



Enhancing the efficiency of solution-processable bulk-heterojunction devices *via* a three-dimensional molecular architecture comprising triphenylamine and cyanopyridone



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ABSTRACT

Through the employment of a three-dimensional molecular geometry, a novel, solution-processable small molecular organic chromophore was designed, synthesized and characterized for application in bulk-heterojunction solar cells. The new chromophore, [(5Z,5'Z,5''Z)-5,5',5''-(((nitro)tris(benzene-4,1-diyl))tris(thiophene-5,2-diyl))tris(methanylylidene))tris(1-(2-ethylhexyl)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile)] (coded as **3D**), was based on a donor-acceptor (D-A) module where a simple triphenylamine unit served as an electron donor, cyanopyridone as an electron acceptor, and a thiophene unit as π -bridge embedded between the donor and acceptor functionalities. The optoelectronic and photovoltaic properties of **3D** were directly compared with those of a structural analogue, [(Z)-5-((5-(4-(diphenylamino)phenyl)thiophen-2-yl)methylene)-1-(2-ethylhexyl)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile)], namely **1D**. The three-dimensional (otherwise termed as non-linear) design, compared to one-dimensional (or linear) design, demonstrated (1) an enhancement of light-harvesting ability by about 50%; (2) an increase in wavelength of the longest wavelength absorption maximum of thin film (633 nm vs. 581 nm) and (3) a narrower optical band-gap (1.53 eV vs. 1.65 eV). Solution-processable bulk-heterojunction devices were fabricated with **3D** and **1D** as donor materials. Studies on the photovoltaic and hole charge mobility properties revealed that the best **3D**-[6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM)-based device showed an impressive enhanced power conversion efficiency of 4.76%, an increase of greater than two-fold with respect to the efficiency of the best **1D**-based device (2.11%), and a higher hole mobility of the order of $3.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Not only is **3D** the first reported example in the literature where cyanopyridone acceptor functionality has been used to generate a three-dimensional donor molecule but the power conversion efficiency reported here is the highest value reported so far for non-linear, star-shaped molecular architectures. These results clearly illustrated that the use of a three-dimensional geometry helped to extend molecular conjugation, thus enhancing the light-harvesting ability and short-circuit current density, while further improving the bulk-heterojunction device performance.

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1. Introduction

Organic solar cells have seen much interest in recent times, mainly due to the recognition that they have a significant potential to be a cheaper alternative to their more traditional inorganic counterparts [1–5]. One particular type of organic solar cell, namely bulk-heterojunction (BHJ), uses a dispersed blend of an

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electron donor and electron acceptor to create the traditional p-n junction, and this design can have advantages over other types of devices such as tandem solar cells. These BHJ devices offer flexibility, low-cost and remote installation to name a few [6–8]. Moreover, unlike other type of photochemical devices, such as dye-sensitized solar cells [9], they don't use any electrolyte system, meaning that they do not suffer from leakage, nor do they dry out over time. However, standalone BHJ devices still lack the efficiencies of dye-sensitized and tandem solar cells. One way to tackle this problem is to find newer and more effective electron donors and acceptors which can be used within the BHJ architecture.

Over the past few years, intensive research efforts in (1) the design and synthesis of new polymeric and small molecular donors, (2) control of active layer morphology and interfacial layers, and (3) exploration of a variety of device architectures have been carried out to achieve an impressive progress in the power conversion efficiency (PCE). For polymeric donors, the PCE has surpassed 10% mark [10–14]. Despite the fact that high PCE numbers are obtained with the use of polymeric entities, there are few main disadvantages in the use of conjugated polymers, such as purity, variations in their molecular weights and purification strategies. To overcome such issues, small molecular electron donors have been developed due to their precisely known structure, defined molecular weight, high purity and good batch to batch reproducibility [15–19]. Solution-processable BHJ devices have shown a competitive outcome too, and the PCE numbers are almost identical when compared to their polymeric counterparts [20]. This outcome is encouraging and provides a strong motivation to continue research on the design and development of small molecular donors for solution-processable BHJ devices.

In their simplest forms, small molecules for use in photovoltaic properties consist of various fragments known as donors (D) – usually these groups are aromatic and with the presence of few electron donating heteroatoms; acceptors (A) – that consist of electron withdrawing groups (for instance nitriles); and a conjugated functionality known as π -spacer which typically separates these D and A groups. Depending on the arrangement of these areas a target chromophore can be labelled, for example, as a D–A, A–D–A, D–A–D and so on. Even though the success of small molecular donors is noteworthy [21–24], incentives remain to develop materials which will not only have better properties than the literature reported, but will also have important characteristics such as solubility, and matching energy levels with the standard soluble fullerene acceptors, [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and its C₇₁ analogue (PC₇₁BM).

One area that is of particular interest is the use of a non-linear design concept, meaning a move towards starburst-type structures as opposed to the traditional linear design. Compounds that use this non-linear design concept, typically called star-shaped molecules, offer insight into a strong relationship between structure and its performance, and although there are several mentions of this design in the literature, they have been somewhat overlooked by the wider research community considering the gains that can be achieved with relatively small efforts. These compounds use a simple core moiety, such as triphenylamine (TPA) or tetraphenylethylene, with electron withdrawing sub-units attached to their ends [21,25,26]. Research into the structure of such compounds using TPA as a central core have shown that this star-shaped design causes an increase in intra-molecular charge transfer (ICT) transition as well as increase to the open circuit voltage [27]. Reports in the literature further suggest that increasing the number of terminal acceptor units enhanced absorption, ICT, hole-mobility and exerted better alignment of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, thus increasing the overall PCE when compared with the

linear counterpart [28]. With such criteria in mind and learnings from the work reported by J. Roncalli, Y. Lin and Y. Li [29–32], we also thought to evaluate the starburst-TPA structural format.

In our own studies of small molecule chromophores/charge transport materials based on a D– π –A design, we have previously shown that the use of a cyanopyridone acceptor fragment has a positive effect on the optoelectronic properties and material performance in photovoltaic devices [33,34]. Similarly, the TPA unit has been reported to possess a three-dimensional propeller structure that makes the TPA-containing molecules exhibit good solubility. It is apparent that many D– π –A structured molecules containing TPA as donor unit have been designed and synthesized for the applications as solution-processable organic photovoltaic donor materials [21–24]. We therefore set out to examine the effect of using TPA and cyanopyridone in a non-linear or three-dimensional geometry in comparison to a linear geometry. We have synthesized two examples [(5Z,5'Z,5''Z)-5,5',5''-(((nitrioltris(benzene-4,1-diyl)) tris(thiophene-5,2-diyl)) tris(methanylylidene)) tris(1-(2-ethylhexyl)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile)] (coded as **3D**) and [(Z)-5-((5-(4-(diphenylamino)phenyl)thiophen-2-yl)methylene)-1-(2-ethylhexyl)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile)] (coded as **1D**) such that both the materials have TPA as a common donor and cyanopyridone (CP) as an acceptor fragment. The design concept of **3D** was motivated by our interest to generate an efficient small molecular donor that can (1) display enhanced solubility, (2) be studied in BHJ devices, (3) exhibit energy levels matching those of the conventional fullerene acceptors, (4) exert better light harvesting properties and (5) provide better BHJ performance when compared with a linear structural analogue. The molecular structures of **1D** and **3D** are depicted in Fig. 1.

A simple thiophene unit was introduced as the π -bridge between D and A parts and our aim was to improve the optoelectronic and photovoltaic properties with the use of three-dimensional molecular arrangement. We further hypothesized that the combination of TPA and CP functionalities in a three-dimensional format can push the film absorption into near-infrared region, thus enhancing photovoltaic properties in terms of current density. In this paper, we report the facile synthesis and characterization of the optical, electrochemical and photovoltaic properties of two small molecules **1D** and **3D**. The materials **1D** and **3D** were synthesized via the Knoevenagel condensation of the appropriate aldehyde with the active methylene group of the CP acceptor functionality and their chemical structures were confirmed by ¹H and ¹³C NMR spectroscopy, and mass spectrometry. Benefitting from the three-dimensional design, compared to one-dimensional or linear design, **3D** demonstrated an enhancement of light-harvesting ability, a narrower optical band-gap and higher hole mobility. The photovoltaic performance of the BHJ device based on a blend of **3D** and PC₆₁BM (1:1, w/w) exhibited an impressive PCE of 4.76%, which is greater than two times with respect to the efficiency of the best **1D**-based device (2.11%), with a short circuit current density (*J*_{sc}) of 8.36 mA/cm², a *V*_{oc} of 0.96 V, and a high fill factor (FF) of 59%, under the illumination of AM.1.5, 100 mW/cm². Not only is **3D** the first reported example in the literature where conjoint use of TPA and CP functionalities has been shown to develop a three-dimensional small molecular donor but the device efficiency (>4.7%) outlined herein is the highest PCE number for solution-processable, star-shaped molecular donors.

2. Experimental details

2.1. Materials and methods

All the reagents and chemicals used, unless otherwise specified,

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