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Diindeno[2,3-*b*]thiophene arene for efficient organic photovoltaics with an extra high open-circuit voltage of 1.14 eV[†]

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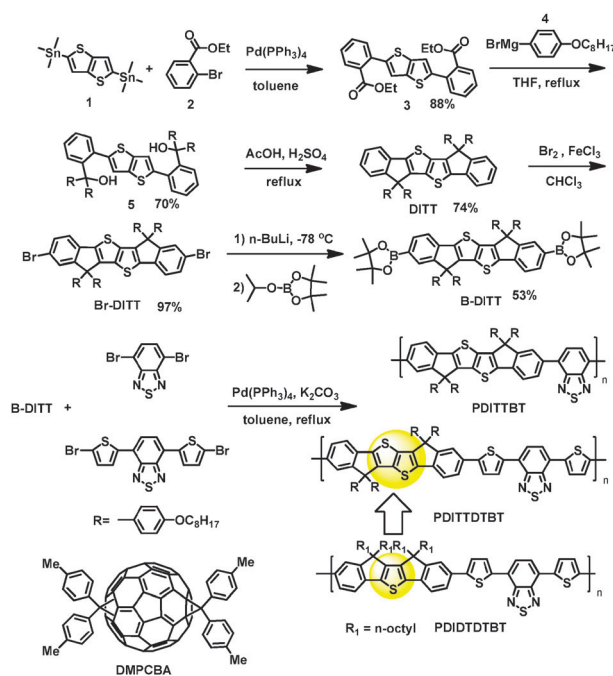
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We report a novel diindeno[2,3-*b*]thiophene ladder-type hexacyclic arene for constructing a donor–acceptor copolymer PDITDTBT. A device based on PDITDTBT:PC₇₁BM exhibited a high V_{oc} of 0.92 V with an impressive PCE of 5.8%, while a PDITDTBT:DMPCBA-based device showed an extra high V_{oc} of 1.14 V.

Over the past decade, considerable progress has been made in the development of organic materials for photovoltaic applications.¹ Bulk heterojunction (BHJ) using n-type and a p-type semiconductor materials in the active layer is the most widely adopted device architecture to ensure maximum internal donor–acceptor (D–A) interfacial area for efficient charge separation.² The most critical challenge at the molecular level is to combine a suitable pair of p-type and n-type semiconductors in the active layer that can simultaneously produce high open-circuit voltage (V_{oc}), short-circuit current (J_{sc}) and fill factor (FF). The most straightforward guideline to enlarge V_{oc} is to lower the donor's highest occupied molecular orbital (HOMO) energy level or raise the acceptor's lowest unoccupied molecular orbital (LUMO) level.³ Thiophene and benzene aromatic rings are the most important structural ingredients to comprise p-type conjugated polymers. Benzene-based units such as tricyclic 2,7-fluorene or 2,7-carbazole units have shown to serve as useful building blocks in the construction of donor–acceptor polymers having deep-lying HOMO energy levels that contribute to yield high V_{oc} (>0.8 V) for PSCs.⁴ However, the intrinsic drawback is that these polymers usually possess relatively large optical band gaps (>2 eV) that limit their ability to harvest sunlight and thus result in moderate J_{sc} . On the other hand, due to the lower aromaticity and easier oxidation, thiophene-based D–A polymers have better light absorption ability to permit greater J_{sc} . However, their V_{oc} values are generally limited to *ca.* 0.6 V as a result of the high-lying HOMO levels.⁵ It has been demonstrated that forced planarization by covalently fastening adjacent aromatic units in the polymer backbone can reduce the band gap and enhance the intrinsic charge mobility.⁶ By extracting benefits from benzene and thiophene moieties to acquire

high V_{oc} and J_{sc} , it is of great interest to integrate benzene units and thiophene units into a molecular entity with forced rigidification to simultaneously extend the conjugation while maintaining the coplanarity. In this regard, we recently developed a pentacyclic diindeno[1,2-*b*:2',1'-*d'*]-thiophene (DITT) unit that was polymerized to afford an alternating poly(diindenothiophene-*alt*-dithienylbenzothiadiazole) copolymer PDITDTBT (Scheme 1).⁷ However, the device using the PDITDTBT/PC₇₁BM (1:2, w/w) blend only gave a V_{oc} of 0.7 V and a J_{sc} of 5.3 mA cm⁻² with a lower PCE of 1.65%.⁷ The thieno[3,2-*b*]thiophene (TT) unit has been an appealing building block for high mobility p-type semiconductors.⁸ This fused structure possesses higher aromatic stabilization energy than a thiophene, which can potentially lower the HOMO level for higher V_{oc} .⁹ Moreover, the C_{2h} symmetry and coplanar geometry allow more ordered packing and stronger interchain interactions to achieve exceptional hole mobility, which is beneficial for J_{sc} .¹⁰ However, introducing the



Scheme 1 Synthetic route of the DITT monomer leading to the targeted PDITBT and PDITDTBT copolymers, and the chemical structures of PDITDTBT and DMPCBA.

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alkyl chains into the β -positions of a thieno[3,2-*b*]thiophene unit to improve the solubility of the resulting polymers imposes a negative effect on the effective conjugation due to severe steric hindrance-induced twisting between the neighboring units.¹¹

By taking aforementioned points into account, in this communication, we have designed and synthesized a novel multi-fused hexacyclic diindenothieno[2,3-*b*]thiophene (**DITT**) unit, where the central **TT** ring is connected with two outer phenyl rings through two embedded cyclopentadienyl (**CP**) rings. The ability of functionalization at bridging carbon allows for incorporating four highly solubilizing side chains without twisting the coplanarity between the central **TT** unit and phenyl rings.

The synthetic route of the **DITT** monomer is depicted in the Scheme 1. Stille coupling of 2,5-bis-trimethylstannylthieno[2,3-*b*]thiophene **1** with 2-bromo-1-ethylbenzoate **2** afforded compound **3**. Double nucleophilic addition of the freshly prepared 4-(octyloxy)phenyl magnesium bromide **4** to the ester groups of **3** led to the formation of tertiary alcohol in **5**. Compound **5** was subjected to intramolecular annulation through Lewis acid-mediated Friedel–Crafts reaction to furnish the multi-fused hexacyclic arene **DITT**. Bromination of **DITT** by $\text{Br}_2/\text{FeCl}_3$ selectively occurred at 2,8 positions to yield **Br-DITT**. Treatment of **Br-DITT** with *n*-butyl lithium followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane successfully afforded **B-DITT** which was polymerized by Suzuki coupling with 4,7-dibromo-2,1,3-benzothiadiazole (**BT**) and 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**DTBT**) acceptors to afford a new class of alternating D–A conjugated polymers **PDITTTBT** ($M_n = 19.0$ kDa, PDI = 1.76) and **PDITTTDTBT** ($M_n = 8.1$ kDa, PDI = 2.10), respectively. **PDITTTBT** showed excellent solubility in common organic solvents, such as THF, chloroform, toluene, dichlorobenzene, while **PDITTTDTBT** is only soluble in hot dichlorobenzene and trichlorobenzene.

The thermal stability of the polymers was analyzed by thermogravimetric analysis (TGA). **PDITTTDTBT** showed higher decomposition temperatures (T_d) of 410 °C than **PDITTTBT** with 377 °C, indicating sufficient thermal stabilities for PSC applications (Fig. S1, ESI[†]). Thermal properties of the polymers were determined by differential scanning calorimetry (DSC). **PDITTTBT** and **PDITTTDTBT** showed glass transition temperatures (T_g) of 216 °C and 197 °C, respectively, without observation of melting point, suggesting that these polymers tend to form amorphous glasses (Fig. S2, ESI[†]).

The absorption spectra of all polymers were measured both in toluene and in thin films (Fig. 1). The shorter wavelength absorbance comes from the π – π^* transition of the **DITT** units, while the lower energy band is attributed to the intramolecular charge transfer (ICT) between the electron-rich and the electron-

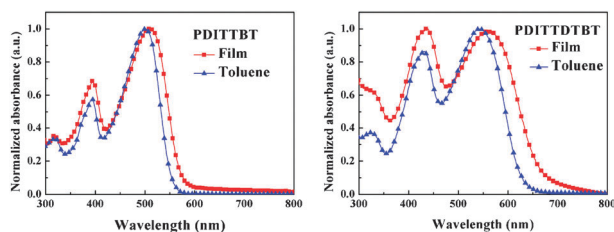


Fig. 1 Normalized absorption spectra of (a) **PDITTTBT** and (b) **PDITTTDTBT** in toluene solution and the solid state.

deficient segments. **PDITTTDTBT** with two additional thiophene rings in the repeating unit exhibited more red-shifted absorption maximum (λ_{max}) in solution at 548 nm than **PDITTTBT** at 501 nm. In addition, the optical band gaps (E_g^{opt}) deduced from the onset of absorption in the solid state are determined to be 2.15 eV for **PDITTTBT** and 1.87 eV for **PDITTTDTBT**. Note that the E_g^{opt} of **PDITTTDTBT**⁷ is 1.85 eV which is lower than that of **PDITTTDTBT**, suggesting that the **TT** unit in **DITT** has higher aromaticity than the thiophene unit in **DITD**. It is also noteworthy that the intensities of the shorter wavelength bands of the two polymers in the solid state are apparently stronger than those in the solution state, which also suggests that the rigid and coplanar **DITT** units increase their extinction coefficient in the solid state.

Cyclic voltammetry (CV) was employed to examine the electrochemical properties (Fig. S3, ESI[†]). Both polymers showed a stable and reversible p-doping/n-doping process in the cathodic and anodic scans. Encouragingly, **PDITTTBT** and **PDITTTDTBT** do show very deep-lying HOMO energy levels of -5.52 eV and -5.40 eV, respectively, which are at an ideal range to assure better air-stability and greater attainable V_{oc} in the device. It should be emphasized that the HOMO level of **TT**-based **PDITTTDTBT** is lower than that of the corresponding thiophene-based **PDITTTDTBT** (-5.40 eV vs. -5.36 eV), again suggesting that the **TT** unit embedded in the structure is indeed capable of increasing the oxidation potential. The LUMO energy levels are approximately located at -3.23 eV for **PDITTTBT** and -3.36 eV for **PDITTTDTBT**.

Bulk heterojunction photovoltaic cells were fabricated by spin-coating the blends with *o*-DCB solutions at various polymer-to-PC₇₁BM ratios on the basis of ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al configuration and their performances were measured under a simulated AM 1.5 G illumination of 100 mW cm⁻². The PC₇₁BM was used due to its stronger light absorption in the visible region than PC₆₁BM.

The *J*–*V* curves of the devices with optimized conditions are shown in Fig. 2. The device based on the **PDITTTBT**/PC₇₁BM (1 : 3.5, w/w) blend exhibited a V_{oc} of 0.88 V, a J_{sc} of 7.46 mA cm⁻², a FF of 41.4% and a moderate PCE of 2.7%. The lower J_{sc} is mainly attributed to the limited absorption coverage of **PDITTTBT**. Encouragingly, the device using the **PDITTTDTBT**/PC₇₁BM (1 : 4, w/w) blend delivered superior performance with a V_{oc} of 0.92 V, a J_{sc} of 10.71 mA cm⁻², a FF of 58.4% with an exceptional PCE of 5.8%. The device characteristics greatly outperformed the **PDITTTDTBT**-based device,⁷ leading to an enhancement of PCE by 3.5 folds (V_{oc} : 0.92 vs 0.7 V; J_{sc} : 10.71 vs 5.3 mA cm⁻²; FF: 58.4 vs 44%, PCE: 5.8 vs 1.65%, see Table S1, ESI[†]).

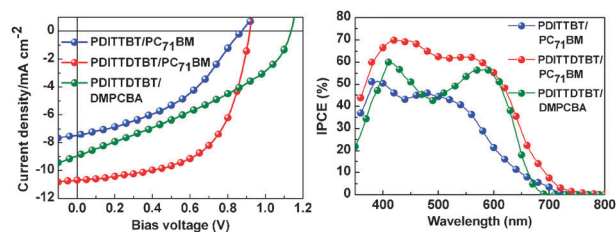


Fig. 2 Current density–voltage characteristics (left) and IPCE spectra (right) of the conventional devices (ITO/PEDOT:PSS/polymer:PC₇₁BM or DMPCEBA/Ca/Al) under illumination of AM 1.5 G, 100 mW cm⁻².

To further evaluate the hole mobility in the **BHJ** active layer, hole-only devices (ITO/PEDOT:PSS/**PDITDTBT**:PC₇₁BM (1:3.5, w/w) or **PDITDTBT**:PC₇₁BM (1:4, w/w)/Au (40 nm)) were fabricated *via* space-charge limit current (SCLC) theory. It is found that the hole mobility of the **PDITDTBT**/PC₇₁BM ($1.41 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is over one order of magnitude higher than that of the **PDITBT**/PC₇₁BM ($7.41 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), which indicates that the polymer with higher thiophene content exhibited higher hole mobility. The enhanced hole mobility of the **PDITDTBT**/PC₇₁BM active layer might be responsible for its better J_{sc} , FF and photovoltaic performance over the **PDITBT**-based device.

It should be emphasized that the hybridization of benzene and thieno[2,3-*b*]thiophene units into a coplanar ladder-type **DITT** structure indeed successfully achieves a superior V_{oc} while maintaining a high J_{sc} value, overcoming the trade-off between V_{oc} and J_{sc} . Bis-adduct C₆₀ derivatives are known to have higher-lying LUMO energy levels leading to very high V_{oc} .¹² Unfortunately, using bis-adduct C₆₀ strategy is only limited to the P3HT-based system. Their extended applications to other low-band gap polymers have been unsuccessful so far. We recently developed a new di(4-methylphenyl)methano-C₆₀ bis-adduct (**DMPCBA**).¹³ The device based on the P3HT:**DMPCBA** blend exhibited a very high V_{oc} of 0.87 V. It is thus highly desirable to combine n-type **DMPCBA** with our newly developed deep-lying p-type **PDITDTBT** polymer. The device incorporating the **PDITDTBT**/**DMPCBA** (1:3.5, w/w) blend exhibited a V_{oc} of 1.14 V with a J_{sc} of 8.97 mA cm⁻², leading to a decent PCE of 3.6%. To the best of our knowledge, the V_{oc} of 1.14 V, almost double than the average V_{oc} (*ca.* 0.6 V) derived from the P3HT/PCBM-based devices, is the highest value ever reported among the single cell BHJ devices. The PCE of 3.6% also represents the best performance of the solar cells incorporating a C₆₀ bis-adduct and a non-P3HT D–A polymer. The morphologies of thin film were evaluated by atomic force microscopy (Fig. S4, ESI†). The images of the **PDITDTBT**/PC₇₁BM (1:4, w/w) blend and the **PDITDTBT**/**DMPCBA** (1:3.5, w/w) blend showed very smooth surfaces and small phase separation domains, suggesting moderately homogeneous morphologies for efficient charge separation and transport. The root-mean-square roughness of the two cases was 1.26 nm and 1.56 nm, respectively.

In conclusion, for the first time, we have successfully designed and synthesized a novel hexacyclic **DITT** arene where a thieno[3,2-*b*]thiophene unit is covalently fastened with two adjacent phenyl rings. The device based on the **PDITDTBT**/PC₇₁BM blend (1:4 in wt%) exhibited a V_{oc} of 0.92 V and a J_{sc} of 10.71 mA cm⁻² with an impressive high PCE of 5.8%, which greatly outperformed the **PDITDTBT**-based device with a PCE of 1.65%. This result clearly indicates that compared to **DIDT**, the **DITT** unit is a much superior molecular design for PSCs. The higher V_{oc} is associated with the deep-lying HOMO energy level of **PDITDTBT** (−5.40 eV) due to the intrinsically larger aromatic stabilization energy of the **DITT** unit, while the coplanar and symmetrical **DITT** resulting in strong UV-visible absorbance and good hole mobility of **PDITDTBT** is responsible for the high photocurrent. Furthermore, by blending **PDITDTBT** with an amorphous C₆₀ bis-adduct **DMPCBA**, a record high V_{oc} of 1.14 V has been

accomplished. We envisage that further improvement is highly achievable through careful morphological optimization. This research provides a guideline for molecular engineering to obtain high V_{oc} without sacrificing J_{sc} .

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