyldithiapryllylidene (DITPY-Ph4)
acts as a hole collecting IFL when introduced in OSCs based on P3HT:PCBM [19]. Inorganic materials have also been studied as hole collecting IFLs, in particular transition metal oxides such as MoO3 [20-22], NiOx [23,24], VOx [25], copper based solutions [26,27] or polyoxometalate [28]. Note that these IFLs can be used either as single layers or in combination with a PEDOT:PSS layer.

In this work, we describe the structural and electronic properties of 2,2',6,6'-tetraphenyl-dipyranylidene (DIPO-Ph4, Fig. 1) and report on its use as an efficient hole-transporting IFL in organic solar cells based on bulk heterojunctions BHJs made of poly(3-hexylthiophene) and [6,6]-phenyl-C61-butyric-acid-methyl-ester (P3HT:PCBM). DIPO-Ph4 is a large planar quinoid compound made of two pyranylidene heterocycles linked together by an exocyclic C=C double bond in 4-40 positions relative to the two O-atoms. DIPO-Ph4 is isoelectronic with tetrathiafulvalene and behaves as a strong \( \pi \)-donor with various acceptors [29]. We reveal here the remarkable needle-like morphology of vacuum-deposited crystalline DIPO-Ph4 thin films and show that it behaves as a more efficient anodic IFL in solar cells as compared to its sulfur analog DITPY-Ph4.

2. Experimental section

2.1. Synthesis and purification of DIPO-Ph4

The synthesis of DIPO-Ph4 has been reported previously [30]. However, we modified the synthetic protocol in order to substantially increase the yield and to improve the purity of the final compound (Scheme 1). Briefly, glutaryl chloride is functionalized by two phenyl groups using a Friedel-Craft acylation, and further oxidized by BF4·Et2O into a pyrylium salt. The latter compound is then reduced by tributylphosphine \( \text{P(C}_4\text{H}_9)_3 \) instead of zinc which is difficult to remove from the final product. The intermediate ylide is finally condensed in basic medium using EtN(i-Pr)2 (DIPEA) to form 2-2'-6-6'-tetraphenylidipyranylidene (DIPO-Ph4) in 85% yield. The raw product is a brownish powder that is purified by Soxhlet extraction in acetonitrile during several days. The final compound is a highly crystalline deep red powder (mp = 325 °C) with shiny metallic reflections (Fig. 1).

2.2. OPV device fabrication

ITO-coated glass substrates (Sigma-Aldrich; 2.5 × 2.5 cm²; \( R = 70–100 \Omega /\text{cm}^2 \)) are patterned by chemical etching with HCl (5% aq.) and sonicated in successively ethanol and acetone during 10 min. The samples are finally exposed to UV-ozone during 10 min in order to remove organic impurities and improve the hydrophobicity of the substrates. The crystalline DIPO-Ph4 is finely divided in a mortar and placed in a quartz boat. DIPO-Ph4 is evaporated at a slow rate (0.1 Å/s) in a thermal vacuum chamber (\( P_0 \approx 10^{-4} \text{ Pa} \)) and the thickness is monitored by a quartz microbalance (Inficon X TM/2). A 5 nm layer of PEDOT:PSS (Sigma-Aldrich; water solution 1.3% in weight) is spin-coated on top of DIPO-Ph4 thin film. P3HT/PCBM bulk layer is prepared by spin-coating from a solution of P3HT (Sigma-Aldrich; purity >98.5%) and PCBM (Sigma-Aldrich; purity 99.5%) dissolved in dichlorobenzene (ratio of \( 1:0.8 \text{ P3HT-PCBM} \)) and sonicated beforehand during 10 min to obtain a homogenous blend solution. The spin-coating conditions are adjusted to obtain...
120 nm P3HT/PCBM thick films. The organic films undergo post-annealing at 110 °C under argon during 10 min. The devices are completed by successive thermal evaporation of LiF (7 Å) and Al (100 nm) through shadows mask with a diameter of 7 mm². The reference cells were prepared by deposition of 20 nm film of PEDOT:PSS on ITO followed by an annealing at 120 °C under argon for 30 min. Successive layers are deposited under the same conditions.

3. Results and discussion

The UV–visible absorption spectrum of DIPO-Ph₄ as recorded in dichloromethane (Fig. 2) shows a structured absorption peak in the visible range (λ_max = 456 nm) with a high molar extinction coefficient 9 × 10⁴ l/mol.cm. An absorption tail of weak intensity is observed from 500 to 600 nm. Vacuum-deposited DIPO-Ph₄ thin films exhibit a much broader absorption over almost the entire visible range, with an absorption edge at 640 nm and several structures assigned to absorption bands. Photoluminescence spectra in solution shows a sharp peak at 606 nm. Whereas DIPO-Ph₄ thin film presents two peaks at the 636 nm and 686 nm. The bandgap of DIPO-Ph₄ (Eg = 1.9 eV) is determined from the absorption spectrum. X-ray diffraction performed on DIPO-Ph₄ single crystals grown from solution reveals a parallel arrangement between neighbouring planar molecules with an intermolecular distance of 3.49 Å [31]. Such a crystal structure is compatible with a π–stacking as well as a widening of the optical absorption spectrum over the entire visible range as compared with that in solution (Fig. 2b).

Cyclic voltammetry (Fig. S1) shows two reversible oxidation
waves at respectively 0.24 V and 0.5 V, corresponding to the successive formation of the radical cation and dication. The HOMO energy level is estimated at \(-4.7 \text{ eV}\) from the first oxidation peak at 0.24 V. \(\text{DIPO-Ph}_4\) has a slightly lower oxidation potential \(E_{\text{ox}} = 0.24 \text{ eV}\) as compared to that of its sulfur analog \(\text{DITPY-Ph}_4\) \(E_{\text{ox}} = 0.30 \text{ eV}\). Therefore the highest occupied molecular orbital (HOMO) of \(\text{DIPO-Ph}_4\) intercalates adequately between ITO and P3HT \(E_{\text{HOMO}} = -5.0 \text{ eV}\) to allow hole transfer from the active layer.

\(\text{DIPO-Ph}_4\) thin films are prepared by slow vacuum-deposition \((0.1 \text{ Å/s})\) onto glass/ITO substrates. Atomic force microscopy (AFM) reveals a highly homogenous surface made of monodisperse grains having an elongated needle shape (Fig. 3). A distribution of the number of grains as a function of their height shows an average height in the range 20–40 nm while the highest needles observed are 70 nm high. The root mean square (RMS) roughness is measured at 13 nm which is much higher than PEDOT:PSS film \((\text{RMS} = 0.9 \text{ nm})\). This particular nanomorphology of \(\text{DIPO-Ph}_4\) considerably increases the contact area between the active material and the anode, thus greatly enhancing hole extraction. However, in order to protect the nanostructure from partial dissolution by the organic solvent during spin-coating deposition of the P3HT:PCBM active layer, a 5 nm thin layer of PEDOT:PSS is spin-coated (from an aqueous solution) on top of the \(\text{DIPO-Ph}_4\) films. AFM images (Fig. S2) confirm that the \(\text{DIPO-Ph}_4\) morphology is preserved \((\text{RMS} = 11.3 \text{ nm})\). A practical advantage of PEDOT:PSS film is its robustness towards organic solvents during fabrication process, making it compatible with most of organic photoactive materials.

Current-sensing atomic force microscopy (CS-AFM) images of \(\text{DIPO-Ph}_4\) films are recorded in contact mode using either positive or negative tip voltages (Fig. 4). For a \(-0.3 \text{ V}\) tip voltage the CS-AFM images exhibit high and homogeneous hole conduction with current intensities up to 10 nA. The hole conduction have preferential pathways through the grain boundaries. In comparison, CS-AFM images recorded on PEDOT:PSS films reveal insulating region and the holes are only diffused in some localized pathways which correspond to individual PEDOT domain (Fig. S3). Current mapping recorded at \(+0.3 \text{ V}\) shows a much weaker conduction of electrons as compare to holes.

We inserted a vacuum-deposited \(\text{DIPO-Ph}_4\) film \((10 \text{ nm})\) as an anodic IFL in combination with a PEDOT:PSS layer \((5 \text{ nm})\) into P3HT:PCBM-based OSC devices (Fig. 5) and compared the PV performance with those of reference cells using a PEDOT:PSS-only IFL.

![Fig. 5.](image-url) Scheme of a solar cell using a double IFL: \(\text{DIPO-Ph}_4\) \((10 \text{ nm, red needles})\) and PEDOT:PSS \((5 \text{ nm, dark grey coating})\). Right) Band diagram of a solar cell using a \(\text{DIPO-Ph}_4\) \((10 \text{ nm})/\text{PEDOT:PSS} (5 \text{ nm})\) double IFL.

![Fig. 6.](image-url) (a) J-V curves measured in the dark and under white light illumination (AM 1.5G; 70 mW/cm²) of two P3HT:PCBM-based solar cells using \(\text{DIPO-Ph}_4\) \((10 \text{ nm; red and cyan lines})/\text{PEDOT:PSS} (5 \text{ nm})\) or \(\text{DIPO-Ph}_4\) \((15 \text{ nm; green line})/\text{PEDOT:PSS} (5 \text{ nm})\) as a double hole injecting IFL. A typical reference cell using a PEDOT:PSS-only IFL is shown for comparison (blue line). b) EQE spectrum (red) of a PV cell using a \(\text{DIPO-Ph}_4\) \((10 \text{ nm})\) PEDOT:PSS \((5 \text{ nm})\) double IFL. The dashed blue line represents the integrated current density corresponding to the red J-V curve of Fig. 6a. The PV characteristics of our devices are summarized in Table 1.

![Fig. 7.](image-url)
All devices have an open circuit voltage (Voc) of ≈0.6 V in agreement with usual values reported for P3HT:PCBM-based devices. The short-circuit current density of the reference cells is Jsc = 7.6 mA cm⁻², resulting in a power conversion efficiency (PCE) of 2.8% (Fig. 6, blue curve). With a 10 nm thick layer of DIPO-Ph₄, the organic solar cell exhibit higher current density. Typical devices exhibit an average current density of Jsc = 9.5 mA cm⁻² and an average PCE of 3.8% (Fig. 6, red curve). These characteristics correspond to a PCE increase of 35% as compare to the reference cell using a PEDOT:PSS-only IFL. In the course of our experiments several double-IFL devices exhibit higher current densities up to Jsc = 11.5 mA cm⁻² with a PCE of 4.6% (Fig. 6, light blue curve) corresponding to a 64% increase as compare to OSCs using a PEDOT:PSS-only IFL.

We assign the enhanced Jsc to the high hole conduction of the DIPO-Ph₄ films, as revealed by CS-AFM (Fig. 4). However, these higher characteristics are sample-dependent due to the difficulty in controlling rigorously the nanomorphology of the DIPO-Ph₄ films, in particular the precise height, shape and density of the crystalline needles. These parameters are extremely sensitive to slight variations in the deposition rate, quality of the substrate and purity of the starting materials. Indeed, devices using higher DIPO-Ph₄ thicknesses (15 nm) show lower Voc (Fig. 6, green curve) and thus a decrease in efficiency (PCE = 2.5%).

4. Conclusions

In summary, highly crystalline thin films of 2,2',6,6'-tetrakis(3-nitropyridyl-2-yl)anthracene (DIPO-Ph₄) have been prepared by vacuum-deposition and used as hole injecting interfacial layers in organic solar cells. The DIPO-Ph₄ thin films are made of vertically-aligned nano-needles. Current-sensing atomic force microscopy (CS-AFM) reveals a considerable increase of the hole-carrying pathways in DIPO-Ph₄ thin films as compare to PEDOT:PSS, thus revealing their hole transporting/electron blocking properties. Inserting a 10 nm thick IFL of DIPO-Ph₄ in combination with a 5 nm thick PEDOT:PSS between the ITO electrode and the P3HT:PCBM film leads to photocurrent densities up to 11.5 mA/cm² under AM1.5G and conversion efficiencies up to 4.6%, that is substantially higher than PEDOT:PSS-only devices. We are currently extending this work by using DIPO-Ph₄ as a HTM in various types of devices, including perovskite solar cells and field-effect transistors [32]. We also engineer the band alignment of DIPO-Ph₄ by chemical design and synthesize a series of dipyranylidene analogs bearing electron-donating or electron-accepting peripheral substituents around the quinoid core.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2017.03.002.


