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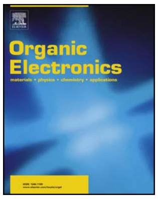

Star-shaped electron acceptors containing a truxene core for non-fullerene solar cells

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ABSTRACT

A series of new electron acceptors containing a truxene core with intense optical absorption were synthesized and used for non-fullerene organic solar cells. Due to the weak electron-donating characteristic of truxene core and thereby weak intramolecular charge transfer interaction from electron-donating core to electron-withdrawing end groups, the resulting new acceptors show relatively wide optical band-gap and high-lying lowest unoccupied molecular orbitals (LUMOs), which consequently lead to complementary light spectra with narrow band-gap donor polymers and high open circuit voltage (V_{oc}) in solar cells. Particularly, **Tr(Hex)$_6$-3BR**, a star-shaped planar acceptor, produced the highest power conversion efficiency of 2.1% with a high V_{oc} of 1.02 V when blended with PTB7-Th.

1. Introduction

Over the past two decades, organic solar cells (OSCs) composed of electron donors and fullerene-based acceptors have attracted enormous attentions and made remarkable progress. The fullerene-based acceptors have high electron affinity and electron mobility, ensuring efficient exciton dissociation and charge transport. Therefore, high performance OSCs with power conversion efficiencies (PCEs) surpassed 11% have been achieved in fullerene-based devices [1,2]. However, fullerene-based acceptors suffer from a few drawbacks such as weak light absorption in the visible spectral region, limited variability in the energy levels, high cost of synthesis, and poor morphological stability in the blend films [3–6]. Recently, non-fullerene acceptors have made great achievements because of their tunable absorption spectra and energy levels, good chemical stability and photostability, as well as better compatibility with donors to form appropriate morphology [7–10]. Encouragingly, impressive PCEs over 13% have been realized by non-fullerene acceptors [11,12].

So far, state-of-the-art non-fullerene acceptors are based on linear acceptor-donor-acceptor (A-D-A) framework with planar conjugated backbone, which contain an electron-rich core and two electron-withdrawing terminal groups [5,6,9–16]. Among these successful materials, 3,9-bis(2-methylene-(3-(1,1-dicyano-methylene)-indanone))-5,5,11,11-tetrakis(4-hexylpheny)-dithieno[2,3-d:2′,3′-d']-*s*-indaceno[1,2-b:5,6-b'] dithiophene (ITIC) [6], and (Z)-5-{[5-(15-{5-[(Z)-(3-Ethyl-4-oxo-2-thioxo-1,3-thiazolidin-5-ylidene)methyl]-8-thia-7.9-diazabicyclo [4.3.0]nona-1(9),2,4,6-tetraen-2-yl}-9,9,18,18-tetrakis(2-ethylhexyl)-5.14-dithiapentacyclo[10.6.0.0^{3,10}.0^{4,8}.0^{13,17}]octadeca-1(12),2,4(8),6,10,13(17),15-heptaen-6-yl)-8-thia-7.9-diazabicyclo [4.3.0]nona-1(9),2,4,6-tetraen-2-yl]methylidene}-3-ethyl-2-thioxo-1,3-thiazolidin-4-one (EH-IDTBR) [14–16] have shined in organic photovoltaics. Following this A-D-A strategy, we are interested in star-shaped planar acceptors rather than linear planar acceptors. Star-shaped molecules are capable of harvesting incident light efficiently owing to their extended dimensionality [17,18], which is beneficial to improving photocurrents in OSCs [19,20]. In addition, star-shaped molecules are able to achieve a proper balance between the size of molecular aggregation in solid state and exciton diffusion length scale to obtain good electronic communication due to moderate intermolecular interactions [20,21].

As an excellent building block for the construction of larger polyarenes, star-shaped molecule of truxene has been recognized and widely used in optoelectronic fields, such as dye-sensitized solar cells [22], perovskite solar cells [23,24], two-photon absorption materials [25], photocatalysts [26], organic light emitting diodes [27], and organic field effect transistors [28]. Moreover, truxene has been successfully

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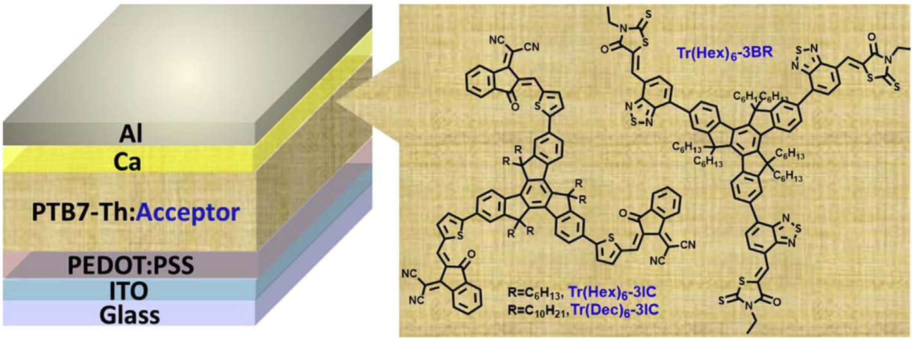

Scheme 1. Device structure employed in this study and the chemical structures of truxene-based acceptors.

employed in constructing electron donors for OSCs [29]. However, truxene has never been used to construct electron acceptors for OSCs. The truxene unit has rigid planar and C_{3h} symmetric structure. As a result, the resulting star-shaped acceptors will be capable of harvesting incident light efficiently due to the extended molecular dimensionality and well-delocalized conjugated structure [30]. Besides, the weak electron-donating characteristic of truxene core and thereby weak intramolecular charge transfer interaction from electron-donating core to electron-withdrawing end groups will endow the resulting new acceptors relatively wide optical band-gap and high-lying lowest unoccupied molecular orbitals (LUMOs), which consequently lead to complementary light spectra with narrow band-gap donor polymers and high open circuit voltage (V_{oc}) in OSCs [31–33].

Based on these considerations, herein we developed three new acceptors with a truxene core, namely **Tr(Hex)$_6$-3IC**, **Tr(Dec)$_6$-3IC**, and **Tr(Hex)$_6$-3BR** (Scheme 1). Among these molecules, **Tr(Hex)$_6$-3IC** and **Tr(Dec)$_6$-3IC** possess the same thiophene π-bridges and terminal electron-withdrawing units of (2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile. Different side chain of hexyl and decyl were introduced onto these two materials because alkyl chain length is proven to be an important factor that determines device performance [34,35]. These two star-shaped materials can be regarded as analogues of ITIC, because they possess the same terminal acceptor units of (2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile. **Tr(Hex)$_6$-3BR** possesses hexyl side chains and double electron withdrawing units of benzo[2,1,3]thiadiazole and 3-ethylrhodanine. This material is a star-shaped analogue of another famous acceptor of EH-IDTBR. Among the three new acceptors, **Tr(Hex)$_6$-3BR** displayed a maximum absorption coefficient as high as 2.9×10^5 cm^{-1} in film. When combined with the widely used narrow band-gap donor polymer of PTB7-Th, the resulting OSCs based on **Tr(Hex)$_6$-3BR** acceptor achieved a PCE of 2.1% with a high V_{oc} of 1.02 V. Moreover, the structure-property relationship with these truxene-based acceptors are discussed in detail in this contribution.

2. Experimental section

2.1. Materials and synthesis

All reagents were obtained from commercial sources and used without further purification, unless otherwise specified. Solvents were dried before use (tetrahydrofuran (THF) from sodium/benzophenone, toluene was washed with H_2SO_4 and then treated with $CaCl_2$, and CH_3CN from CaH_2). Scheme 2 shows the synthetic routes of the truxene-based acceptors. The detailed synthesis procedures are described as following.

2.1.1. Compound **1**

1-Indanone (20.0 g, 151 mmol) was dissolved in the mixture solution of acetic acid (120 mL) and concentrated hydrochloric acid (60 mL). The solution was heated to 120 °C and refluxed for 24 h. The hot mixture was poured into 1 L ice water, then sodium carbonate was added slowly with stirring for 1 h. The yellow precipitate was filtered, and washed with water, acetone, and dichloromethane to give an off-white powder (11 g, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.98 (d, 3H), 7.71 (d, 3H), 7.51 (t, 3H), 7.40 (t, 3H), 4.29 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.21, 142.13, 137.54, 135.71, 127.35, 126.73, 125.56, 122.31, 36.98.

2.1.2. Compound **2a**

In a three-necked flask containing compound **1** (10 g, 29 mmol) under argon protection, anhydrous THF (200 mL) was added and the suspension was stirred at −78 °C. *n*-BuLi (115.2 mL, 2.5 M) was added dropwise and the mixture was kept at −78 °C for 2 h. 1-Bromohexene (48.2 g) was injected slowly. The mixture was allowed to warm to room temperature and stirred overnight. After that, the mixture was poured into 1 L saturated NH_4Cl aqueous solution to quench the excess *n*-BuLi. The water phase was exacted with ethyl acetate, and then the combined organic phase was dried over $MgSO_4$. After the solvent was removed, the crude product was subjected to silica gel column with hexane as eluent to give an off-white powder **2a** (R = C_6H_{13}, 22 g, 95%). It was used directly in the next step without characterization.

2.1.3. Compound **2b**

Compound **2b** was synthesized similarly to compound **2a** with a yield of 92% by using 1-bromodecane to react with compound **1**.

2.1.4. Compound **3a**

A mixture of compound **2a** (2.4 g, 2.8 mmol), anhydrous $FeCl_3$ (5 mg) and chloroform (15 mL) was stirred. And then a solution of bromine (0.5 mL, 10 mmol) in 5 mL of chloroform was added dropwise under stirring at 0 °C, then kept overnight. Na_2SO_3 aqueous solution (50 mL) was added to remove excess bromine. The mixture was exacted with dichloromethane for three times, and the organic phase was dried over $MgSO_4$. After the solvent was removed, the yellow residue was recrystallized from ethanol to yield an off-white powder (2.65 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.18 (d, 3H), 7.56 (d, 3H), 7.52 (dd, 3H), 2.87 (m, 6H), 2.04 (m, 6H), 0.93 (m, 36H), 0.63 (m, 18H), 0.46 (m, 14H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 156.02, 145.04, 139.00, 137.77, 129.51, 126.04, 125.66, 121.18, 56.13, 36.95, 31.59, 29.51, 24.02, 22.40, 14.01.

2.1.5. Compound **3b**

Compound **3b** was synthesized similarly to compound **3a** from compound **2b**. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.17 (d, 3H), 7.72 (d, 3H), 7.56 (dd, 3H), 2.83 (m, 6H), 2.04 (m, 6H), 0.91 (m, 102H), 0.51 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 156.22, 145.11, 139.02, 137.55, 129.55, 126.24, 125.67, 121.28, 56.35, 36.98, 32.29, 29.99, 29.97, 29.80, 29.70, 29.61, 24.32, 23.10, 14.28.

2.1.6. Compound **4a**

A mixture of compound **3a** (0.615 g, 0.568 mmol), (5-(1,3-dioxolan-2-yl)thiophen-2-yl)trimethylstannane (1.136 g, 2.556 mmol), tetrakis (triphenylphosphine)palladium(0) (146 mg) were dissolved in toluene (70 mL) and degassed with argon for 30min. The mixture was refluxed