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Synthesis and photovoltaic properties of two star-shaped molecules involving phenylquinoxaline as core and triphenylamine and thiophene units as arms

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ABSTRACT

Two novel star-shaped D–A-type small molecules of TPA–PQ–T and TPA–PQ–2T were designed and synthesized, in which the hole-transporting moieties of triphenylamine (TPA) and thiophene (T) or double thiophene (2T) were used as arms and donor units, phenylquinoxaline (PQ) moiety was used as central core and acceptor unit, respectively. Their optical, thermal, electrochemical and photovoltaic properties were investigated. Both compounds films show a strong absorption peak in the range 250–600 nm, and a high thermal stability at more than 430 °C, respectively. The highest power conversion efficiency (PCE) of 1.28% with a short-circuit current density (J_{sc}) of 6.13 mA/cm^2, an open circuit voltage (V_{oc}) of 0.74 V and a fill factor (FF) of 32% was obtained in the solution-processed TPA–PQ–2T-based solar cells using [6,6]-phenyl-C-61-butyric-acid-methyl-ester ($PC_{61}BM$) as acceptor under the illumination of AM 1.5 G, 100 mW/cm^2. The PCE and J_{sc} values are 2.98 and 2.59 times higher than those of the TPA–PQ–T-based cells, respectively.

1. Introduction

Organic solar cells (OSCs) have received considerable attention in recent years as promising alternatives for photovoltaic conversion solar energy, due to their advantages of low-cost, light weight, flexible substrates [1–3]. Over the past decade, numerous efforts have been dedicated to the development of new polymer materials to enhance the performance of the device [4–10]. To date, a record of power conversion efficiency (PCE) has been reached up to 10.8% by using low band gap polymers in bulk heterojunction (BHJ)-structured OSCs [11]. However, there are two major defects based on conjugated polymers: the purity of the materials and the molecular weights of the conjugated polymers [12]. Obviously, this kind of material of photovoltaic properties is difficult to reproduce.

Recently, a number of research efforts have been focused on the development of novel small-molecule donors, due to their advantages of definite molecular weight, well-definite molecular structure, and high purity without batch to batch variations [13], as compared with polymers. More recently, various design rules and interesting new materials have been explored, including linear π-conjugated small molecules [14,15] and star-shaped small molecules [16–21]. As is well known, star-shaped small molecules have shown many advantages over linear conjugated small molecules, such as monodispersity, excellent solubility and vast structures with different functional groups [20,21]. So far, the PCE exceeding 5.81% with using star-shaped small molecule donor materials in BHJ-OSCs has been achieved [19], representing a promising important advance in the development of solution processable OSCs. In particular, compared to the linear small molecule donor materials, the star-shaped small molecule donor materials present a wider spectral absorption that can absorb more sunlight to improve the PCEs of small-molecule donors [22].

As a well-known high solution process ability and good electron-donating moiety, triphenylamine (TPA) has been widely used to design donor–acceptor (D–A) polymers and small molecules for the applications in OSCs [23]. To date, many TPA-based linear and star-shaped small molecules for OSCs have been reported, and most of them showed good photovoltaic performances [24–27]. For instance, a D–A–D-type small molecule with TPA as the donor unit and thiazolothiazole as acceptor group based on the small molecule showed a best PCE of 3.61% [24]. And it is also reported that BHJ solar cells based on a small molecule with TPA as the core and dicyanovinyl units as the terminating group

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yielded a PCE as high as 5.40% [27], which indicates that the organic small molecules containing TPA as donor unit are promising as high efficiency photovoltaic materials for the application as donor in the BHJ-OSCs.

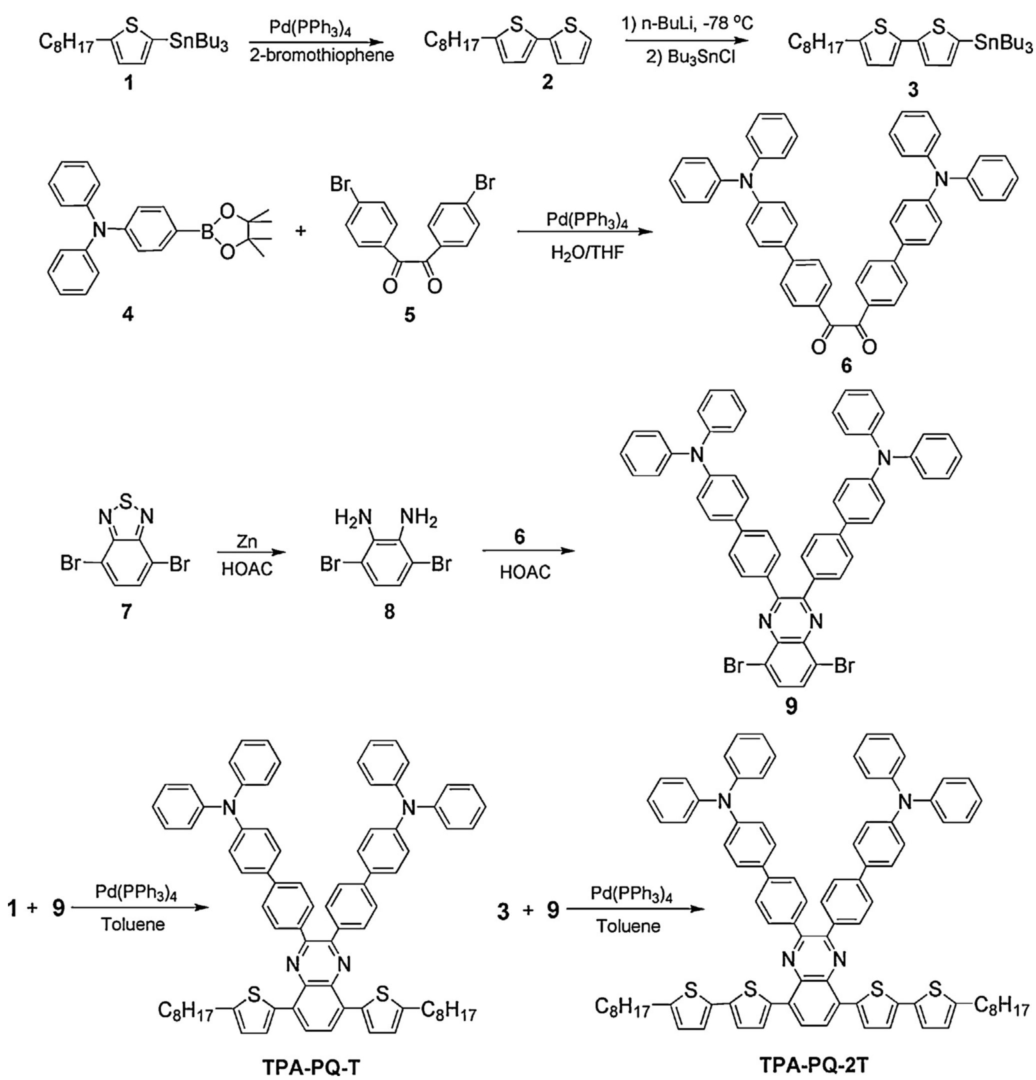
Meanwhile, the phenylquinoxaline (PQ) moiety has attracted great interest as acceptor building block for conjugated polymers in photovoltaic application, due to its electron-withdrawing property of two imine nitrogens and relatively stable quinoid structure [28–33]. A notable PCE up to 8.0% was obtained in the quinoxaline-polymer based device by Chen et al. [33]. However, to our knowledge, there is less reported on PQ-based small molecules as central core and acceptor unit for application in OSCs [34].

With the above considerations in mind, the combination of TPA and PQ units is expected to provide promising low band gap molecules due to the strong intramolecular interaction between donor unit and acceptor unit. Furthermore, the energy levels and aggregation state of the star-shaped molecules can be fine-tuned by introducing thiophene (T) or double thiophene (2T) as donor units onto the PQ group, which provides the advantage of a low band gap and could thus improve electron injection and transport performances [35]. Hence, in this text, two star-shaped small molecules of TPA–PQ–T and TPA–PQ–2T were designed and synthesized. Both TPA–PQ–T and TPA–PQ–2T presented good thermal stability, in which T_d was over 430 °C. Their photophysical, electrochemical and photovoltaic performances were preliminary studied. The highest PCE of 1.28%, with a short-circuit current density (J_{sc}) of 6.13 mA/cm^2, an open circuit voltage (V_{oc}) of 0.74 V and a fill factor (FF) of 32% was obtained in the solution-processed TPA–PQ–2T-based solar cells using PC$_{61}$BM as acceptor, under the illumination of AM 1.5, 100 mW/cm^2. The PCE and J_{sc} values are 2.98 and 2.59 times higher than those of the TPA–PQ–T-based cells, respectively. In particular, the PCE level of TPA–PQ–2T is 2.8 times higher than that of the TH-Q-based device [34]. Obviously, TPA group into the PQ is available for increasing the PCE level of the small molecules. Our study offered a useful and important guideline for designing PQ-based small molecules for high-performance OSCs.

2. Experimental

2.1. Materials

All reagents and chemicals were purchased from commercial sources (Aldrich, Acros, TCI) and used without further purification unless stated otherwise. Tetrahydrofuran (THF) was distilled over sodium and benzophenone under an inert nitrogen atmosphere. The synthetic routes of TPA–PQ–T and TPA–PQ–2T are shown in Scheme 1, and the detailed procedures of monomers and the target



Scheme 1. Synthetic routes for TPA–PQ–T and TPA–PQ–2T.