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

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A B S T R A C T

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′-tetraphenyl-dipyranylidene (DIPO-Ph_4), 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-Ph_4 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-Ph_4 thin films as compare to PEDOT:PSS, thus revealing their hole transporting/electron blocking properties. Inserting a 10 nm thick IFL of DIPO-Ph_4 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/cm^2 under AM 1.5G and conversion efficiencies up to 4.6%, that is substantially higher than PEDOT:PSS-only devices.

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 propysilanes [15], and graphene oxide [16–18]. In a previous work, we reported that 2,2′,6,6′-tetraphenyldithiapyranylidene (DITPY-Ph_4)

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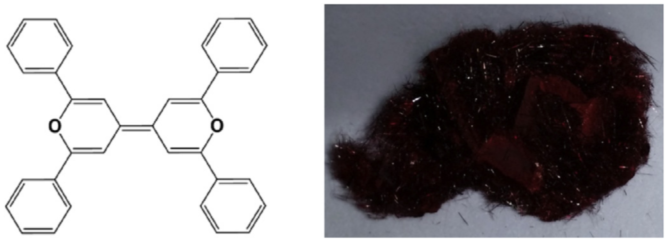
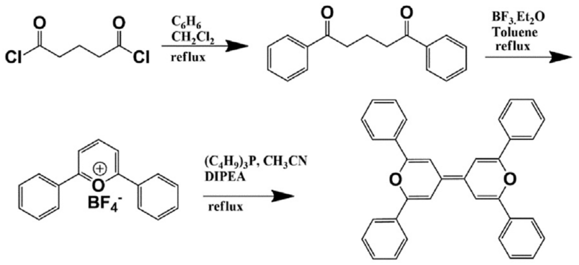


Fig. 1. Left: Chemical structure of 2,2′,6,6′-tetraphenyldipyranylidene (DIPO-Ph_4). Right: Deep-red shiny crystalline powder of DIPO-Ph_4 after purification by Soxhlet extraction in acetonitrile.



Scheme 1. Synthetic pathway to 2,2′,6,6′-tetraphenyldipyranylidene (DIPO-Ph_4).

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-Ph_4, 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-Ph_4 is a large planar quinoïd compound made of two pyranylidene heterocycles linked together by an exocyclic C=C double bond in 4-4′positions relative to the two O-atoms. DIPO-Ph_4 is isoelectronic with tetrathiafulvalene and behaves as a strong π-donor with various acceptors [29]. We reveal here the remarkable needle-like morphology of vacuum-deposited crystalline DIPO-Ph_4 thin films and show that it behaves as a more efficient anodic IFL in solar cells as compared to its sulfur analog DITPY-Ph_4.

2. Experimental section

2.1. Synthesis and purification of DIPO-Ph_4

The synthesis of DIPO-Ph_4 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 $BF_4.Et_2O$ into a pyrylium salt. The latter compound is then reduced by tributylphosphine $P(C_4H_9)_3$ instead of zinc which is difficult to remove from the final product. The intermediate ylide is finally condensed in basic medium using $EtN(i\text{-}Pr)_2$ (DIPEA) to form 2-2′-6-6′-tetraphenyldipyranylidene (DIPO-Ph_4) 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 cm^2; R = 70–100 Ω/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 hydrophilicity of the substrates. The crystalline DIPO-Ph_4 is finely divided in a mortar and placed in a quartz boat. DIPO-Ph_4 is evaporated at a slow rate (0.1 Å/s) in a thermal vacuum chamber (P_0~10^{-4} 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-Ph_4 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 P3HT-PCBM) and sonicated beforehand during 10 min to obtain a homogenous blend solution. The spin-coating conditions are adjusted to obtain

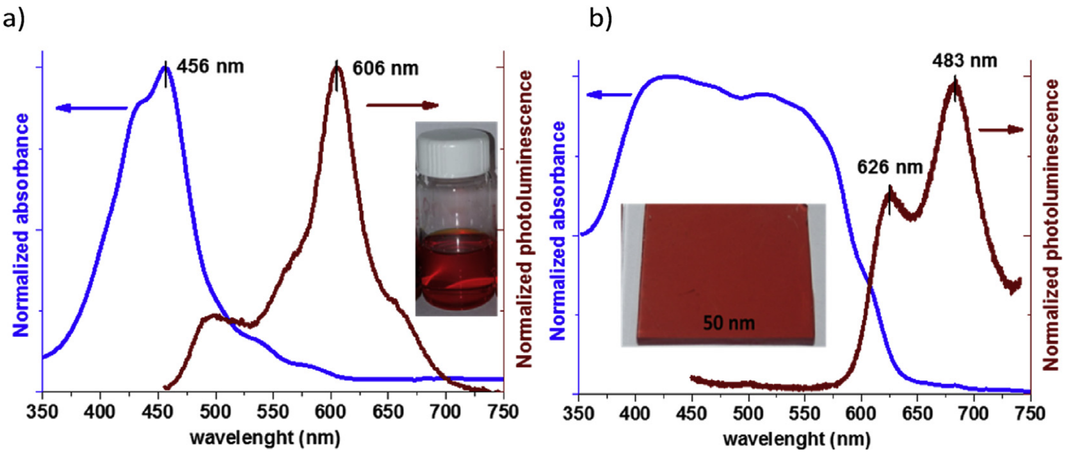


Fig. 2. a) Optical absorption (blue) and photoluminescence (red) spectra of DIPO-Ph_4 a) in solution in dichloromethane and b) as a 50 nm thin film vacuum-deposited on quartz. Inserts: photographs of the respective DIPO-Ph_4 solution and thin film.