

A new ladder-type benzodi(cyclopentadithiophene)-based donor-acceptor polymer and a modified hole-collecting PEDOT:PSS layer to achieve tandem solar cells with an open-circuit voltage of 1.62 V[†]

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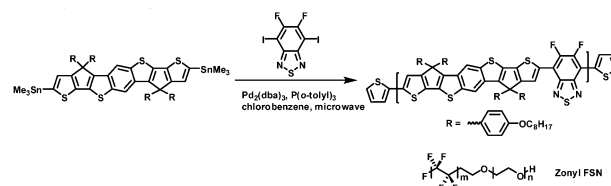
We have developed a new ladder-type conjugated polymer PBDCPDT-FBT and a robust interconnecting layer (ICL) integrating a hole-collecting m-PEDOT:PSS layer with an electron-collecting ZnO layer. The inverted device using PBDCPDT-FBT exhibited a high power conversion efficiency (PCE) of 5.76% with a V_{oc} of 0.81 V, a J_{sc} of 12.82 mA cm⁻², and a FF of 55.5%. The inverted tandem device incorporating the PBDCPDT-FBT and ICL achieves a V_{oc} of 1.62 V leading to a PCE of 7.08%.

Organic photovoltaic cells (OPVs) have attracted growing attention in the past decade on account of their advantages of low cost, light weight, flexibility and capability of large-area processing.¹ Achieving high-performance OPVs critically relies on the combination of superior organic materials and advanced device engineering.^{1,2} One of the current challenges at the molecular level is the insufficient absorption coverage of a single polymer, resulting in limited utilization of sunlight. Research on tandem cells stacking two single cells in series has attracted considerable attention in anticipation of attaining synergistic device characteristics.³ Maximizing light-harvesting capability is particularly a beneficial feature for a tandem cell, because one subcell can incorporate a broad band-gap polymer (BBGP) to mainly absorb UV-visible light, while the other subcell utilizes a lower band-gap polymer (LBGP) to specifically capture photons with longer wavelengths.³ Furthermore, the overall open-circuit voltage (V_{oc}) of an in-series tandem cell can be as large as the summation of the V_{oc} values of the two corresponding single cells. Judicial selection of suitable p-type and n-type materials in the two independent active layers to tailor their optical and electronic properties plays a pivotal role in determining the macroscopic device parameters. Crystalline poly(3-hexylthiophene) P3HT is an ideal BBGP for a tandem cell considering its high hole mobility and easy availability. Nevertheless, development of a new LBGP

with superior molecular properties is highly desired. Benzodithiophene (BDT) derivatives have been demonstrated to be the most successful building blocks for making p-type polymers to achieve the state-of-the-art efficiencies.⁴ By taking advantage of the BDT intrinsic properties, we designed a new ladder-type benzodi(cyclopentadithiophene) (BDCPDT) arene, where 3,7-positions of the central BDT subunit are covalently bridged with 3-positions of the two outer thiophenes by two carbon atoms. The BDCPDT arene features a coplanar and extended conjugated ladder-type framework that can elongate up to an effective conjugation length and facilitate intrinsic charge mobility.⁵ The synthesis of distannylated BDCPDT monomer is shown in Fig. S1 (ESI[†]).⁶ The distannylated BDCPDT monomer was copolymerized with the 4,7-diiodo-5,6-difluoro-2,1,3-benzothiadiazole (FBT) acceptor by the palladium-catalyzed Stille polymerization to afford an alternating copolymer, PBDCPDT-FBT (Scheme 1).

The physical properties are summarized in Table 1, and the computed molecular orbital properties are described in the ESI.[†] PBDCPDT-FBT exhibited a significant red-shift of λ_{onset} by 20 nm from solution to solid states, indicating stronger intermolecular interactions in the solid state due to the highly planarized structure of BDCPDT units (Fig. 1a). As shown in Fig. 1b, in comparison with P3HT, PBDCPDT-FBT exhibited not only a lower optical bandgap of 1.67 eV but also a broader absorption window, indicating that PBDCPDT-FBT can function as a suitable BBGP to pair with P3HT for a tandem solar cell.

In this research, we focused our investigation on inverted tandem cells, because the devices with an inverted architecture have much better device stability.⁷ At the beginning, an indene



Scheme 1 Palladium-catalyzed Stille polymerization of BDCPDT and FBT monomers and the structure of Zonyl FSN.

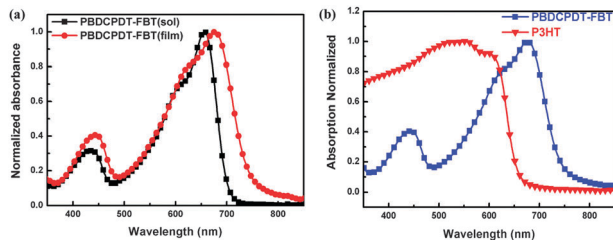
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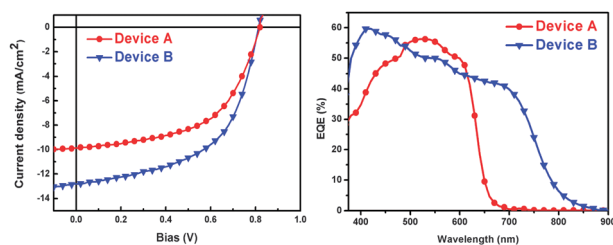
Table 1 Summary of the physical properties of PBDCPDT-FBT

Polymer	M_n (kDa)	M_w (kDa)	PDI	E_g^{opt} (eV)	λ_{max} (nm)		$E_{\text{ox}}^{\text{onset}}$ (V)	HOMO ^a (eV)	$E_{\text{red}}^{\text{onset}}$ (V)	LUMO ^a (eV)
					Toluene	Film				
PBDCPDT-FBT	49.9	74.2	1.48	1.67	658	677	0.55	−5.35	−1.32	−3.48

^a HOMO = $-(4.8 + E_{\text{ox}}^{\text{onset}})$ eV, LUMO = $-(4.8 + E_{\text{red}}^{\text{onset}})$ eV.

**Fig. 1** (a) Normalized absorption spectra of PBDCPDT-FBT in toluene solution and thin films, (b) comparison of absorption spectra of PBDCPDT-FBT and P3HT in thin films.

C₆₀ bis-adduct fullerene (IC₆₀BA)⁸ with a much high-lying LUMO energy level of −3.7 eV was combined with HBG P3HT to fabricate a single-junction inverted device A (ITO/ZnO/P3HT:IC₆₀BA (1 : 1, w/w)/m-PEDOT:PSS/Ag). Meanwhile, the LBG PBDCPDT-FBT copolymer was paired with PC₇₁BM to make another single inverted device B (ITO/ZnO/PBDCPDT-FBT:PC₇₁BM (1 : 3, w/w)/MoO₃/Ag). The current density–voltage characteristics and EQE spectra of the devices A and B are illustrated in Fig. 2 and their photovoltaic performances are listed in Table 2. The P3HT:IC₆₀BA-based device A yielded a PCE of 4.50%, with a V_{oc} of 0.82 V, a J_{sc} of 10.01 mA cm^{−2}, and a FF of 54.9%. On the other hand, the inverted device B exhibited a high PCE of 5.76% with a V_{oc} of 0.81 V, a J_{sc} of 12.82 mA cm^{−2}, and a FF of 55.5%. As determined by space-charge limited current (SCLC) theory, the hole mobility of PBDCPDT-FBT was estimated to be 6.4×10^{-5} cm² s^{−1} V^{−1}, indicating its superior capability of transporting holes. By comparing the EQE spectra of the PBDCPDT-FBT:PC₇₁BM-based device B with that of the P3HT:IC₆₀BA-based device A, an additional ~25% EQE contribution in the region of 650–800 nm was found for device B, indicating that the broader absorption of the low band-gap polymer PBDCPDT-FBT can increase the carrier output leading to a much higher J_{sc} of 12.8 mA cm^{−2}. This result demonstrates that P3HT:IC₆₀BA and PBDCPDT-FBT:PC₇₁BM active layers can be suitably used in the front cell and the rear cell of a tandem cell.

**Fig. 2** Current density–voltage characteristics (left) and EQE (right) spectra of single-junction cells based on P3HT:IC₆₀BA or PBDCPDT-FBT:PC₇₁BM under illumination of AM 1.5 G at 100 mW cm^{−2}.**Table 2** Photovoltaic performance of device A: ITO/ZnO/P3HT:IC₆₀BA (1 : 1, w/w)/m-PEDOT:PSS/Ag (inverted). Device B: ITO/ZnO/PBDCPDT-FBT:PC₇₁BM (1 : 3, w/w)/MoO₃/Ag and devices C ITO/ZnO/P3HT:IC₆₀BA/m-PEDOT:PSS/ZnO/PBDCPDT-FBT:PC₇₁BM/MoO₃/Ag

Device	V_{oc} (V)	J_{sc} (mA cm ^{−2})	FF (%)	PCE (%)
Device A	0.82	10.01	54.9	4.50
Device B	0.81	12.82	55.5	5.76
Device C ^a	1.62	8.03	54.4	7.08

^a Thickness of P3HT:IC₆₀BA blend = 190 nm, thickness of PBDCPDT-FBT:PC₇₁BM blend = 90 nm.

In addition to photoactive materials, a series-connected tandem cell requires an interconnecting layer (ICL) to function as a charge recombination zone where holes from the front cell and electrons from the rear cell combine. The most formidable challenge in assembling an inverted tandem cell is to technically incorporate a central ICL with high transmittance and good conductivity. To address this issue, we developed a robust ICL integrating a modified PEDOT:PSS hole-collecting layer and a layer of electron-collecting ZnO.

PEDOT:PSS is widely used as a hole conducting layer in the conventional solar cells. Nevertheless, hydrophilic PEDOT:PSS faces difficulty in depositing on top of a hydrophobic active layer, hindering its use in the inverted devices. To circumvent this deficiency, PEDOT:PSS solution was modified by adding a fluorinated surfactant, Zonyl FSN (Scheme 1) to form a m-PEDOT:PSS. In comparison with the pristine PEDOT:PSS, the m-PEDOT:PSS showed substantially improved miscibility with organic materials due to the fact that the amphiphilicity of Zonyl FSN can decrease the surface energy of the m-PEDOT:PSS significantly. Therefore, the aqueous m-PEDOT:PSS solution can be easily deposited on the active layer of a front cell by spin-coating. More encouragingly, the m-PEDOT:PSS possesses a much higher conductivity of 7.4×10^{-1} S cm^{−1} than the pristine PEDOT:PSS (10^{-3} S cm^{−1}).⁹ The average transmittance of the m-PEDOT:PSS (100 nm)/ZnO (20 nm) film from 350 to 800 nm reaches 85%, revealing its high transparent characteristics (Fig. S2, ESI†). Consequently, multilayer tandem cells with ITO/ZnO/P3HT:IC₆₀BA/m-PEDOT:PSS/ZnO/PBDCPDT-FBT:PC₇₁BM/MoO₃/Ag configuration were successfully fabricated by consecutive solution processing. The conduction band of ZnO corresponds well with the LUMO energy level of IC₆₀BA. Meanwhile, instead of m-PEDOT:PSS, MoO₃ was selected as a hole transporting layer for the rear cell because its valence band (*ca.* −5.4 eV) fits well with the HOMO energy of PBDCPDT-FBT (−5.3 eV).¹⁰ Overall, the energy offsets at the interfaces have been minimized to ensure the good transportation of carriers in the device. The current density *versus* voltage (*J–V*) characteristics of the tandem solar cell under AM 1.5 G illumination are shown in Fig. 3 and the device characteristics are summarized in Table 2.

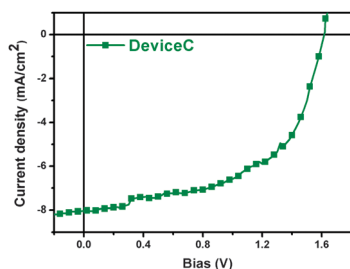


Fig. 3 J - V curves of the tandem cell (ITO/ZnO/P3HT:IC₆₀BA/m-PEDOT:PSS/ZnO/PBDCPDT-FBT:PC₇₁BM/MoO₃/Ag).

To optimize the absorption management by modulating the thickness of active layers, device C exhibited a high PCE of up to 7.08% with a very high V_{oc} of 1.62 V and an improved J_{sc} of 8.03 mA cm⁻². The V_{oc} of device C is nearly equal to the sum of the two single cells, confirming the efficient coupling of the two subcells in series. To the best of our knowledge, this magnitude is one of the highest V_{oc} values reported in the literature.

In conclusion, we have developed a new conjugated polymer, PBDCPDT-FBT, which exhibited a high hole mobility and complementary absorption coverage to P3HT. An inverted device using PBDCPDT-FBT exhibited a high PCE of 5.76% with a V_{oc} of 0.81 V, a J_{sc} of 12.82 mA cm⁻², and a FF of 55.5%. An interconnecting layer (ICL), integrating a layer of hole-collecting PEDOT:PSS modified by Zonyl FSN with a layer of electron-collecting ZnO, was also developed. The enhanced hydrophobicity of m-PEDOT:PSS overcomes the difficulties of fabricating layer-by-layer inverted tandem cells. This ICL possesses high transmittance and good conductivity, which paves the way for successfully fabricating high-performance tandem solar cells. The inverted tandem device with ITO/ZnO/P3HT:IC₆₀BA/m-PEDOT:PSS/ZnO/PBDCPDT-FBT:PC₇₁BM/MoO₃/Ag configuration achieved a V_{oc} of 1.62 V leading to a PCE of 7.08%, which performs superiorly than their individual subcells. The V_{oc} of 1.62 V is among one of the highest values ever reported.

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