

Benzobisthiazole Polymer with Resonance-assisted Hydrogen Bonds for High-performance Transistor and Solar Cell Applications

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Electronic Supplementary Information

Abstract Benzobisthiazole polymer with resonance-assisted hydrogen bonds (RAHBs) has been synthesized for both organic field-effect transistor and polymer solar cell applications. The properties of the hydrogen bonded polymer are compared with the reference polymer without RAHBs. Single-crystal X-ray diffraction analyses of the building block reveal that the RAHB interactions are formed between the carbamate hydrogen and imine nitrogen of the thiazoles. The hydrogen donor and acceptor are connected by π -conjugated molecular framework and the hydrogen-bridged quasi aromatic rings lock the conformation of the building block. The building block adopted a layered sandwich packing in crystal instead of slipped herringbone stacking which was often found in the crystal of benzobisthiazole derivatives. The polymer **PCBTZ-TT** with RAHBs showed deeper HOMO/LUMO energy level (about 0.2 eV) than reference polymer. The **PCBTZ-TT** demonstrated the hole mobility of $0.96 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in field-effect transistor devices and achieved power conversion efficiency of 13.6% in solar cell devices with **Y6** as acceptor without any additive.

Keywords Resonance-assisted hydrogen bonding; Benzobisthiazole; Thiazole; OFET; OPV

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INTRODUCTION

Conjugated polymers have attracted great attention as semiconducting materials for applications in electronic devices, such as, organic field-effect transistors (OFETs), organic solar cells (OSCs) and various sensors.^[1–4] The conjugated polymers are aromatic/unsaturated units linked by single bonds.^[2] The free rotation of the single bonds often causes conformational disorder in the main chain, which can limit the delocalization of π electrons.^[5] So, conformational control has always been the key issue in the design and synthesis of conjugated polymers.^[6] Coplanar structure can enhance π -electron delocalization, facilitate inter-chain interactions, and reduce the energy band

gap of polymer.^[7]

Thiazole with electron-withdrawing imine nitrogen is widely studied as replacement for thiophene in conjugated polymers.^[8–10] Thiazole is electron deficient compared with thiophene.^[11] Therefore, thiazole polymers show improved chemical stability against p-doping in ambient.^[8,12–14] The absence of hydrogen atom on one of the β -positions in the thiazole could relieve some steric hinder between the repeating units, resulting in improved coplanarity.^[6] Recently, we found that the imine nitrogen atoms in thiazolothiazole were good hydrogen acceptors for intramolecular hydrogen bonds.^[15] When hydrogen donor and acceptor are connected by π -conjugated molecular framework, these π -resonance-assisted hydrogen bonds can be significantly stronger (3–5 times) than classical hydrogen bonds, and show substantial covalent characteristic.^[16] Gilli suggested the synergism of π -electron delocalization and H-bonding as one of the main features of this type resonance-assisted hydrogen bonding (RAHB).^[17–21] This concept which connected π -conjugation and hydrogen bonding has found important applica-

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tions in chemistry and life science.^[16,22] The study on thiazolo-thiazole-based conjugated polymers has demonstrated that RAHB had a profound influence on the packing motifs of repeating units, optical and redox properties of the semiconducting polymers.^[15] Benzobisthiazole (**BTZ**) with a benzene ring inserted between two thiazoles is a large ring-fused hetero-arene.^[23] The **BTZ** compounds often show strong intermolecular π - π stacking interactions and long-range ordered because of extended planar structure and sulfur/nitrogen intermolecular contacts.^[24] It has been studied as building blocks for organic semiconducting and showed relatively low energy loss and high power conversion efficiency in solar cell devices, recently.^[25–29] However, relatively low field-effect mobility and limited solubility of **BTZ** based materials still hindered their broad applications in solution-processed organic electronics (Table S3 in the electronic supplementary information, ESI).^[30–37]

Herein, we present a new **BTZ** building block with RAHB interactions, the carbamate functionalized thiophene-benzobisthiazole-thiophene (**CBTZ**) (Fig. 1). Single-crystal X-ray diffraction analyses of the building block reveal that the RAHB interactions are formed between the carbamate hydrogen and imine nitrogen of the thiazoles. It shows completely different packing characteristics from previously reported **BTZ-TT**, which does not have hydrogen bonding (Fig. 1). The new π -conjugated polymer based on **CBTZ** has also been synthesized. The polymer **PCBTZ-TT** was compared with known polymer **PBTOT** which had the same backbone but without RAHB interactions. The introduction of RAHB reduced the optical band gap of **PCBTZ-TT** and deepened its HOMO/LUMO energy levels (~ 0.2 eV) compared with **PBTOT**. The **PCBTZ-TT** demonstrated high-performances in both organic field-effect transistors and polymer solar cells. The OFET devices based on **PCBTZ-TT** gave the highest/average hole mobility of $0.96/0.92 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, much higher than those of the devices based on the reference polymer **PBTOT** ($0.002\sim 0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). Bulk hetero-junction solar cells with **PCBTZ-TT:Y6** as active layer without any additive gave a power conversion efficiency (PCE) of 13.6% under $100 \text{ mW}\cdot\text{cm}^{-2}$ AM 1.5G sunlight illumination.

EXPERIMENTAL

General Considerations

The chemicals were reagent grade and purchased from Sigma-Aldrich, Adamas, Accela ChemBio Co., and Bide Pharmatech Ltd. Toluene and tetrahydrofuran (THF) were freshly distilled over sodium wire under a nitrogen atmosphere. 2-Formylthiophene-3-carboxylate and PEI-Zn were synthesized according to the literature.^[38] **Y6** was obtained from Solarmer Materials Inc. Flash column chromatography was performed on silica gel (300–400 mesh). Indium tin oxide (ITO)-coated glass substrates were acquired from CSG Holding Co., Ltd., Shenzhen.

^1H - and ^{13}C -NMR spectra were recorded on a Bruker 400 MHz spectrometer with tetramethylsilane as an internal reference at room temperature. Elemental analyses were carried out on an Elementar Vario EL Cube. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (MS) analyses were performed on a Bruker Autoflex. Single crystal X-ray diffraction analysis was performed on a Bruker D8 VENTURE X-ray diffractometer. UV-Vis spectra were obtained with a Perkin Elmer Lambda 20 UV-Vis spectrophotometer. Cyclic voltammetry (CV) measurements were performed with a CS-150 electrochemical analyzer under a nitrogen atmosphere in a deoxygenated anhydrous acetonitrile solution of *tetra*-butylammonium hexafluorophosphate (*n*-Bu₄NPF₆, 0.1 mol/L) at the scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$. A three-electrode cell was used in all measurements. A platinum disk electrode was used as the working electrode, a platinum wire was used as the counter electrode, and an Ag/Ag⁺ (AgNO₃, 0.01 mol·L⁻¹ in acetonitrile) electrode was used as the reference electrode. The cell was calibrated with the ferrocene/ferrocenium (Fc/Fc⁺) redox couple (4.8 eV below vacuum level) as an external standard which was measured under the same conditions before and after the measurement of samples. The polymer film was coated on the surface of a platinum disk electrode. Gel permeation chromatography (GPC) analysis of polymer was carried out on a Waters HPLC with a polystyrene gel column (Agilent PL gel 5 μm , MIXEDC) at room temperature. A polystyrene standard kit was used for calibration, and THF was used as the eluent. Thermogravimetric analyses

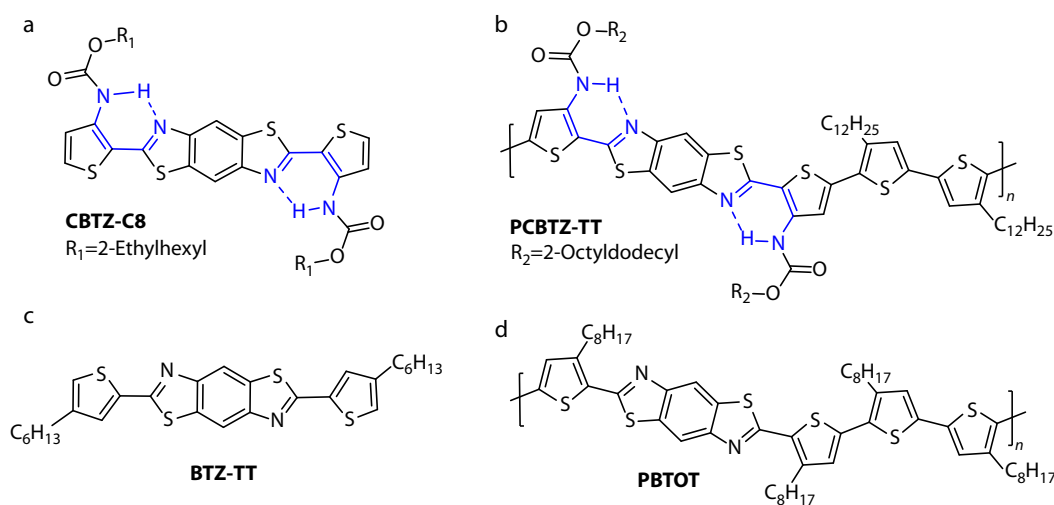


Fig. 1 Molecular structures of (a) **CBTZ-C8**, (b) **PCBTZ-TT**, (c) **BTZ-TT**, and (d) **PBTOT**.

(TGAs) was conducted with a PerkinElmer Pyris 1 at a heating rate of 20 °C·min⁻¹ under nitrogen. Atomic force microscopy (AFM) images of polymer thin-films were obtained from a Bruker JPK atomic force microscope.

Synthesis of Monomer and Polymer

Synthesis of diethyl-2,2'-(benzo[1,2-d:4,5-d']bis(thiazole)-2,6-diyl)bis(thiophene-3-carboxylate) (**1**)

Ethyl-2-formylthiophene-3-carboxylate (3.202 g, 17.401 mmol) and 2,5-dimercapto-1,4-phenylenediamine dihydrochloride (2.031 g, 8.286 mmol) were dissolved in DMSO (17.0 mL). Triethylamine (2.420 mL, 17.401 mmol) was added to the mixture. The reaction was heated to 200 °C for 5 h, and was cooled to room temperature. The precipitate was filtered and washed with ethanol to give the titled compound as a dark yellow solid (1.822 g, 44%). The crude product was used directly in next step without further purification. HRMS MALDI-TOF: *m/z* calcd. for C₂₇H₁₆Br₂N₂O₄S₄, 500.6200; Found, 501.0055.

Synthesis of 2,2'-(benzo[1,2-d:4,5-d']bis(thiazole)-2,6-diyl)bis(thiophene-3-carboxylic acid) (**2**)

A mixture of **1** (0.600 g, 1.200 mmol) and potassium hydroxide (2.020 g, 36.000 mmol) in tetrahydrofuran/1,4-dioxane/water (50.0 mL/20.0 mL/10.0 mL) was heated to 100 °C for 24 h. The solvent was evaporated under reduced pressure to approximately half of its original volume. Water (300.0 mL) was added to the solution, and the pH of the mixture was adjusted to about 5 by addition of aqueous hydrochloric acid solution (1.0 mol/L). The precipitate was filtered and washed with water to give the titled compound as a brown solid (0.488 g, 92%). ¹H-NMR (400 MHz, DMSO-d₆, δ, ppm): 8.84 (s, 2H), 7.89 (d, *J*=5.3 Hz, 2H), 7.55 (d, *J*=5.3 Hz, 2H). ¹³C-NMR (101 MHz, DMSO-d₆, δ, ppm): 164.71, 160.61, 150.12, 142.13, 136.47, 132.39, 131.46, 130.83, 115.79. HRMS MALDI-TOF: *m/z* calcd. for C₁₈H₈N₂O₄S₄, 443.9367; Found, 443.2616.

Synthesis of bis(2-octyldodecyl)(benzo[1,2-d:4,5-d']bis(thiazole)-2,6-diylbis(thiophene-2,3-diyl))di-carbamate (**CBTZ**)

Compound **2** (0.311 g, 0.700 mmol), 2-octyldodecanol (10.0 mL), triethylamine (0.390 mL, 2.800 mmol) and diphenylphosphoryl azide (DPPA) (0.43 mL, 1.820 mmol) were added to a round-bottom flask (50 mL). The mixture was stirred at 90 °C overnight. After the mixture was cooled to room temperature, a yellow precipitate was formed and collected by filtration. The solid was recrystallized in petroleum ether to a yellow powder (0.354 g, 49%). ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 10.74 (s, 2H), 8.35 (s, 2H), 7.98 (s, 2H), 7.41 (d, *J*=5.4 Hz, 2H), 4.18 (d, *J*=6.0 Hz, 4H), 1.80 (m, 2H), 1.44–1.23 (m, 68H), 0.91–0.85 (m, 12H). ¹³C-NMR (101 MHz, CDCl₃, δ, ppm): 162.73, 153.67, 150.84, 140.33, 132.27, 128.44, 122.43, 113.83, 113.77, 68.74, 37.58, 31.93, 31.39, 30.08, 29.75, 29.69, 29.65, 29.40, 29.39, 26.82, 22.70, 14.12. HRMS MALDI-TOF: *m/z* calcd. for C₅₈H₉₀N₄O₄S₄, 1034.5845; Found, 1034.5868.

Synthesis of bis(2-octyldodecyl)(benzo[1,2-d:4,5-d']bis(thiazole)-2,6-diylbis(5-bromothiophene-2,3-diyl))-dicarbamate (**CBTZ-Br**)

The bromination procedure was adopted from the literature method.^[39] **CBTZ** (0.403 g, 0.390 mmol) was dissolved in chloroform (15.0 mL) in a round-bottom flask (50 mL) and iodine (0.198 g, 0.780 mmol) was added. Bromine (0.140 g, 0.860

mmol) in chloroform (15 mL) was added to the flask. After the reaction was stirred at 25 °C for 10 h, a saturated aqueous solution of sodium hydroxide was added. The organic layer was separated and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (dichloromethane/petroleum ether=1:2, V:V) to afford an yellow powder (0.200 g, 43%). ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 10.67 (s, 2H), 8.26 (s, 2H), 8.02 (s, 2H), 4.18 (d, *J*=5.9 Hz, 4H), 1.80 (s, 2H), 1.45–1.23 (m, 66H), 0.92–0.86 (m, 12H). ¹³C-NMR (101 MHz, CDCl₃, δ, ppm): 161.36, 153.41, 150.64, 139.82, 132.26, 125.58, 117.08, 114.70, 113.83, 68.95, 37.58, 31.94, 31.37, 30.08, 29.76, 29.70, 29.65, 29.40, 26.82, 22.71, 14.13. HRMS MALDI-TOF: *m/z* calcd. for C₅₈H₈₈Br₂N₄O₄S₄, 1193.4140; Found, 1193.4147.

Synthesis of polymer **PCBTZ-TT**

Compound **CBTZ-Br** (0.098 g, 0.082 mmol), 4,4'-didodecyl-2,2'-bithiophene-5,5'-diylbis(trimethylstannane) (0.067 g, 0.082 mmol), Pd₂(dba)₃ (0.002 g, 0.0021 mmol), P(*o*-tolyl)₃ (0.003 g, 0.0084 mmol) and anhydrous toluene (7.0 mL) were placed in a Schlenk tube under nitrogen. The reaction was stirred at 100 °C for 1 h. After the mixture was cooled to room temperature, it was poured slowly into methanol. The precipitate was filtered and washed with methanol, acetone, and petroleum ether in a Soxhlet. The product was extracted with chloroform. The solution was concentrated and precipitated in methanol. The polymer was collected as a dark solid with metallic luster (0.096 g, 77%). *M_n*=291.6 kDa; *M_w*=755.3 kDa; PDI=2.6. Anal. Calcd. for C₈₉H₁₃₈N₄O₄S₄: C 70.37%; H 9.15%; N 3.68%. Found: C 70.06%; H 9.09%; N 3.56%.

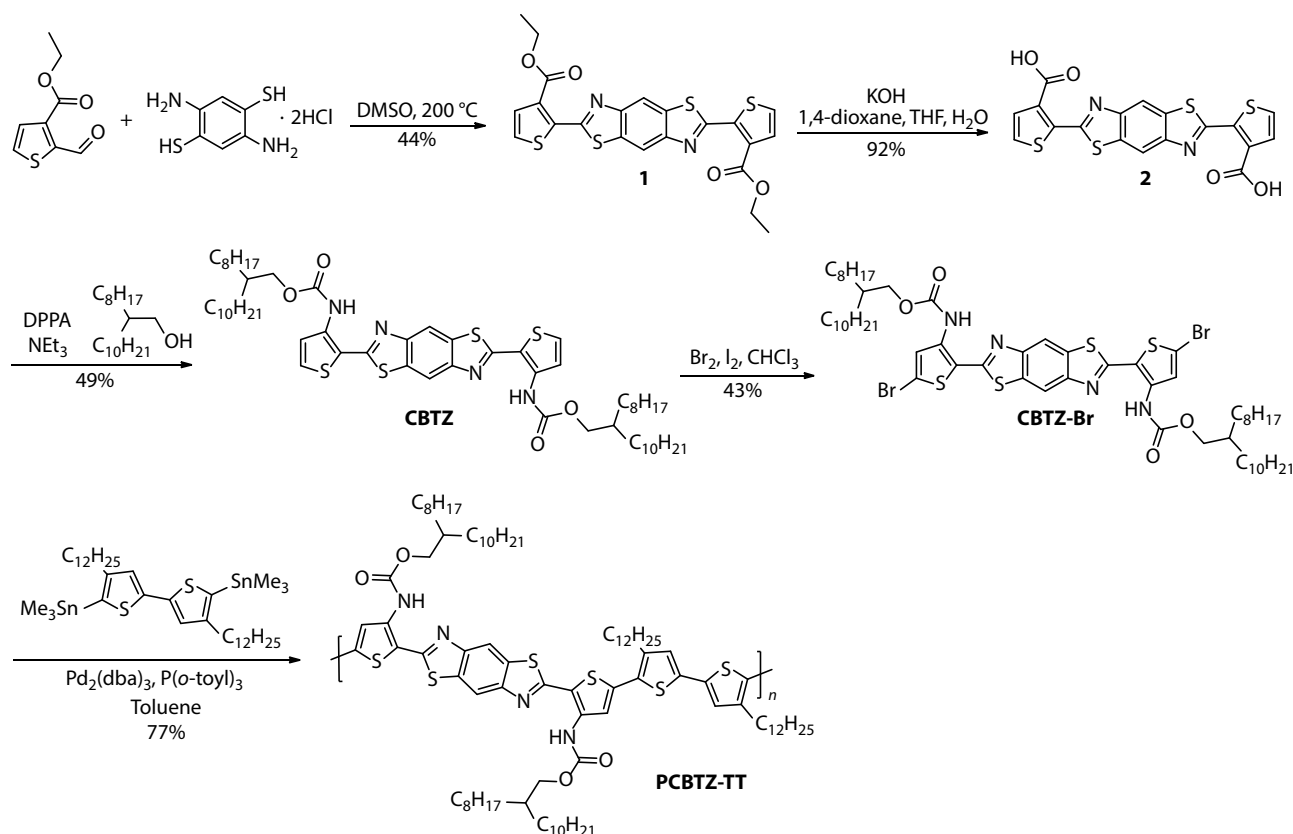
RESULTS AND DISCUSSION

Synthesis and Thermal Stability

The synthesis of the new monomer **CBTZ-Br** is shown in Scheme 1. Diethyl 2,2'-(benzo[1,2-d:4,5-d']bis(thiazole)-2,6-diyl)bis(thiophene-3-carboxylate) (**1**) was prepared by condensation of 2-formylthiophene-3-carboxylate and 2,5-dimercapto-1,4-phenylenediamine dihydrochloride in dimethyl sulfoxide. Compound **1** was hydrolyzed in aqueous potassium hydroxide solution and was neutralized by addition of hydrochloric acid solution to give bis-carboxylic (**2**). Bis-carbamate **CBTZ** was synthesized by one-pot reactions of acyl azide formation and Curtius rearrangement in an alcohol solvent. The **CBTZ-C8** was synthesized in the same manner for the single-crystal X-ray diffraction study. The **CBTZ** was brominated to give **CBTZ-Br**. The polymer was synthesized by Stille cross-coupling reactions. The number-average molecular weight (*M_n*) of **PCBTZ-TT** was 291.6 kDa, and polydispersity indexes (PDIs) of **PCBTZ-TT** was 2.6. The polymer was readily soluble in common solvents such as tetrahydrofuran, chloroform and chlorobenzene. The thermal stability of the polymer was evaluated by thermogravimetric analysis (TGA). The decomposition temperatures (*T_d*) (at 5% weight loss) for **PCBTZ-TT** was 278 °C (Fig. S2 in ESI). The thermal stability of the polymer was adequate for organic semiconducting device applications.

X-ray Crystallography

The single crystal of **CBTZ-C8** was grown from chloroform solution by the solvent evaporation method in ambient air. The conditions for cultivating single crystals mainly included the



Scheme 1 Syntheses of monomer and polymer.

concentration of 1 mg/mL, the temperature of 6–13 °C, and the local humidity of 50%–65%. The structure and crystal data of **CBTZ-C8** (CCDC: 2054199) are shown in Fig. 2 and Table S4 (in ESI). The **CBTZ-C8** adopted a centrosymmetric conformation with sulfur atoms of thiophenes and the sulfur atoms of thiazolothiazole on the same sides. The dihedral angle (S1A–C5A–C4A–S2) was only 4.9°. The distances of N2A–H, N2A···N1A and H···N1A were 1.05, 2.82, and 1.99 Å, respectively. These bond distances corresponded to the typical structures with medium strength RAHBs. The hydrogen bonds in **CBTZ-C8** were in conjugated systems (N=C–C=C–N–H). The hydrogen bonds were a part of the six membered rings, and the delocalization of π -electrons also occurred in the six membered rings. The hydrogen-bridged quasi aromatic rings lock the conformation of **CBTZ-C8**, and enhance the rigidity and planarity of the building block, and thereby facilitate the delocalization of π -electrons in the molecule. The crystal structure of the related compound **BTZ-TT** (with alkyl side chains on C4 of thiophenes) was reported in the literature before (Fig. 2). The **BTZ-TT** displayed a different conformation in crystal, which had sulfur atoms of thiophenes and the nitrogen atoms of thiazoles on the same sides because of the absence of the intramolecular hydrogen bonding and the conformation was completely coplanar.

The arrangements of the **CBTZ-C8** and the **BTZ-TT** in the crystals are very different. For the **CBTZ-C8**, there are six molecules in a unit cell (Fig. 2b). Two molecules in the center po-

sition are perpendicular to the plane, and four coplanar molecules are distributed around them. However, there are only two perpendicular molecules in the unit cell for **BTZ-TT** (Fig. 2e). The **CBTZ-C8** adopts layered sandwich packing structures (Fig. 2c). This packing motif increases the overlapping area of π orbitals between molecules. The **BTZ-TT** adopted a classical herringbone packing in the crystal (Fig. 2f) and this type stacking diminished intermolecular π -orbital overlap. The inter-planar π - π stacking distances are 3.4 Å for **CBTZ-C8** and 3.7 Å for **BTZ-TT**. The **CBTZ-C8** displayed close and compact stacking in solid-state because of the introduction of carbamate groups and the highly polarizable intramolecular hydrogen bonds to the π -conjugated molecules. The compact packing of **CBTZ-C8** in solid state enhanced intermolecular π - π interactions and the packing features of **CBTZ-C8** in solid state were favorable for charge transporting.

Optical and Electrochemical Properties of Polymer

To investigate the effects of temperature on the aggregation properties of the **PCBTZ-TT**, we carried out temperature-dependent absorption measurements on the **PCBTZ-TT**. Absorption spectra of **PCBTZ-TT** in chloroform solvent at eight different temperatures from 28 °C to 98 °C are shown in Fig. 3. With the increase of temperature, the intensity of the 0-0/0-1 absorption peaks decreases gradually. The results indicated that the intermolecular aggregates of **PCBTZ-TT** were weakened at elevated temperature. At room temperature, the dilute solution

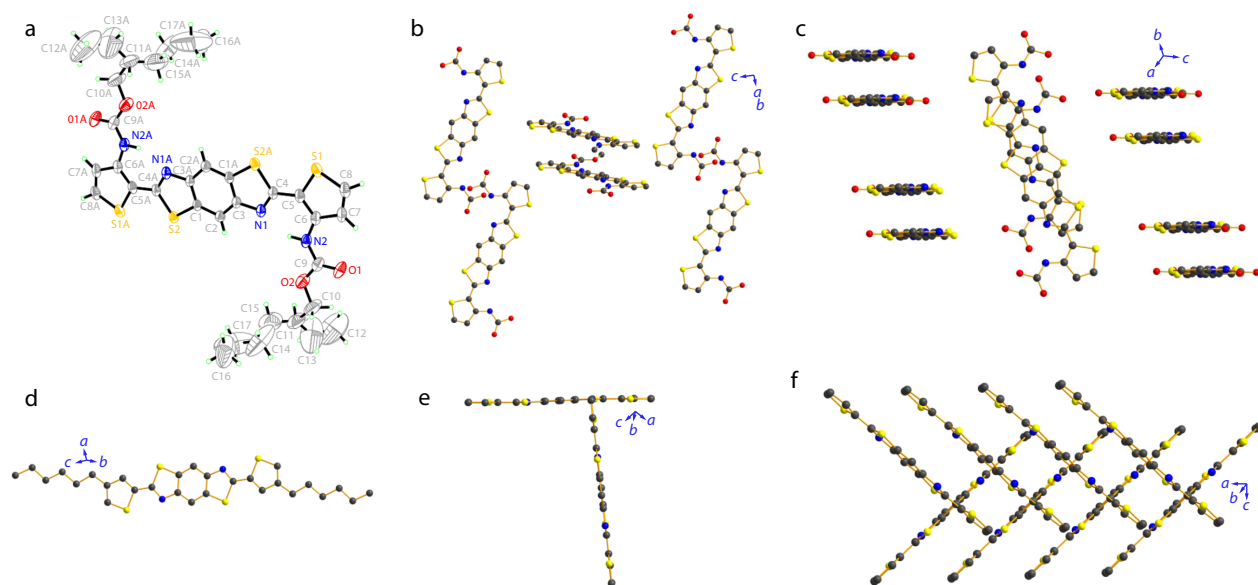


Fig. 2 Crystal structures (a, d), unit cell diagram (b, e) and packing structure (c, f) for **CBTZ-C8** and **BTZ-TT**, respectively; the red-, blue-, yellow- and gray-colored atoms represent O, N, S and C, respectively. All hydrogen atoms and alkyl chains have been omitted for clarity.

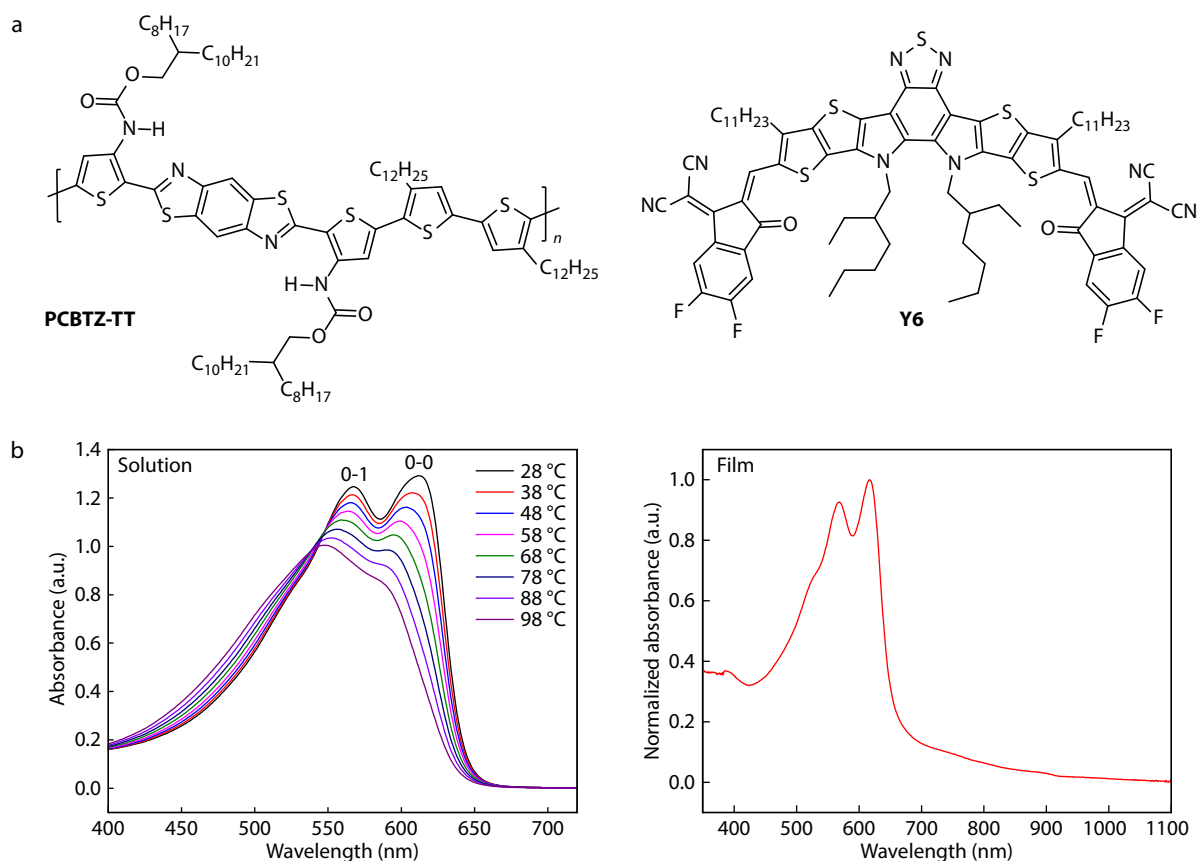


Fig. 3 The structures of **PCBTZ-TT** and **Y6** (a), UV-Vis absorption spectra of **PCBTZ-TT** in chlorobenzene at different temperatures and as thin-films (b).

of **PCBTZ-TT** showed the absorption maximum at 613 with a molar extinction coefficient of $3.2 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ and another peak at 568 nm and the corresponding data are

summarized in Table 1. The ratio of 0-0/0-1 vibronic peaks for **PCBTZ-TT** was greater than unity for both solution and thin-film spectra, and these indicated dominant J-aggregates for **PCBTZ-TT**.

Table 1 Optical and electrochemical properties of the polymers.

Polymer	$\lambda_{\text{max}}^{\text{Solution}}$ (nm)	$\lambda_{\text{max}}^{\text{Film}}$ (nm)	$\lambda_{\text{onset}}^{\text{Film}}$ (nm)	$E_{\text{g}}^{\text{opt a}}$ (eV)	HOMO ^b (eV)	LUMO ^c (eV)
PCBTZ-TT	568, 613	570, 617	670	1.85	−5.41	−3.56
PBTOT	500	551, 602	639	1.94	−5.20	−3.30

^a Band gaps calculated from the onset absorptions of thin films $E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$ (eV); ^b $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} - E^{1/2}(\text{Fc}/\text{Fc}^+) + 4.8)$ eV, $E^{1/2}(\text{Fc}/\text{Fc}^+) = 0.09$ eV;

^c $E_{\text{LUMO}} = (E_{\text{HOMO}} + E_{\text{g}}^{\text{opt}})$ eV

TT. The optical bandgap ($E_{\text{g}}^{\text{opt}}$) of **PCBTZ-TT** was 1.85 eV calculated from the onset absorptions of thin-film spectra. The absorption properties of **PCBTZ-TT** and the reference polymer **PBTOT** are compared in Table 1. **PCBTZ-TT** and **PBTOT** have the same conjugated main chains, but **PBTOT** has alkyl side chains on the thiophenes, so there is no RAHB interaction in this polymer (Fig. 1). The **PBTOT** solution showed the absorption maximum at 500 nm and a shoulder absorption around 580 nm.^[31] The $E_{\text{g}}^{\text{opt}}$ of the reference **PBTOT** was reported to be 1.94 eV. Its absorption curve was blue-shifted compared with that of **PCBTZ-TT**. Two vibronic peaks were also observed in the thin-film spectrum of **PBTOT**, but the ratio of 0-0/0-1 vibronic peak for **PBTOT** was smaller than unity which indicated H-aggregate. It was known that J-aggregation in thin films indicated large intra-chain exciton coupling.^[40] The introduction of RAHBs altered the aggregation types of polymers, even though they had the same conjugated backbones.

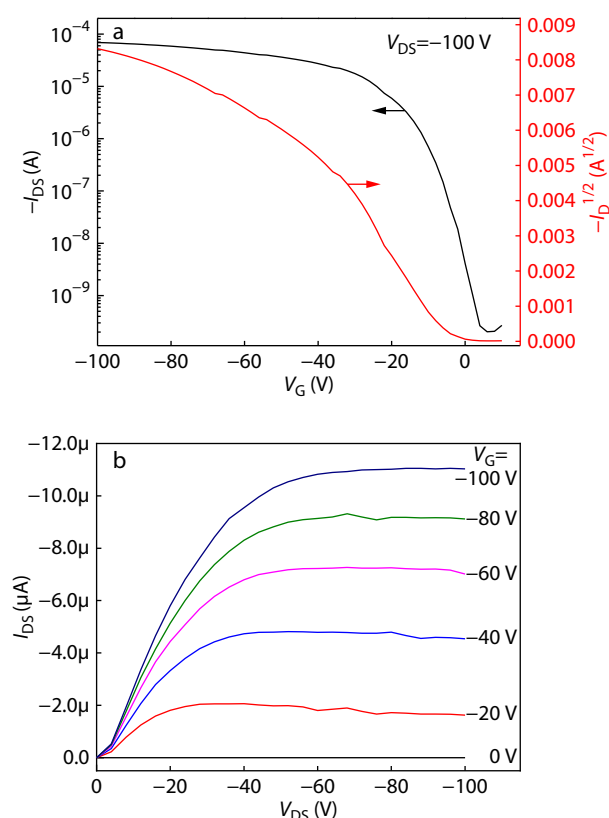
The electrochemical properties of the polymer thin-films were studied by cyclic voltammetry (Fig. S3 in ESI and Table 1). The HOMO energy levels were estimated from the onsets of the first oxidation waves, and the LUMO energy levels were calculated from the HOMO levels and the optical band gaps. The HOMO and LUMO energy levels of **PCBTZ-TT** were −5.41 and −3.56 eV, respectively. The HOMO and the LUMO energy levels of **PBTOT** were −5.20 and −3.30 eV reported in the literature.^[31] Both HOMO and LUMO energy levels of **PCBTZ-TT** were deepened about 0.2 eV in comparison with those of **PBTOT**. This suggested that the carbamate substituents combined with RAHBs acted as a electron-withdrawing moieties lowered the HOMO/LUMO levels of the polymer.

OFET Device Properties and Characterization

To investigate the charge-transport properties of the new polymer, the bottom-gate/top-contact (BGTC) OFETs were fabricated using Si/SiO₂/OTS/active layer/Au device configuration. The transfer and output characteristics of **PCBTZ-TT** are shown in Fig. 4. All OFET devices exhibited typical p-type carrier transport (Table 2). The polymer **PCBTZ-TT** film deposited at room temperature exhibited the hole mobility of 0.39 cm²·V^{−1}·s^{−1}. The mobilities of OFET devices increased steadily after annealing at 80 °C, 120 °C, and reached the highest values at 160 °C. The **PCBTZ-TT** exhibited the mobility ($\mu_{\text{aver}}/\mu_{\text{max}}$) of 0.92/0.96 cm²·V^{−1}·s^{−1} with the threshold voltage (V_{T}) of −10 V to −14 V after annealing at 160 °C. The reference polymer **PBTOT** showed the hole mobility of 0.002–0.01 cm²·V^{−1}·s^{−1} with the V_{T} of −5.2 V to −19 V after annealing at 200 °C.^[29] With the introduction of RAHBs, the polymer **PCBTZ-TT** achieved the highest field-effect mobility among all the reported benzobisthiazole containing polymers (Table S3 in ESI).

Photovoltaic Properties of Polymers

Photovoltaic devices with the configuration of ITO/PEI-

**Fig. 4** Transfer (a) and output (b) characteristics of **PCBTZ-TT**.**Table 2** Performances of **PCBTZ-TT** and **PBTOT** based OFETs.

Polymer	T_{anneal} (°C)	μ (cm ² ·V ^{−1} ·s ^{−1}) Max ^a (avg)	V_{T} (V)	$I_{\text{on}}/I_{\text{off}}$
PCBTZ-TT	As-spun	0.39 (0.37±0.01)	−16~−21	10 ⁶ ~10 ⁷
	80	0.49 (0.47±0.01)	−19~−27	10 ⁶ ~10 ⁷
	120	0.64 (0.62±0.01)	−18~−25	10 ⁶ ~10 ⁷
	160	0.96 (0.92±0.02)	−10~−14	10 ⁶ ~10 ⁷
PBTOT	200	0.002~0.01	−5.2~−19	10 ⁶

^a The average values with standard deviations obtained from 12 devices are in parentheses.

Zn/**PCBTZ-TT:Y6**/e-MoO₃/Ag were fabricated.^[36] The organic photovoltaic (OPV) devices were measured under a simulated solar illumination of 100 mW·cm^{−2} AM 1.5G under a nitrogen atmosphere. The current density-voltage (J - V) curves, external quantum efficiency (EQE) spectra are displayed in Fig. 5, and the solar cell device parameters are summarized in Table 3, Tables S1 and S2 (in ESI). The devices were optimized by varying the thickness of the active layer, donor/acceptor mass ratios, and the amount of additive. The devices showed the highest PCE at the film thickness of 100 nm (Table S1 in ESI). The **PCBTZ-TT:Y6**

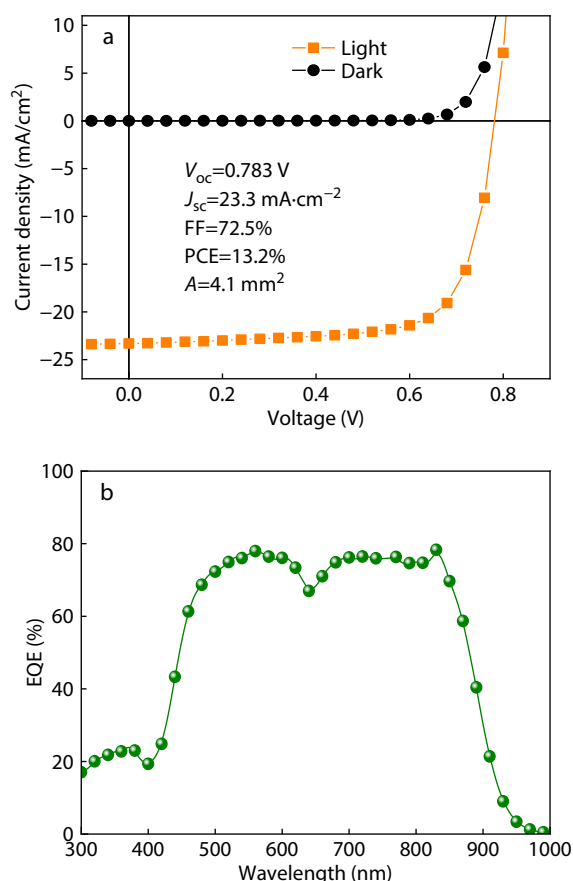


Fig. 5 J - V characteristics (a) and EQE spectra (b) of the OPV devices for **PCBTZ-TT:Y6**.

Table 3 Photoelectrical parameters of the solar cells.

PCBTZ-TT/Y6 ratios	V_{oc}^a (V)	J_{sc}^a ($\text{mA}\cdot\text{cm}^{-2}$)	FF ^a (%)	PCE ^a (%)
1:1	0.777±0.001 (0.778)	22.0±0.5 (22.5)	69.4±0.4 (69.7)	11.9±0.3 (12.2)
1:1.2	0.783±0.002 (0.784)	23.3±0.7 (23.9)	72.5±0.2 (72.6)	13.2±0.4 (13.6)
1:1.5	0.780±0.003 (0.783)	23.7±0.3 (23.9)	68.4±0.5 (68.9)	12.6±0.3 (12.9)
1:2	0.774±0.003 (0.775)	23.5±0.3 (23.6)	60.5±0.4 (60.9)	11.0±0.1 (11.1)

^a The average values with standard deviations are obtained from 12 devices, and the values in parentheses are the highest values.

mass ratio of 1:1.2 gave the best device performances (Table 3). The addition of 1-chloronaphthelene (CN) did not improve the device performances (Table S2 in ESI). The device exhibited the best performance with a PCE of 13.6%, an open-circuit voltage (V_{oc}) of 0.78 V, a J_{sc} of 23.9 $\text{mA}\cdot\text{cm}^{-2}$, and an FF of 0.72. This is a high PCE achieved for benzobisthiazole containing polymers in organic solar cells. The results demonstrated that the RAHB is a useful design strategy for high performance donor polymers.

The EQE curve of the blended film is shown in Fig. 5. The blended film showed a high photo-conversion efficiency in the range of 400–950 nm, with the maximum EQE of 76.5% at 830 nm. The electron and hole mobilities of the blend films were measured by a space-charge-limited current (SCLC)

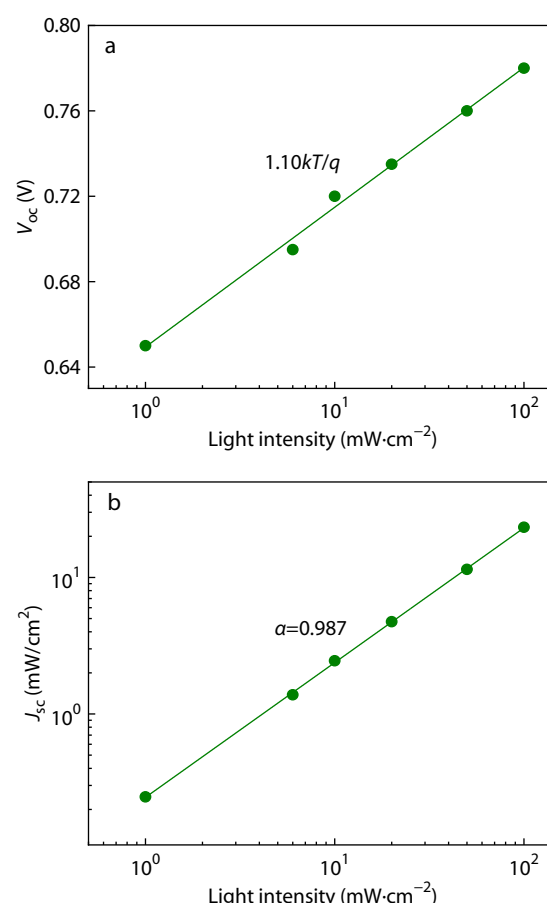


Fig. 6 Light intensity dependence of V_{oc} (a) and light intensity dependence of J_{sc} (b) of the solar cells based on **PCBTZ-TT**.

method. The device configurations were ITO/PEDOT:PSS/active layer/e-MoO₃/Ag for holes and ITO/PEI-Zn/active layer/PFN-Br/Ag for electrons (Fig. S1 in ESI). The electron and hole mobilities were 3.78×10^{-2} and 6.01×10^{-4} $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$, respectively. To investigate the properties of carrier recombination, we measured the light intensity dependence of J and V characteristic (Figs. 6a and 6b). In Fig. 6(a), the slope of the device is $1.10kT/q$, which implied that at open circuit, bimolecular recombination was dominant. As shown in Fig. 6(b), the α value was close to unity for **PCBTZ-TT**-based devices, which indicated that such bimolecular recombination was negligible in this device.

Surface Morphologies of the Active Layers

To investigate the influence of morphology on the OFET device performances, the polymer films were probed by atomic force microscopy (AFM). As shown in Fig. 7, after annealing, the images of **PCBTZ-TT** thin films display rod-like features at nanometer scales which self-assembled into worm-like patterns. The 160 °C-annealed **PCBTZ-TT** film shows few grain boundaries compared with as-spun film, and this morphology could be beneficial for the charge transfer.

The AFM of **PCBTZ-TT:Y6** blended film was also investigated (Fig. 8). **PCBTZ-TT** and **Y6** showed good miscibility, and the thin-film displayed a relatively smooth surface with an arithmetic mean (R_a) roughness of 1.4 nm. The AFM phase

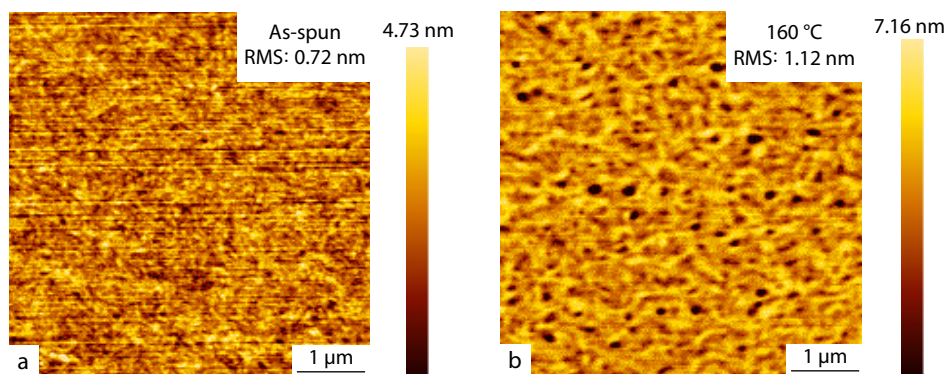


Fig. 7 AFM images of the **PCBTZ-TT** thin films as-spun (a) and annealed at 160 °C (b).

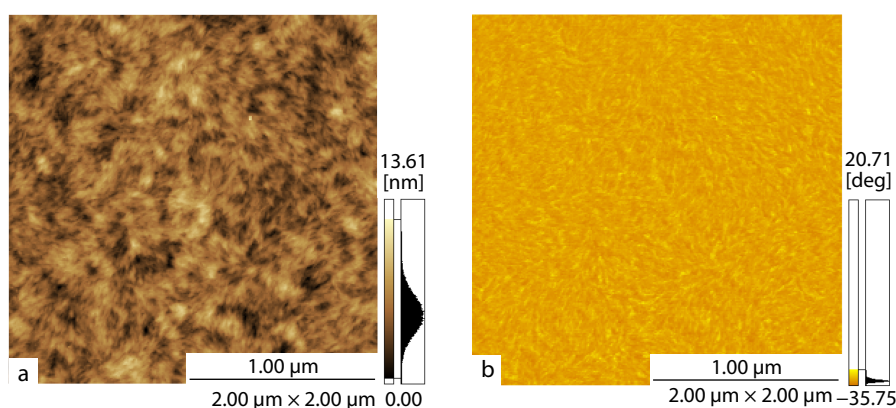


Fig. 8 AFM images of the **PCBTZ-TT:Y6** (1:1.2) thin film: (a) height and (b) phase.

image of the thin-film shows nearly uniform crystalline grains with suitable phase-separation sizes which could facilitate the charge separation and transport in the active layers.

CONCLUSIONS

In conclusion, we have synthesized a new building block **CBTZ** with RAHB interactions for conjugated polymers. Single-crystal X-ray diffraction analyses revealed that the RAHB not only facilitated the co-planarity of **CBTZ** but also altered the conformation of molecules in crystals. The **CBTZ** adopted a layered sandwich packing in crystal instead of slipped herringbone stacking which was often found in the crystal structures of benzobisthiazoles. The polymer **PCBTZ-TT** with RAHBs showed deeper HOMO/LUMO energy level (about 0.2 eV) than reference polymer. The carbamate substituents together with RAHBs acted as an electron-withdrawing moiety. The RAHBs significantly improved the semiconducting properties of the polymers in comparison with other known benzobisthiazole polymers. The field-effect mobility of **PCBTZ-TT** ($0.96 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) is nearly two orders of magnitude greater than that of the reference polymer **PBTOT** ($0.002\text{--}0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). The polymer **PCBTZ-TT** also showed high performance in organic solar cells. The photovoltaic devices with **PCBTZ-TT** as donor and **Y6** as acceptor achieved a PCE of 13.6% without any additive. These results have indicated that combining nitrogen heterocycle and RAHB can be a useful

strategy for designing high-performance for both OFET and OPV applications.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2662-z>.

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