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# Benzobisthiazole-substituted terpolymers for non-halogenated solvent-processed polymer solar cells with enhanced efficiency, thermal stability and mechanical robustness†

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High power conversion efficiency (PCE), eco-friendly processing, and long-term stability are essential for the commercialization of polymer solar cells (PSCs). In this study, we develop PM6-based terpolymer donors (PM6-DTzBX, where  $X = 5-20$ ), by substituting the benzodithiophene-dione (BDD) unit with the benzobisthiazole (DTzB) unit, which aims to tune the crystalline properties of the polymers as well as achieving a blend morphology with sufficient intermixed domains. The DTzB-incorporating polymer donors ( $P_D$ s) demonstrate stronger intermolecular interactions with a Y6-BO small molecule acceptor (SMA) and exhibit more pronounced crystalline properties than the reference PM6  $P_D$ . Consequently, PM6-DTzB10  $P_D$ -based PSCs achieve a higher PCE of 16.8% compared to that of PM6-based PSCs (15.6%) when processed in a non-halogenated *ortho*-xylene solvent. Furthermore, under thermal stress at 100 °C for 100 h, PM6-DTzB10-based PSCs maintain 88% of the initial PCE and exhibit enhanced thermal stability compared to PM6-based PSCs, which retain 72% of the initial PCE. Additionally, the PM6-DTzB10:Y6-BO blend films demonstrate a 7-fold increase in stretchability with a crack onset strain (COS) of 11.7%, compared to the PM6:Y6-BO blend films (COS = 1.7%). These enhancements in the PCE, thermal stability, and mechanical robustness can be mainly ascribed to the formation of a well-intermixed  $P_D$ :SMA blend morphology and enhanced crystalline properties of PM6-DTzB  $P_D$ s. This study highlights the potential of the terpolymer strategy in developing efficient, thermally stable, and mechanically robust PSCs.

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## 1. Introduction

Polymer solar cells (PSCs) are gaining attention as a promising next-generation energy source due to their advantages including semi-transparency, and cost-effective large-area fabrication through solution processing.<sup>1-4</sup> Various polymer donors ( $P_D$ s) and small-molecule acceptors (SMAs) have been developed to enhance the power conversion efficiency (PCE) of PSCs, with some achieving PCE values exceeding 19%.<sup>5-13</sup> However, the commercialization of PSCs necessitates the

replacement of hazardous halogenated solvent-based processing, such as the use of chloroform and chlorobenzene, with more eco-compatible alternatives.<sup>14-21</sup> However, solution processing based on non-halogenated solvents results in PSCs with lower PCE values than those processed with halogenated solvents, mainly due to unoptimized  $P_D$ :SMA blend morphologies.

The unfavorable blend morphology primarily stems from the lower solubilities of  $P_D$ s and SMAs and their unoptimized aggregated structures in non-halogenated solvents.<sup>14,22,23</sup> In particular, molecular incompatibility between the  $P_D$  and SMA often leads to severe phase separation between their respective domains during the film formation process. This unoptimized blend morphology adversely affects charge generation and transport in PSCs, resulting in decreased PCEs. In addition, an excessively phase-separated morphology is prone to degrade under external stresses such as light and heat, resulting in decreased photo, thermal, and mechanical stabilities of the PSCs.<sup>24-27</sup> Therefore, the design of active layer materials with sufficient solubilities in non-halogenated solvents and

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improved donor/acceptor interactions is imperative to simultaneously achieve both high performance and stability of the PSCs. For example, pairing donor and acceptor materials with improved molecular compatibility can prevent excessive separation between domains by reducing the thermodynamic penalty for formation of large donor–acceptor interfaces. The presence of sufficient donor–acceptor interfaces and intermixed domains can enhance the exciton dissociation and charge generation efficiency, resulting in higher short-circuit current density ( $J_{sc}$ ), fill factor (FF), and PCE values in the PSCs.<sup>28</sup> Importantly, the  $P_D$ :SMA blend film with sufficient intermixed domains can prevent the occurrence of cracks at the  $P_D$ :SMA interfaces by effectively dissipating mechanical stress, and enhancing the mechanical robustness of the PSCs.<sup>29–31</sup>

The design of terpolymer-type  $P_D$ s featuring D–A<sub>1</sub>–D–A<sub>2</sub> type backbones has proven to be an effective strategy for enhancing the molecular compatibility of typical alternating-type  $P_D$ s (D–A<sub>1</sub>) with SMAs by replacing the A<sub>1</sub> block with a carefully selected A<sub>2</sub> block.<sup>32–40</sup> A suitable proportion of the A<sub>2</sub> block in the terpolymer-type  $P_D$  can effectively control its surface tension, which determines the enthalpic interaction with the SMA at the donor–acceptor interfaces. For instance, Cao *et al.* designed a random terpolymer-type  $P_D$  (JD40-BDD20) by adjusting the molar ratio of dithienobenzothiadiazole (TBT) and benzodithiophene-dione (BDD) units.<sup>23</sup> The use of the JD40-BDD20 terpolymer resulted in a reduced phase separation with the PJTVT acceptor compared to the control JD40  $P_D$  due to its higher miscibility with the acceptor. As a result, the JD40-BDD20-based PSC demonstrated a higher PCE of 16.35% than that (14.05%) of the JD40-based PSC in *ortho*-xylene (*o*-xylene) processing. As another example, our group introduced ethyl thiophene-3-carboxylate units into the D18  $P_D$  backbone to yield terpolymer-type  $P_D$ s (PBET 10–50), which enabled a  $P_D$ :Y6-BO SMA blend morphology with sufficient intermixed domains compared to that with the reference D18.<sup>33</sup> PBET 10–50 enabled solution processing in *o*-xylene to construct a PSC with a PCE of 15.5%, whereas solution processing of D18  $P_D$  was nearly impossible due to its very poor solubility in *o*-xylene. These studies suggest that developing terpolymer-type  $P_D$ s can effectively increase their solubility in non-halogenated solvents and improve the molecular compatibility with SMAs. However, most random terpolymers inevitably exhibit reduced crystalline properties compared to alternating copolymers because random incorporation of the third A<sub>2</sub> unit into the  $P_D$  polymer results in the distortion of the molecular conformation and interferes with the effective formation of intermolecular assembly.<sup>22,35</sup> This decreased crystallinity of  $P_D$ s can negatively influence the charge transport properties of the film, compromising the PCE values of the PSCs. Therefore, it is essential to design and incorporate an appropriate third unit into the  $P_D$  backbone that not only ensures higher crystalline and electrical properties but also maintains its sufficient processability in eco-friendly solvents.

In this study, we develop a new series of terpolymer-type  $P_D$ s (PM6-DTzBX,  $X = 5, 10, \text{ and } 20$ ) by incorporating the benzo[1,2-*d*:4,5-*d'*]bis(thiazole) (DTzB) unit into the PM6  $P_D$  backbone, replacing the BDD unit. Then, we utilize them to produce

efficient and stable PSCs using non-halogenated solvent-based processing. We select the DTzB unit as the third component in the  $P_D$  for the following reasons: (1) the DTzB unit, containing nitrogen atoms, offers higher polarity and hydrophilicity than the BDD unit, thereby enhancing the molecular compatibility of the  $P_D$ s with SMAs.<sup>41–43</sup> (2) The thiazole units in the DTzB block facilitate strong molecular interactions with adjacent thiophenes through a N–S noncovalent bonding.<sup>44–47</sup> This improved intra- and inter-molecular interaction can overcome the inherent limitations of random terpolymers, resulting in  $P_D$ s with higher crystallinity and superior charge transport properties. As a result, with *o*-xylene solvent-based processing, PM6-DTzB10  $P_D$ -based PSCs achieve a higher PCE of 16.8% compared to PM6-based PSCs (PCE = 15.6%). This increase is mainly attributed to higher crystallinity and hole mobility of the PM6-DTzB10. In addition, the PM6-DTzB10:SMA blend exhibits decreased domain size and purity compared to those of the reference PM6:SMA blend. This improved morphology of the PM6-DTzB10:SMA blend contributes to enhanced thermal stability and mechanical robustness through the formation of large donor–acceptor interfaces. Under continuous heating at 100 °C for 100 h, PM6-DTzB10-based PSCs maintain 88% of the initial PCE and exhibit enhanced thermal stability compared to PM6-based PSCs retaining 72% of the initial PCE. Moreover, the PM6-DTzB10:Y6-BO blend film exhibits remarkably enhanced stretchability with a higher crack onset strain (COS) value of 11.7%, compared to the PM6:Y6-BO blend film (COS = 1.7%). This study highlights the importance of selecting the third unit in terpolymer  $P_D$ s to simultaneously enhance the  $P_D$  crystallinity and  $P_D$ –SMA interaction for achieving highly efficient and stable PSCs.

## 2. Results and discussion

### 2.1. Synthesis and characterization of materials

To explore the impact of the incorporated DTzB unit in the  $P_D$  chain on polymer properties and photovoltaic performance, PM6-DTzBX ( $X = 5, 10, \text{ and } 20$ ) terpolymers were synthesized. Here,  $X$  represents the molar fraction of the DTzB unit relative to the benzodithiophene (BDT) unit in the  $P_D$  backbone. The planar-structured DTzB unit was chosen to yield the PM6-DTzBX terpolymers for several reasons. (1) The nitrogen atoms in the DTzB unit can effectively enhance the polarity of the resulting polymers, reducing the thermodynamic immiscibility between the PM6-DTzBX terpolymers and SMAs.<sup>41,48</sup> (2) The thiazole units in the DTzB block promote strong N–S noncovalent bonding with thiophene, enhancing intra- and inter-molecular interactions between  $P_D$ s.<sup>42</sup> (3) Importantly, the DTzB unit has a fused ring structure without an alkyl solubilizing group, which helps to reinforce the backbone planarity of the PM6-DTzBX terpolymers.<sup>49,50</sup> These factors can synergistically improve the crystallinity of the  $P_D$ , thereby enhancing its charge-transporting capability.

Fig. 1a presents the chemical structures of the  $P_D$  and 2,2'-(2Z,2'Z)-((12,13-bis(2-butyloctyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-*e*]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*]indole-2,10-diyl)



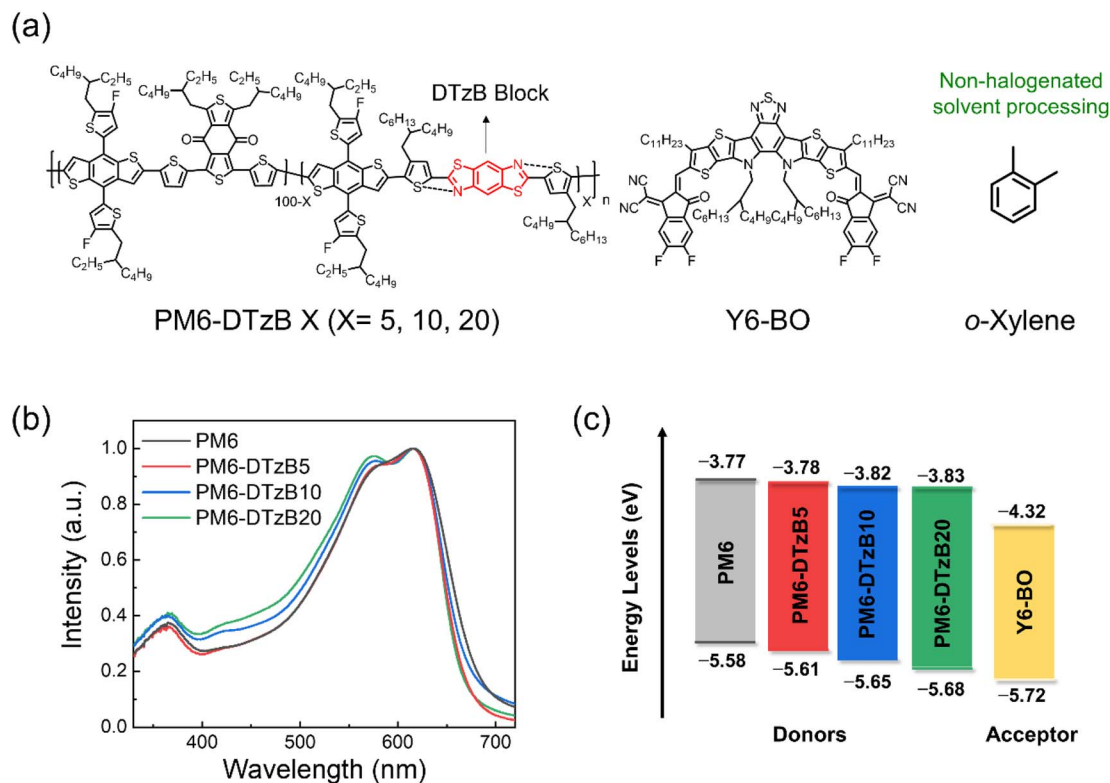


Fig. 1 (a) Chemical structures of the materials and a processing solvent used in this study. (b) UV-vis absorption spectra of  $P_D$  films. (c) Energy levels of the materials used in this study.

bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (Y6-BO) SMA. Y6-BO was selected as a SMA due to its excellent light absorption ability, electron mobility, and sufficient solubility in processing solvents including *o*-xylene. The synthetic details of the DTzB monomer and  $P_D$ s are provided in the Experimental section of the ESI (Fig. S1 and S2<sup>†</sup>). All  $P_D$ s were synthesized to have similar number-average molecular weight ( $M_n$ ) values ranging from 46 to 49 kg mol<sup>-1</sup> (Table 1). We also confirmed that all  $P_D$ s exhibited sufficient solubility in *o*-xylene (>40 mg mL<sup>-1</sup>).

Ultraviolet-visible (UV-vis) absorption spectra of the  $P_D$ s in film and solution are shown in Fig. 1b and S3,<sup>†</sup> respectively. Interestingly, with an increase in the quantity of DTzB units within the  $P_D$  backbone,  $P_D$ s exhibited enhanced light absorption in a broad range spectrum, including wavelengths from 400 to 550 nm. While the maximum absorption wavelengths ( $\lambda_{\text{max}}^{\text{film}}$ ) of

the  $P_D$ s were similar in a range of 615–617 nm, the wavelengths at their absorption edges ( $\lambda_{\text{max}}^{\text{edge}}$ ) gradually blue-shifted with increasing DTzB content in the  $P_D$ s. For example, the  $\lambda_{\text{max}}^{\text{edge}}$ s of PM6, PM6-DTzB5, PM6-DTzB10, and PM6-DTzB20 were 685, 678, 677, and 673 nm, respectively. As a result, the optical bandgap ( $E_g^{\text{opt}}$ ) of the  $P_D$ s gradually increased with increasing content of the DTzB units (Table 1). The frontier molecular orbital energy levels of the  $P_D$ s were measured by cyclic voltammetry (Fig. 1c and S4<sup>†</sup>). Increasing the content of DTzB units gradually downshifted the highest occupied molecular orbital (HOMO) energy levels of the  $P_D$ s. For example, the HOMO energy levels of PM6, PM6-DTzB5, PM6-DTzB10, and PM6-DTzB20 were –5.58, –5.61, –5.65, and –5.68 eV, respectively. Energy levels, which were estimated from density functional theory (DFT) calculations performed at the B3LYP/6-31G(d,p) level, supported the energy level trend observed in CV measurements (Fig. S5<sup>†</sup>). For example,

Table 1 Properties of the materials used in this study

Material	$M_n(D)^a$ [kg mol <sup>-1</sup> ]	$\lambda_{\text{max}}^{\text{film}b}$ [nm]	$\epsilon_{\text{max}}^{\text{film}} [\times 10^5 \text{ cm}^{-1}]$	$\lambda_{\text{film}}^{\text{edge}b}$ [nm]	$E_g^{\text{opt}c}$ [eV]	$E_{\text{HOMO}}^d$ [eV]	$E_{\text{LUMO}}^e$ [eV]
PM6	48.8 (2.6)	615	0.64	685	1.81	–5.58	–3.77
PM6-DTzB5	46.0 (2.5)	615	0.63	678	1.83	–5.61	–3.78
PM6-DTzB10	47.8 (3.6)	617	0.65	677	1.83	–5.65	–3.82
PM6-DTzB20	45.9 (3.2)	617	0.62	673	1.84	–5.68	–3.83
Y6-BO	—	829	1.13	886	1.40	–5.72	–4.32

<sup>a</sup> Determined by gel permeation chromatography eluting in 1,2,4-trichlorobenzene relative to polystyrene standards. <sup>b</sup> Estimated from the UV-vis spectra of the thin film state spin-coated from the *o*-xylene solution. <sup>c</sup> Estimated from the absorption onsets in thin films spin-coated from the *o*-xylene solution using  $E_g^{\text{opt}} = 1240/\lambda_{\text{film}}^{\text{edge}}$ . <sup>d</sup> Calculated from the cyclic voltammetry spectra. <sup>e</sup> LUMO = HOMO +  $E_g^{\text{opt}}$ .

the BDT-DTzB structure possessed a lower HOMO energy level ( $-5.24$  eV) compared to that of the BDT-BDD structure (HOMO =  $-5.15$  eV) in the simulation.<sup>41,44</sup> In addition, the BDT-DTzB structure exhibited a larger bandgap value ( $E_g = 2.92$  eV) than the BDT-BDD structure ( $2.71$  eV). Therefore, the downshifted HOMO energy levels of the  $P_D$ s are attributed to the strong electron-withdrawing properties of DTzB units and an increased bandgap of the polymers. The down-shifted HOMO energy levels of the  $P_D$ s are advantageous in achieving high  $V_{oc}$  of the PSCs.

The aggregation properties of the  $P_D$ s were investigated by measuring temperature-dependent UV-vis absorption spectra in *o*-xylene solution (Fig. S6†). The degree of aggregation was quantified by comparing the ratio of maximum intensity at  $100$  °C to that at  $20$  °C ( $I_{max}^{100\text{ °C}}/I_{max}^{20\text{ °C}}$ ). PM6-DTzB  $P_D$ s showed stronger aggregation ( $I_{max}^{100\text{ °C}}/I_{max}^{20\text{ °C}} = 0.84\text{--}0.88$ ) compared to PM6  $P_D$  ( $I_{max}^{100\text{ °C}}/I_{max}^{20\text{ °C}} = 0.77$ ) (Table S1†). This result suggests that introducing the DTzB unit into the  $P_D$  backbone enhances the intermolecular interaction between  $P_D$  chains, leading to a higher degree of aggregation.<sup>41</sup>

The crystalline properties of neat  $P_D$  films were investigated using grazing incidence X-ray scattering (GIXS). In the GIXS 2D image and line-cut profiles, all  $P_D$ s predominantly exhibited a face-on packing orientation, as evidenced by distinct (100)

peaks in the in-plane (IP) direction and (010) peaks in the out-of-plane (OOP) direction (Fig. S7 and S8†).<sup>51</sup> For a quantitative comparison of the relative crystallinity of the  $P_D$ s, their coherence length ( $L_c$ ) values for the (010) scattering peaks in the OOP direction ( $L_{c(010)}$ ) were estimated using Scherrer's equation (Table S2†).<sup>52</sup> Interestingly,  $P_D$ s containing DTzB units exhibited higher  $L_{c(010)}$  values ( $1.2$  nm for PM6-DTzB10 and  $1.3$  nm for PM6-DTzB20) than PM6 ( $L_{c(010)} = 0.6$  nm), suggesting relatively larger crystal sizes in the film. The higher crystallinity of PM6-DTzB  $P_D$ s compared to PM6 may be attributed to their stronger aggregation in solution, which helps forming well-ordered intermolecular assemblies during the film formation by solution processing.<sup>53</sup>

The charge transport abilities of  $P_D$  films were assessed by measuring the space charge limited current (SCLC) (Table S3†). The hole mobilities ( $\mu_{hs}$ ) of neat  $P_D$ s gradually increased with increasing DTzB content. For example, the  $\mu_{hs}$  of PM6, PM6-DTzB10, and PM6-DTzB20 were  $1.36 \times 10^{-4}$ ,  $1.63 \times 10^{-4}$ , and  $1.72 \times 10^{-4}$   $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ , respectively. The enhanced electrical properties of the DTzB-containing  $P_D$ s compared to PM6 correlate with their enhanced aggregation and crystalline properties. It is notable that, while most random terpolymer-type  $P_D$ s exhibited reduced crystalline and electrical properties

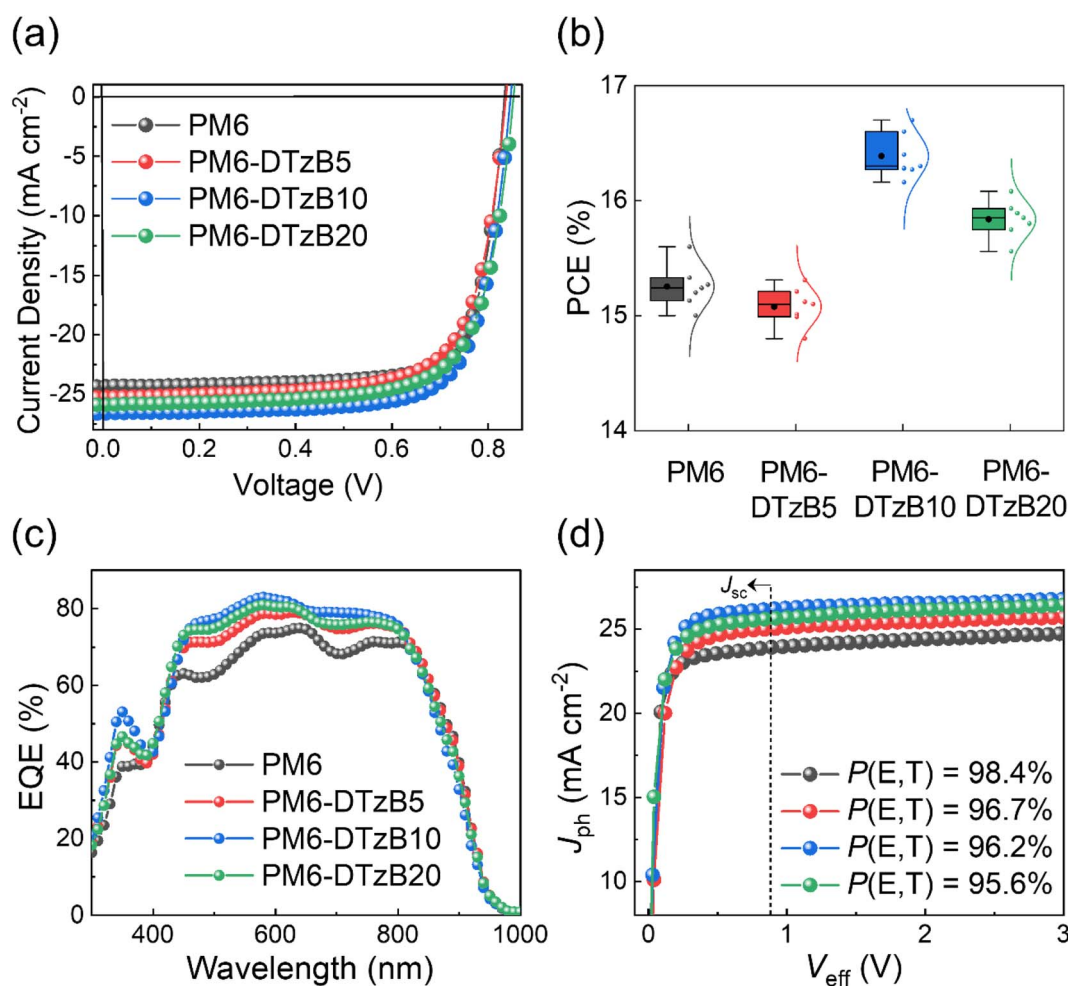


Fig. 2 (a)  $J$ - $V$  curves, (b) PCE distributions, (c) EQE spectra, and (d)  $J_{ph}$ - $V_{eff}$  curves of  $P_D$ :Y6-BO PSCs.





compared to the alternating copolymers owing to reduced structural regularity,<sup>23,36,54</sup> incorporation of the DTzB units does not compromise those properties.

## 2.2. Photovoltaic properties

The photovoltaic properties of all  $P_D$ :Y6-BO systems were investigated by fabricating conventional-type PSCs. The device architecture and fabrication procedure of PSCs are described in the Experimental section of the ESI.† All  $P_D$ :Y6-BO PSCs were processed in the *o*-xylene solvent. The current density-voltage ( $J$ - $V$ ) curves are shown in Fig. 2, and the corresponding photovoltaic parameters of the PSCs are presented in Table 2. Notably, the introduction of the DTzB unit instead of the BDD unit into PM6  $P_D$  sequentially increased the open-circuit voltage ( $V_{oc}$ ) of PSCs (0.830 V for PM6, 0.839 V for PM6-DTzB5, 0.842 V for PM6-DTzB10, and 0.856 V for PM6-DTzB20). This  $V_{oc}$  trend is correlated with the lower HOMO levels of DTzB-incorporating  $P_D$ s than PM6 (Table 1). As a result, PM6-DTzB10-based PSCs exhibited a higher PCE (16.8%) than that of the control  $P_D$  (PM6, 15.6%), mainly owing to a higher  $V_{oc}$  value (0.842 V) and  $J_{sc}$  of 25.14 mA cm<sup>-2</sup>, in comparison to PM6-based PSCs ( $J_{sc}$  = 24.03 mA cm<sup>-2</sup>). However, a further increase in the content of DTzB units led to a decreased PCE value (16.1% for PM6-DTzB20:Y6-BO). The PCE distributions of PSCs fitted with Gaussian functions are displayed in Fig. 2b, indicating that all systems showed consistent PCEs. The external quantum efficiency (EQE) spectra of the PSCs are shown in Fig. 2c. The PM6-DTzB-based PSCs exhibited higher EQE responses in both the  $P_D$  absorption range (400–650 nm) and SMA absorption range (650–900 nm). This result supports higher  $J_{sc}$  values in DTzB-incorporating  $P_D$ :Y6-BO PSCs than PM6:Y6-BO PSCs. The calculated  $J_{sc}$  values matched well with the  $J_{sc}$ s measured from the PSCs with errors within 2% (Table 2).

To elucidate the origin of the different photovoltaic properties, we investigated the charge generation, dissociation, transport, and recombination behaviors of the  $P_D$ :Y6-BO blends. To investigate charge generation behaviors, the free charge carrier generation rate ( $G(E,T)$ ) of the PSCs was evaluated. The  $G(E,T)$  can be determined from the maximum exciton generation rate ( $G_{max}$ ) and exciton dissociation probability ( $P(E,T)$ ).<sup>55</sup> The calculation procedure of  $G_{max}$ ,  $P(E,T)$  and  $G(E,T)$  is described in the Experimental section of the ESI.† The incorporation of an appropriate proportion of DTzB in  $P_D$ s increased the  $J_{sat}$  and  $G_{max}$  of the blend film. For example, the  $G_{max}$  values of the PM6-DTzB5-, PM6-DTzB10-, and PM6-DTzB20-based blends were 1.89, 1.97 and 1.94 cm<sup>-3</sup> s<sup>-1</sup>,

respectively, surpassing that of the PM6 based blend (1.81 cm<sup>-3</sup> s<sup>-1</sup>). Therefore, the  $G(E,T)$  values of the PM6-DTzB-based blends were higher than that of the PM6-based blend (Fig. 2d and Table S4†). This result indicates that the incorporation of the DTzB unit in the  $P_D$  facilitates the charge generation and contributes to a higher  $J_{sc}$  during PSC operation.

The charge recombination properties of the PSCs were investigated by measuring their light intensity ( $P$ )-dependent  $J_{sc}$  and  $V_{oc}$  values (Fig. S9†).<sup>56</sup> All the blends exhibited similar slopes ( $\alpha$ ) in the  $\log J_{sc}$ - $\log P$  plots, indicating similar bimolecular recombination properties. The slope ( $S$ ) in the  $V_{oc}$ - $\log P$  plots exhibited comparable values in PM6- (1.10 kT  $q^{-1}$ ) and PM6-DTzB10-based PSCs (1.09 kT  $q^{-1}$ ), indicating that the introduction of an appropriate amount of DTzB does not cause monomolecular/trap-assisted recombination.<sup>57</sup> The SCLC hole and electron mobilities of the  $P_D$ :Y6-BO blend films were measured to evaluate their charge transport abilities (Table S5†). All the blends showed similar  $\mu_h$  values ( $2.1$ – $2.3 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). Interestingly, the electron mobility ( $\mu_e$ ) was the highest in the PM6-DTzB10 blend ( $1.55 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) among all blends, resulting in the most balanced mobility ratio ( $\mu_h/\mu_e$  = 1.50) compared to other blends.<sup>58</sup>

## 2.3. Structural and morphological properties

The morphological properties of the  $P_D$ :Y6-BO blends were analyzed using GIXS, resonant soft X-ray scattering (RSOXS), and *in situ* UV-vis spectroscopy. We first measured the GIXS profiles of a neat Y6-BO film (Fig. S10 and S11†). Interestingly, the GIXS 2D image and line-cut profile of the Y6-BO neat film exhibited a much sharper and more distinct (010) peak along the OOP direction after annealing, which is attributed to its strong crystalline property. Subsequently, the GIXS profiles of the  $P_D$ :Y6-BO blend films were compared (Fig. 3a, b and S12†). All  $P_D$ :Y6-BO blend films displayed IP (100) and OOP (010) peaks around  $q_{xy}$  = 0.28–0.29 Å<sup>-1</sup> and  $q_z$  = 1.45–1.95 Å<sup>-1</sup>, respectively. Therefore, we assessed the relative degree of crystallinity (rDoC) of the (010) peaks of the  $P_D$ :Y6-BO blend films in the blend GIXS profiles (Fig. 3b and Table 3). The  $r$ -DoC<sup>(010)</sup> values increased in the following order: PM6:Y6-BO (0.65) < PM6-DTzB10:Y6-BO (0.87) < PM6-DTzB20:Y6-BO (1.00).<sup>59</sup>

To investigate the degree of phase separation between the  $P_D$  domain and Y6-BO domain, RSOXS measurements were performed, using a beam energy of 285.0 eV to maximize the contrast between the components in the blend films (Fig. 3c). The domain size and relative domain purity ( $r$ -DP) of the blends were estimated from their RSOXS profiles. Both the PM6:Y6-BO

Table 2 Photovoltaic performances of  $P_D$ :Y6-BO PSCs

$P_D$	$V_{oc}^a$ [V]	$J_{sc}^a$ [mA cm <sup>-2</sup> ]	Cal. $J_{sc}^b$ [mA cm <sup>-2</sup> ]	FF <sup>a</sup>	PCE <sub>max</sub> (avg) <sup>a</sup> [%]
PM6	0.830	24.03	23.53	0.76	15.60 (15.13 ± 0.18)
PM6-DTzB5	0.839	24.59	24.33	0.73	15.37 (15.04 ± 0.21)
PM6-DTzB10	0.842	25.14	25.19	0.76	16.81 (16.14 ± 0.27)
PM6-DTzB20	0.856	25.02	24.65	0.74	16.08 (15.73 ± 0.18)

<sup>a</sup> Average values were obtained from 10 independent devices. <sup>b</sup> Calculated from EQE profiles.



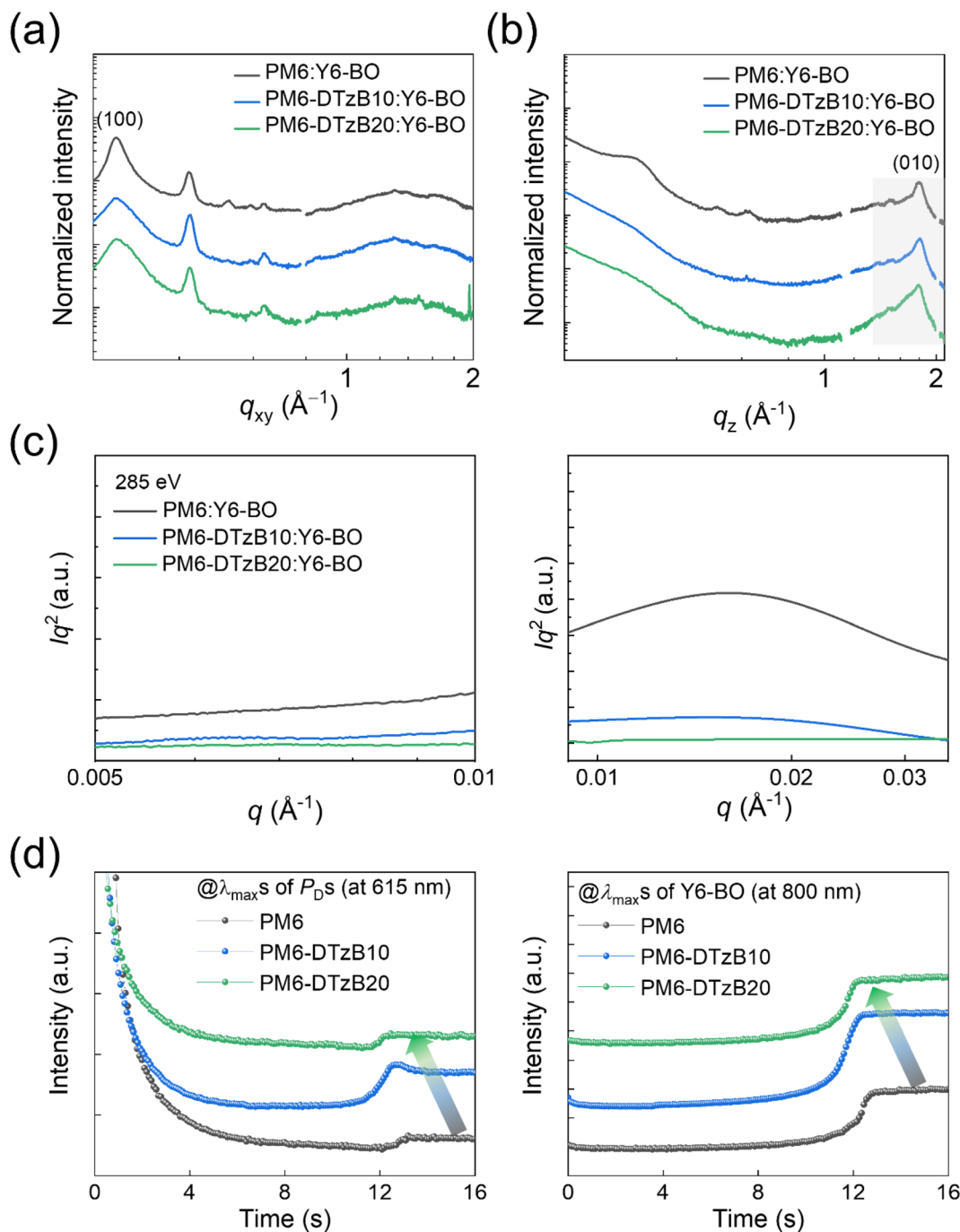


Fig. 3 GIAXS line-cut profiles of  $P_D$ :Y6-BO blends in (a) the IP and (b) OOP directions. (c) RSoXS profiles of  $P_D$ :Y6-BO blends. (d) Time evolution of the UV-vis absorption intensity change of  $P_D$ :Y6-BO blends at 615 and 800 nm, respectively, during spin-coating.

blend (37.2 nm) and PM6-DTzB10:Y6-BO blend (33.1 nm) exhibited appropriate domain sizes for charge transport, while the PM6-DTzB20:Y6-BO blend showed no distinguishable peak. The  $r$ -DP was significantly higher for the PM6:Y6-BO blend (1.00) compared to the PM6-DTzB10-based blend (0.58) and PM6-DTzB20-based blend (0.50) (Table 3). A large interfacial area between donor and acceptor domains in a blend film is advantageous for charge generation and exciton dissociation. Therefore, the well-intermixed domain in the PM6-DTzB10:Y6-BO blend facilitates both higher  $J_{sc}$  and FF values compared

to other blends.<sup>60–63</sup> At the same time, the incorporation of the DTzB unit into the PM6-DTzB  $P_D$ s increased their crystalline properties, enhancing the charge transport properties and the PCE values in the PSCs. However, the PM6-DTzB20:Y6-BO blends exhibited an excessive amount of intermixed domains with lower domain size and purity, resulting in decreases of charge transport properties and photovoltaic performance.

The *in situ* UV-vis absorption measurements during the spin coating process were performed to investigate the film formation kinetics of different  $P_D$ :SMA blend systems and understand



Table 3 Morphological characteristics of  $P_D$ :Y6-BO blends

$P_D$	$r$ -DOC <sup>(010)</sup> <sup>a</sup>	Domain size <sup>b</sup> [nm]	$r$ -DP <sup>b</sup>	$t_{\text{sat}}$ at $\lambda_{\text{max}}$ of $P_D$ <sup>c</sup> [s]	$t_{\text{sat}}$ at $\lambda_{\text{max}}$ of Y6-BO <sup>c</sup> [s]
PM6	0.65	37.2	1	13.2	12.8
PM6-DTzB10	0.87	33.1	0.58	12.6	12.4
PM6-DTzB20	1	—	0.50	12.4	12.2

<sup>a</sup> Estimated from the OOP (010) peak of GIXS line-cut profiles in the range of 1.45–1.95 Å<sup>−1</sup>. <sup>b</sup> Estimated from the RSoXS profiles. <sup>c</sup> Estimated from the *in situ* UV-vis spectroscopy profiles of  $P_D$ :Y6-BO blends.

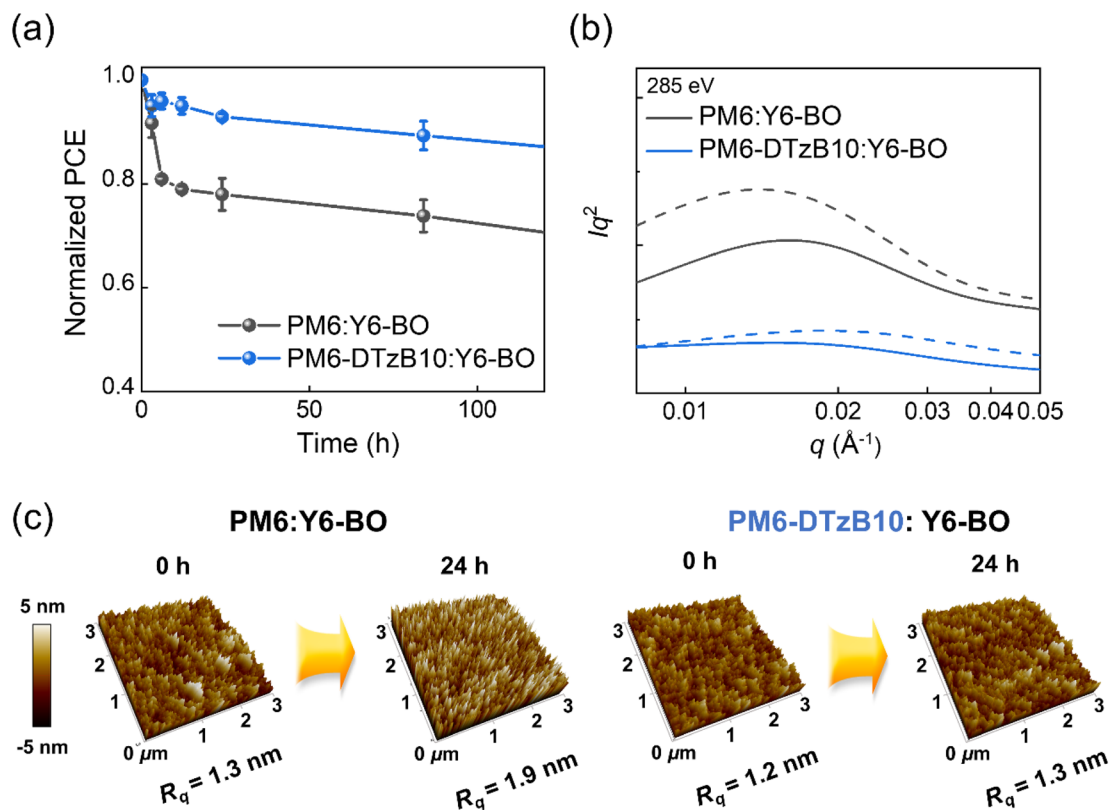


Fig. 4 (a) Thermal stability of  $P_D$ :Y6-BO PSCs under a 100 °C heating condition. (b) RSoXS profiles of the  $P_D$ :Y6-BO blend in the initial state (solid line) and after (dotted line) thermal annealing at 100 °C for 72 h. (c) AFM height images of  $P_D$ :Y6-BO blend films before (left) and after (right) thermal annealing at 100 °C for 24 h. Each image size is 3  $\mu\text{m}$   $\times$  3  $\mu\text{m}$ .

its impact on the blend morphology (Fig. 3d, S13,† and Table 3). Extended quenching time in film solidification generally leads to a higher degree of liquid–liquid phase separation, typically resulting in more distinct phase separation between  $P_D$  and SMA domains.<sup>64</sup> The saturation times ( $t_{\text{sat}}$ s) in the absorption intensities at the maximum absorption wavelengths ( $\lambda_{\text{max}}$ ) of  $P_D$ s and Y6-BO were tracked. At the  $\lambda_{\text{max}}$  of  $P_D$ s,  $t_{\text{sat}}$  values decreased in the following sequence: PM6 (13.2 s) > PM6-DTzB10 (12.6 s) > PM6-DTzB20 (12.4 s). These reduced  $t_{\text{sat}}$  values of PM6-DTzB  $P_D$ s could be attributed to the stronger aggregation of PM6-DTzB  $P_D$ s in *o*-xylene solvent compared to PM6, as shown in Fig. S6.† Similarly, the  $t_{\text{sat}}$  value of Y6-BO in the blend solution also followed a decreasing trend: PM6 (12.8 s) > PM6-DTzB10 (12.4 s) > PM6-DTzB20 (12.2 s). These results suggest that the incorporation of DTzB into the  $P_D$ s accelerated the solidification of both the  $P_D$  and Y6-BO domains during film

formation. This acceleration mitigates excessive phase separation and promotes the development of sufficiently intermixed domains.

To further investigate the changes in the molecular compatibility between the  $P_D$  and SMA depending on the terpolymer structure, we conducted contact angle measurements to estimate the interfacial tensions between the  $P_D$  and SMA (Fig. S14 and Table S6†).<sup>65,66</sup> The contact angles of water droplets on neat  $P_D$  films decreased in the order of PM6 (103.1°) > PM6-DTzB10 (100.9°) > PM6-DTzB20 (99.5°). Correspondingly, the surface tension values of  $P_D$ s linearly increased from PM6 (19.2 mN m<sup>−1</sup>) to PM6-DTzB10 (20.5 mN m<sup>−1</sup>) and finally to PM6-DTzB20 (21.2 mN m<sup>−1</sup>). These results are consistent with the previous studies where polymers containing DTzB units, such as PBB1 and PBB2 polymers, exhibited higher hydrophilicity than the reference polymers PM6 and PM7.<sup>41,43</sup> The surface tension value of the Y6-



BO SMA film was measured to be  $24.8 \text{ mN m}^{-1}$ . Thus, interfacial tension ( $\gamma^{\text{D-A}}$ ) values between the  $P_D$  and Y6-BO decreased sequentially in the order of PM6:Y6-BO (0.79), PM6-DTzB10:Y6-BO (0.50), and PM6-DTzB20:Y6-BO blends (0.38). This result supports the view that the inclusion of DTzB units into the  $P_D$ s reduces molecular incompatibility with the Y6-BO SMA, thereby thermodynamically facilitating the formation of larger donor-acceptor interfaces and intermixed domains.

#### 2.4. Thermal stability

Next, to assess the influence of the polymer structure on the thermal stability of PSCs, the changes in the PCEs of both PM6- and PM6-DTzB10-based PSCs were monitored under continuous heating at  $100^\circ\text{C}$  (Fig. 4a). The difference in PCE changes

between the two blend systems was evident. This degradation was mainly attributed to the unstable initial morphology associated with the poor miscibility between the PM6  $P_D$  and SMA.<sup>67,68</sup> PM6:Y6-BO-based PSCs showed a notable PCE decrease within 24 hours, maintaining less than 80% of their initial efficiency (PCE = 12.0%). In contrast, PM6-DTzB10:Y6-BO-based PSCs retained 93% of their initial PCE (PCE = 15.6%) under identical conditions.<sup>33,69,70</sup>

To elucidate the difference in thermal stability, morphological changes during the thermal annealing were compared through RSoXS and atomic force microscopy (AFM) measurements (Fig. 4 and Table S7†). RSoXS profiles revealed significant phase separation in the PM6:Y6-BO blend under thermal stress, with  $r$ -DP increasing from 0.65 to 1.00 (Fig. 4b). In contrast, the PM6-DTzB10:Y6-BO blend maintained a relatively consistent

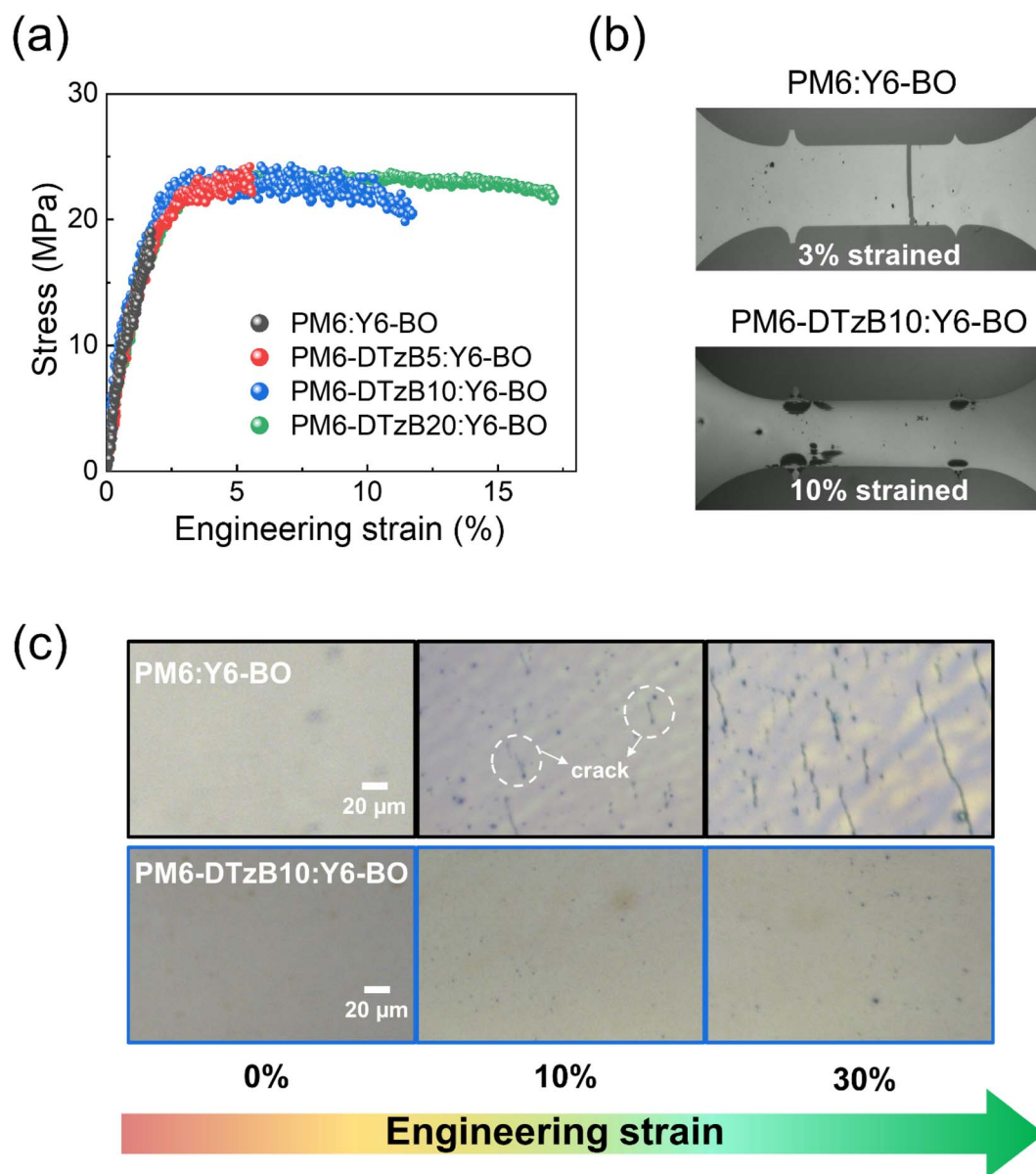


Fig. 5 (a) Stress-strain curves of  $P_D$ :Y6-BO blend films. Optical microscope (OM) images of the blend films (b) during the tensile test and (c) on TPU substrates under stretching.





domain purity ( $\sim 0.4$ ), both before and after thermal annealing.<sup>71,72</sup> This consistency suggests that the PM6-DTzB10:Y6-BO blend preserved its initial morphology mainly due to enhanced  $P_D$ -SMA interaction and more strongly developed crystalline domains. Also, a similar trend was observed in their AFM height images. The root-mean-square averaged roughness ( $R_q$ ) value of the PM6:Y6-BO blend increased from 1.3 to 1.9 nm after 24 h of heating. The increased  $R_q$  values and the formation of agglomerates on the PM6:Y6-BO blend are indicative of its unstable initial blend morphology. In contrast, the PM6-DTzB10:Y6-BO blend exhibited almost the same  $R_q$  value from 1.2 to 1.3 nm under identical heating conditions. These results confirm that the PM6-DTzB10:Y6-BO-based PSCs maintain their initial PSC performance under thermal stress by preserving their blend morphology.<sup>73</sup>

### 2.5. Mechanical properties

The mechanical robustness of the PSCs is a critical factor for their application as power suppliers in wearable devices.<sup>74,75</sup> At first, we evaluated the stretchability of neat  $P_D$  films using a pseudo free-standing tensile test (Fig. S15 and Table S8†).<sup>76,77</sup> Interestingly, both the COS value and toughness were enhanced with the incorporation of the DTzB unit into the  $P_D$  backbone. Specifically, the COS values increased in the following order: PM6 (16.9%) < PM6-DTzB5 (20.7%) < PM6-DTzB10 (23.1%) < PM6-DTzB20 (28.0%) films. This improvement in the mechanical properties in the PM6-DTzB  $P_D$  could be attributed to its random terpolymer structure and increased intermolecular interaction between  $P_D$ s, compared to PM6  $P_D$ .

Next, we compared the stretchability of the  $P_D$ :Y6-BO blend films (Fig. 5a and Table S9†). All active layers were spin-coated using the same process for device fabrication. Since the SMA molecules typically exhibit unconnected brittle domains due to their inherent rigid structure, it is important to dissipate mechanical stress to prevent crack propagation in the SMA domains and at the interfaces between the  $P_D$  and SMA domains.<sup>78</sup> For example, the PM6:Y6-BO exhibited a relatively low COS of only 1.7%. In contrast, well-intermixed  $P_D$ :SMA domains have advantages in enhancing the film stretchability.<sup>23</sup> With an increasing content of the DTzB unit, the COS value increased from 5.5% for PM6-DTzB5:Y6-BO, to 11.7% for PM6-DTzB10:Y6-BO, and 17.0% for PM6-DTzB20:Y6-BO. Similarly, the toughness values also increased in the order of  $0.2 \text{ MJ m}^{-3}$  for PM6:Y6-BO,  $1.0 \text{ MJ m}^{-3}$  for PM6-DTzB5:Y6-BO,  $2.5 \text{ MJ m}^{-3}$  for PM6-DTzB10:Y6-BO, and  $3.7 \text{ MJ m}^{-3}$  for PM6-DTzB20:Y6-BO. Fig. 5b shows the optical microscope (OM) images of the PM6:Y6-BO and PM6-DTzB10:Y6-BO blend films upon stretching during a tensile test. The PM6:Y6-BO blend showed distinct crack formation even at a small strain of 3%. In contrast, the PM6-DTzB10:Y6-BO blend displayed plastic deformation without any observable cracks at a strain of 10%. This improvement in mechanical properties of DTzB-incorporated  $P_D$ -based blends is mainly attributed to the presence of a larger fraction of intermixed  $P_D$ :SMA domains, which effectively dissipates mechanical stress and suppresses crack propagation. Especially, the PM6-DTzB10:Y6-BO blend and PM6-DTzB20:Y6-

BO blend contained more intermixed blend domains than the PM6:Y6-BO blend, as shown in RSoXS profiles (Fig. 3c). These well-intermixed  $P_D$ :SMA blend domains can facilitate the dissipation of mechanical stress on the brittle Y6-BO domains and at fragile  $P_D$ :SMA interfaces.<sup>23</sup>

Additionally, the crack formation behavior while stretching the  $P_D$ :Y6-BO blend films on the thermoplastic polyurethane (TPU) substrate was compared to assess the potential of the DTzB-incorporated  $P_D$ s in stretchable PSC applications (Fig. 5c).<sup>79–81</sup> For the PM6:Y6-BO blend, cracks were clearly observed at only 10% strain and rapidly propagated under 30% strain, despite the stress dissipation from the elastomer support. In contrast, the PM6-DTzB10:Y6-BO blend film did not show any visible cracks during stretching up to 30% strain.

## 3. Conclusions

We developed a series of PM6-DTzB terpolymers by introducing the planar structured DTzB unit into the PM6  $P_D$  backbone and achieved efficient, thermally-stable, and mechanically robust PSCs by non-halogenated solvent processing. The introduction of an appropriate amount of the DTzB unit into the  $P_D$  backbone resulted in improved molecular compatibility with the Y6-BO SMA as well as enhanced crystalline and electrical transport abilities of the  $P_D$  film. This led to the formation of the blend morphology with sufficient  $P_D$ :SMA intermixed domains as well as well-developed crystalline domains of  $P_D$ s and SMAs, enhancing both the charge generation and transport properties in the PSCs. Therefore, PM6-DTzB10:Y6-BO PSCs exhibited a higher PCE of 16.8% compared to that of PM6:Y6-BO PSCs (PCE = 15.6%) with solution processing in *o*-xylene. The optimized blend morphology of the PM6-DTzB10:Y6-BO was also beneficial in suppressing the burn-in degradation of PSCs while significantly improving the stretchability of the active layer. The PM6-DTzB10-based PSCs showed a higher thermal stability against annealing at 100 °C than the PM6-based PSCs. Moreover, the PM6-DTzB10:Y6-BO blend films demonstrated superior mechanical properties, exhibiting 7 times higher stretchability (COS = 11.7%) compared to the PM6-based blend (COS = 1.7%).

## Author contributions

S. S. and H. J. contributed equally to this work. S. S. and H. J. conceptualized this research, performed the investigation, and wrote the original draft. E. S. O., C. L., T. H.-Q. N., and T. N.-L. P. supported the investigation. J.-W. L., D. J., M. J. L., and T.-S. K. supported editing the draft. B. J. K. led data curation, project administration, funding acquisition, and editing the draft.

## Conflicts of interest

The authors declare no conflict of interest.

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