#### RESEARCH ARTICLE



# Dialkylthienosilole and *N*-alkyldithienopyrrole-based copolymers: Synthesis, characterization, and photophysical study

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#### Abstract

We synthesized and characterized a set of  $D-\pi$ -A conjugated copolymers containing thiophene  $\pi$ -bridge. While benzothiadiazole serves as an acceptor (A) unit, the 4,4-dialkyldithieno[3,2-b:2',3'-d]silole (**DTSi**) or *N*-alkyldithieno[3,2-b:2',3'-d]pyrrole (**DTP**) act as a donor (**D**) unit. The copolymers were synthesized via the commonly Stille cross-coupling reaction and exhibited molecular weights of 18.6 to 31.3 kg/mol. The main structural differences among the copolymers are the type of donor moiety (DTSi or DTP) and the position of hexyl side chains on the thiophene  $\pi$ -bridge units between the **D** and A moieties. The ultimate goal of this work is to explore the effect of three structural factors that could control the photophysical properties of polymers in order to help in the rational design of polymers having specific properties used in optoelectronic devices. The physical properties include thermal stability, photophysical, and electrochemical properties. The structural factors are (a) the power of donor moiety, (b) the position of alkyl side chain on the thiophene  $\pi$ -bridge, and (c) the nature of the alkyl side chain. Also, we utilized the density functional theory calculations to calculate the geometric and electronic structures. A good agreement was remarked between the experimental and theoretical findings.

#### K E Y W O R D S

D-π-A, DFT calculations, donor-acceptor polymers, DTSi and DTP, Stille cross-coupling

## **1** | INTRODUCTION

The design and realization of new  $\pi$ -conjugated organic semiconductors have been attracted significant attention from several research groups in the past decade.<sup>[1]</sup> Polycondensed benzenoids, polyacetylenes, and (oligo) polyheteroaromatics represent prominent examples of such materials.<sup>[1,2]</sup> Among these, the silole-based polymers outperformed owing to their high fluorescent efficiency, photostability, and chemical stability.<sup>[3–5]</sup> One privilege of silole-based polymer over the carbon-fused analog is the enhancement of solid-state ordering as a result of their stronger  $\pi$ -stacking interaction. This could improve the charge transport, which is favorable to obtain a higher JSC value.<sup>[6]</sup>

Rasmussen and co-workers pioneered the use of Nalkyldithieno[3,2-b:2',3d]pyrrole (**DTP**) as a promising fused aromatic building block for electronic materials.<sup>[5,7]</sup> DTP has an utterly flat crystal structure, indicating good  $\pi$ -conjugation across the fused rings. Upon polymerization, poly(*N*-alkyldithieno[3,2-*b*:2',3'-*d*]pyrrole) (**PDTPs**) exhibited excellent stability in their oxidized state, low bandgaps, and efficient red fluorescence in solution.<sup>[8]</sup> The nitrogen atom in the DTP molecule enhances the electron-donating nature in the resulting polymer.<sup>[9]</sup> Meanwhile, inserting  $\pi$ -bridges to form a **D**- $\pi$ -**A** structure with extended conjugation is a widely spread method to modulate the optoelectronic properties of the polymers.<sup>[10]</sup> It has been demonstrated that light absorption, energy levels, charge transport, and photovoltaic performances can be efficiently adjusted by introducing different  $\pi$ -bridges.<sup>[11]</sup> The **D**- $\pi$ -**A** copolymers incorporating DTP moieties are described as low bandgap donor materials, which were realized in organic photovoltaic and organic field-effect transistor applications.<sup>[12-16]</sup>

Benzothiadiazole-based copolymers with different kinds of electron-rich and/or electron-deficient units showed narrow bandgaps and exhibited high Power Conversion Efficiencies (PCEs).<sup>[17–19]</sup> We have recently reported the synthesis of a series of alternating  $\pi$ -conjugated copolymers based on 2,1,3-benzothiadiazole and different numbers of hexylthiophene units via Pd-mediated Stille cross-coupling and C–H arylation methodologies.<sup>[20]</sup> The introduction of the benzothiadiazole acceptor unit into polymer chains showed a pronounced impact on each of the photophysical and electrochemical properties.

In continuation to our interest towards the synthesis of  $\pi$ -conjugated polymeric materials and small molecules for optoelectronic applications,<sup>[20,21]</sup> we introduced here a simple synthetic design to prepare a set of  $\pi$ -conjugated copolymers based on comonomers 4,7-bis(3,3'/4,4'-hexylthiophene-2-yl)benzo[c][2,1,3]thiadiazole (**HT-BT-HT**) moieties along with other donors such as **DTP** and

DTSi moieties via the commonly used palladiumcatalyzed Stille cross-coupling method. Besides, the position of alkyl side chains at  $\pi$ -bridge is another essential structural factor that has recently been employed to control the planarity of the **D**- $\pi$ -**A** copolymers.<sup>[22]</sup> For example, the 4-position anchoring of alkyl chains on the flanking thiophene units in di-2-thienvl-2.-1,3-benzothiadiazole has negligible impact on the steric hindrance relative to that of 3-position anchoring.<sup>[23]</sup> Inspired by these findings, in this work, the effect of moving the hexyl chains on thiophene units from the 3-position to the 4-position on the photophysical and electrochemical properties of the copolymers was investigated. Due to the similar structure between the examined polymers and our previously studied polymer **PBTHT**,<sup>20a, c, d</sup> a comparative study was performed in this respect.

#### 2 | RESULTS AND DISCUSSION

# 2.1 | Synthesis of comonomers and polymers

Figure 1 shows the chemical structure of four precursory comonomers, 4,7-bis(5-bromo-3,3'/4,4'-hexylthiophene-2-yl)benzo[c][2,1,3]thiadiazoles (**HT-BT-HT**; **1** and **3**), and their corresponding tributylstannyl derivatives (**2** and **4**), as building blocks to construct the title copolymers. These comonomers were synthesized via our recently reported methods.<sup>20a</sup>

Scheme 1 shows the synthetic pathways for the preparation of another set of donors, synthesized by some modifications of reporting procedures, which also used as precursors for the synthesis of the target polymers. Lithiating of 3,3',5,5'-tetrabromo-2,2'-bithiophene (**6**), prepared by brominating 2,2'-bithiophene (**5**) with bromine,<sup>15</sup> with *n*-butyllithium (*n*-BuLi) selectively at the 3,3'-positions at 90°C followed by treating with chlorotrimethylsilane at the same temperature afforded 3,3'-dibromo-5,5'-bis (trimethylsilyl)-2,2'-bithiophene (**7**) in 73% yield. On lithiating **7** with *n*-BuLi at 80°C followed by the reaction with dichlorodi-hexyl or ethylhexylsilane, the corresponding 4,4-di-hexyl or ethylhexyl-5,5'-bis



FIGURE 1 Structures of HT-BT-HT comonomers



SCHEME 1 Synthetic pathways for the synthesis of DTSi and DTP derivatives

(trimethylsilyl)dithieno[3,2-b:2',3'-d]silole (**8a,b**) was obtained in 55% and 60% yields, respectively. 4,4-Di-hexyl and/or ethylhexyl-5,5'-dibromo-dithieno[3,2-b:2',3'-d] silole (**9a,b**) was finally obtained in high yields (94% and 91%, respectively) by brominating **8a,b** with NBS in THF at room temperature.

Reagents and conditions: (a)  $Br_2$ , *glac*. AcOH/CHCl<sub>3</sub>, reflux; (b) Zn-dust/EtOH/*glac*. AcOH, reflux; (c) (CH<sub>3</sub>)<sub>3</sub>SiCl/THF, -90°C; (d) (R)<sub>2</sub>SiCl<sub>2</sub>/THF, -80°C; (e) NBS/THF, 0°C to room temp.; (f) *t*-NaOBu, Pd<sub>2</sub>dba<sub>3</sub>,

BINAP/Toluene 110°C, RNH<sub>2</sub>; and (g) *n*-Bu-Li/ $-80^{\circ}$ C,(-Bu)<sub>3</sub>SnCl/ $-80^{\circ}$ C to room temperature.

The HT-BT-HT comonomers are used as building blocks for synthesizing a variety of low bandgap copolymers (P1-P8) via the commonly used Pd-catalyzed Still cross-coupling method as shown in (**Scheme 2**). The polymerization reaction was catalyzed by Pd (PPh<sub>3</sub>)<sub>4</sub> under microwave reaction conditions in *N*,*N*dimethylformamide (DMF). Stille cross-coupling of equimolar amounts of comonomer **2** with dibromo-



**SCHEME 2** General synthetic pathways for the synthesis of  $\pi$ -conjugated copolymers **P1-P8** 

hexyl or ethylhexyl of DTSi (9a,b) afforded the corresponding copolymers P1 and P2 in 86% and 85% yields, respectively. Under the same reaction conditions, copolymerization of comonomers 1 and 2 with each of 13 or 12b afforded the copolymers P3 and P4 in 81% and 79% yields, respectively. Similarly, copolymers P5 and P6 were prepared by Pd-catalyzed Stille cross-coupling of dibromo-hexyl or ethylhexyl of DTSi (9a,b) with comonomer 4. Finally, copolymerization of comonomers 3 and 4 with each of 13 or 12b afforded the copolymers P7 and P8 in 88% and 83% yields, respectively. For comparison, copolymer PBTHT was prepared by our previously reported method via Stille cross-coupling polymerization.<sup>20a</sup> For the convenience of discussion, sometimes, the 3,3'- and 4,4'-positions of hexyl groups on the thiophene  $\pi$ -bridge units in the synthesized copolymers are named as  $\alpha, \alpha'$ - and  $\beta, \beta'$ positions, respectively (see Scheme 2).

After precipitation in methanol, the crude copolymers were filtered off and washed extensively with methanol, followed by Soxhlet extraction with methanol and acetone successively to remove byproducts and oligomers. Analysis of the polymers showed that the palladium catalyst was wholly removed from the polymers. The chemical structures of the resulting copolymers were confirmed by <sup>1</sup>H NMR spectroscopy. The findings showed that all data are entirely consistent with the proposed structures. On the other hand, all copolymers showed excellent solubility at room temperature in common organic solvents, such as chloroform, chlorobenzene, and dichlorobenzene (>5 mg/mL<sup>-1</sup>). The excellent solubility could be attributed to the presence of solubilizing side chains on thiophene moieties. All copolymers have higher molecular weight distribution with a number-average molecular weight  $(M_n)$  relative to **PBTHT** (Table 1). Except for **P8**, all **DTSi**-based polymers had a higher tendency to aggregate to form a bigger size. The observed relatively lower  $M_n$  values of copolymers **P5-P8** compared with **P1-P4** are probably due to the relatively steric hindrance effect resulting from the hexyl chains at the  $\beta$ , $\beta'$ -positions in the thiophene rings with the alkyl chains in the **DTSi** or **DTP** units. However, there should be a much less steric hindrance effect in the Stille coupling reaction in the case of using comonomers **1** or **2**.

## 2.2 | Thermal properties

The thermal stability of the copolymers was explored by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), under nitrogen atmosphere. TGA of copolymers reveals that the residual weights of copolymers **P1**, **P3**, **P4**, **P7**, and **P8** are greater than 50% when the temperature rises to 800°C (Figure 2). The polymers exhibited good thermal stability with onset decomposition temperatures ( $T_d$ , 95 wt% residues) corresponding to a 5% weight loss in the range of 306.62 to 405.06°C (Table 1), indicative of high thermal stabilities, which could be assigned to side-chain decomposition upon heating processes.<sup>[24]</sup> The three polymers **P3**, **P4**, and **P6** have the best thermal stability with onset decomposition temperatures ( $T_d$ ) corresponding to a 5% weight loss at 400.68, 392.91, and 405.06 °C, respectively.

The glass transition temperature  $(T_g)$  of copolymers **P1-P8** along with **PBTHT** data are also summarized in

Polymer	$M_{\rm n}$ ,kg/mol <sup>b</sup>	PDI, $M_{\rm w}/M_{\rm n}^{\rm b}$	Yield % <sup>c</sup>	$T_{\mathbf{d},} ^{\circ}\mathbf{C})^{\mathbf{d}}$	$T_{g,} \circ C)^{e}$
PBTHT <sup>f</sup>	18.63	2.10	87	365.80	72.40
P1	26.89	2.29	86	375.25	53.54
P2	22.63	1.64	85	306.62	51.98
P3	31.31	1.72	81	400.68	121.94
P4	27.89	1.75	79	392.91	87.73
P5	21.49	1.37	82	362.16	87.00
P6	19.82	1.61	78	405.06	80.02
P7	24.18	1.68	88	355.05	165.38
P8	20.19	1.55	83	336.86	128.85

TABLE 1 Characterization results of copolymers PBTHT and P1-P8<sup>a</sup>

Abbreviation: TGA: thermogravimetric analysis.

<sup>a</sup>All polymerizations were carried out using the Stille cross-coupling method in dry DMF in the presence of Pd (PPh<sub>3</sub>)<sub>4</sub>under microwave conditions.

<sup>b</sup>Determined by gel permeation chromatography with polystyrene as standard and CHCl<sub>3</sub>, as eluent.

<sup>c</sup>Based on the weight of the polymer obtained after Soxhlet extraction and drying under vacuum.

<sup>d</sup>Onset decomposition temperature (5% weight loss) measured by TGA under nitrogen atmosphere at a heating rate of 10°C/min.

<sup>e</sup>Determined by DSC under the nitrogen atmosphere at a heating rate of 10°C/min.

<sup>f</sup>Data were taken from our previously published work.<sup>20a</sup>



FIGURE 2 Thermogravimetric analysis thermograms of copolymers P1-P8

Table 1, while their DSC curves are presented in Figure 3. The copolymer samples were heated up to 300°C, and the DSC data were obtained from the second heating cycle. DSC analysis revealed that PBTHT, P1, P2, P4, P5, and P6 are amorphous materials with a glass transition temperature at 72.40, 53.48, 51.98, 87.73, 87.00, and 80.02°C, respectively. The amorphous nature of the P1, P2, P5, and P6 can be understood from the 4,4'dihexyl groups of the DTSi moieties protruding out of the polymer backbone planes. The otherwise stated polymers exhibited  $T_g$  values in the range of 121.94 to 165.38°C. Interestingly, **PBTHT** showed the lowest  $T_{g}$ value along all of the other polymers except for P1 and **P2**. More interestingly, the  $T_g^{s}$  of the copolymers increases with incorporating the DTP moiety in the copolymer backbones than that of polymer containing DTSi moiety (Table 1). This owes to the extra



**FIGURE 3** Differential scanning calorimetry curves of copolymers **P1-P8** 

intermolecular interactions and the increasing interchain regularity caused by introducing **DTP** to copolymer main chains. The high thermal stability of the copolymers could prevent the deformation of their morphology and the degradation of their polymeric active layer under applied electric fields. Thus, the synthesized polymers might be considered as good candidates for device applications, especially for light-emitting diodes, organic thinfilm transistors, and solar cell applications.

#### 2.3 | Optical properties

The optical absorption spectra of copolymers **P1-P8** in chlorobenzene solutions and as thin films cast on glass slides were extensively investigated (Figures 4 and 5). The corresponding optoelectronic properties are summarized in Table 2. The optical bandgaps  $(E_g^{op})$  of the copolymers were deduced from their absorption onsets. Each polymer is characterized by two major absorption peaks, a feature that is commonly observed for alternating **D-A** copolymers. The low-wavelength peak can be attributed to a  $\pi$ - $\pi$ <sup>\*</sup> transition, while the high-wavelength transition is believed to be related to an intramolecular **D-A** charge transfer.

Upon inspection of Figure 4, one can explore the effect of three structural factors on the spectral features of the examined polymers as the following:

1. The power of donor moiety: The structure of **PBTHT** is very similar to those of **P5** and **P7**. They differ only in the structure of the donor moiety. The replacement one of benzothiadiazole moieties of **PBTHT** by **DTP** or **DTSi** species has a dramatic impact on geometry, spectral profile, and spectroscopic parameters (such as in  $\lambda_{max}$ ,  $\lambda_{onset}$  and  $E_g^{op}$ ), as shown in Figure 4A and Table 2. The power of donor moieties,



FIGURE 4 Ultraviolet-visible spectra of the studied polymers P1-P8 in chlorobenzene



FIGURE 5 Ultraviolet-visible spectra of the studied copolymer thin films P1-P8 in comparison with PBTHT

benzothiadiazole, **DTSi**, and **DTP** was computed by B3LYP/6-311+G(d,p) as their ionization energy, 9.67, 8.49, and 7.98 eV, respectively. Accordingly, the lower the ionization potential moiety, the easier to remove an electron from it and can be described as a stronger donor group. This could explain the significant bathochromic shift in  $\lambda_{max}$  (~50 nm) upon the structural replacement by benzothiadiazole moiety in **PBTHT** copolymer by **DTSi** (**P5**) or **DTP** (**P7**). Strictly speaking, this result is not attributed only to the increase of donating ability but also because of increasing the twisting angle  $\varphi$ 1 (angle between the donor moiety and thiophene ring) from ~2 to ~ -25° as shown by our density functional theory (DFT) results. The synergistic effect of both factors can control the ICT leading to the findings. Also, the vast shift in the  $\lambda_{onset}$ , ie, reached 109 nm, as well as the reduction in  $E_g^{op}$  was observed. This shed light on the proper choice of donor moiety to enhance the light-harvesting efficiency. As an extension to the power of donor moiety, the effect of replacement of silicon atom in the tricyclic-ring by nitrogen one was studied. In the inspection of Table 2 and Figure 4B, we can divide the studied copolymers into two subsets, **P1-P4** and **P5-P8**, based on the position of the hexyl chain. Compared with the **P5-P8** subset, a relatively significant

#### TABLE 2 Optical and electrochemical properties of polymers PBTHT and P1-P8<sup>[a]</sup>

	UV-vis absorption								
	Solution			Film			Cyclic Voltammetry <sup>[c]</sup>		
Polymer	$\lambda_{max}$ , nm	$\lambda_{onset}$ , nm	$E_g^{op}, \mathbf{eV}^{[\mathbf{b}]}$	$\lambda_{max}$ , nm	$\lambda_{onset}$ , nm	$E_g^{op}, \mathbf{eV}^{[\mathbf{b}]}$	HOMO, eV	LUMO, eV	$E_g^{ec}$ , eV
PBTHT <sup>[d]</sup>	513	593	2.09	532	644	1.92	-5.66	-3.37	2.29
P1	519	616	2.01	541	654	1.82	-5.36	-3.48	1.88
P2	497	600	2.06	508	681	1.89	-5.46	-3.34	2.12
P3	545	645	1.92	569	794	1.56	-5.16	-3.37	1.79
P4	538	643	1.92	578	720	1.72	-4.98	-3.34	1.64
P5	564	685	1.81	614	779	1.59	-4.97	-3.36	1.61
P6	550	673	1.84	564	720	1.72	-5.36	-3.53	1.83
P7	561	702	1.77	578	802	1.55	-4.91	-3.29	1.62
P8	555	686	1.80	589	804	1.54	-5.02	-3.35	1.67

Abbreviations: CV: cyclic voltammetry; UV-vis: ultraviolet-visible.

<sup>a</sup>All data are for those polymers prepared by microwave polymerization reaction conditions.

<sup>b</sup>Optical bandgap  $(E_{e}^{op})$  was calculated from the intersection of the tangent on the low energetic edge of the absorption spectrum with the baseline.

<sup>c</sup>The onset potentials are obtained from the intersection of the two tangents down at the rising current and the baseline changing current of the CV curves. <sup>d</sup>Data were taken from our previously published work.<sup>20a</sup>

change in the spectral properties mainly  $\lambda_{max}$  (26 and 41 nm) and  $\lambda_{onset}$  (29 and 43 nm) was observed in the **P1-P4** subset upon the replacement of **DTP** by **DTSi** moiety. On the other hand, a limited effect was observed in the **P5-P8** subset on  $\lambda_{max}$  (~3 and 5 nm) and  $\lambda_{onset}$  (~17 and 13 nm) because of the antiinterference effect of another structural factor. Further details will be discussed in the next section.

2. The positioning effect of hexyl side chains on thiophene *rings*: When changing the hexyl side chains in the  $\pi$ bridge (thiophene unit) from the  $\alpha, \alpha'$ - to the  $\beta, \beta'$ -positions, the low-energy peak is significantly red-shifted, while the high-energy peak remains almost unchanged. These results suggest that the  $\beta$ , $\beta'$ positions induce a more pronounced coupling between the D and A units, enhancing charge transfer and reducing the  $E_{q}^{op}$ . This effect works more significantly in the DTSi-based polymers, ie, P1, P2, P5, and P6, compared with the DTP-based polymers (Figure 4C). For instance, a significant bathochromic shift in  $\lambda_{max}$ , 45, and 53 nm, was observed ongoing from P1 to P5 and from P2 to P6, respectively, as a result of moving the alkyl side chains from  $\alpha, \alpha'$ - to the  $\beta$ ,  $\beta'$ -positions. On the other hand, a limited shift, 16 and 17 nm, was remarked ongoing from P3 to P7 and from P4 to P8, respectively. A considerable shift in  $\lambda_{onset}$  (range: 43-73 nm) and reduction in  $E_g^{op}$ (range: 0.12-0.22 eV) were noticed as a result of this structural change. A similar attitude was observed in the ultraviolet-visible (UV-Vis) absorption spectra of similar polymers.<sup>[22]</sup>

We can conclude some points: (a) whatever the donor moiety is, the movement of the position of hexyl side chain from  $\alpha, \alpha'$ - to the  $\beta, \beta'$ -positions lead to a bathochromic shift in  $\lambda_{max}$  and  $\lambda_{onset}$  as well as a reduction in  $E_g^{op}$ . This is attributed to the stronger coupling of electron-donating hexyl groups in  $\beta, \beta'$ -positions together with the donor moiety, which enhances the ICT; (b) the stronger donating ability of **DTP** relative to **DTSi** led to stronger ICT with the acceptor and thiophene bridge carrying hexyl chain in  $\beta,\beta'$ -positions. This highlights the considerate selection of the position of the alkyl chain on  $\pi$ -bridge because their proper choice is essential to enhance the efficiency of light-harvesting.

3. The nature of alkyl chains on the DTSi or DTP moieties: As shown in Figure 4D, the replacement of hexyl by ethylhexyl chain in DTP donor moiety, for example, leaves almost constant absorption spectra for polymers P3 and P4. However, a slight blue shift from 6 to 23 nm in the high-wavelength peak was observed as a result of this structural change between each pair of the following polymers P1 and P2, P3 and P4, P5 and P6, and P7 and P8. This shift may indicate a larger twist between the neighboring rings induced by the more bulky ethylhexyl side chains.

Similarly, the absorption spectra of polymer thin films are mostly affected by the alkyl side-chains positioning rather than by the chain chemical structure, as illustrated in Figures 5A and 5B and Table 2. However, a significant red-shift ongoing from the solutions to the solid films was remarked. The spectral shift is generally attributed to the intermolecular  $\pi$ - $\pi$  stacking interactions between conjugated main chains in the solid-state. Changing alkyl side chains from the  $\alpha, \alpha'$ - to the  $\beta, \beta'$ -position leads, as expected, to a significant reduction (~0.20 eV) of the polymer energy bandgap. The resulting 1.54- and 1.55-eV optical bandgap of both P7 and P8 is very close to the optimal value for single-junction photovoltaic devices<sup>[25]</sup> and makes these polymers highly promising for photovoltaic applications. Interestingly, in the case of polymer thin films P3, P5, P7, and P8, the shoulder results in cutoff wavelengths were found to be of 794, 779, 802, and 804 nm, respectively, corresponding to a bandgap of 1.56, 159, 1.55, and 154 eV. These strong broad absorptions are ideal for PV applications due to favorable overlap with the AM1.5 solar spectrum. It is worth mentioning that the absorption spectra of all copolymer films with hexyl groups at  $\beta$ ,  $\beta'$ -positions (**P2**, **P4**, **P6**, and **P8**) in the thiophene  $\pi$ -bridge units are red-shifted than those corresponding polymers with hexyl side chains  $\alpha, \alpha'$ positions (P1, P3, P5, and P7) (see Figures 5A and 5B), indicating a more planar structures due to reduced steric hindrance in those polymers. More interestingly, copolymers P3, P5, P7, and P8 have optical bandgaps of 1.56, 1.59, 1.55, and 1.54 eV, respectively, which are close to the ideal value of 1.5 eV for PSC application. This redshift might be attributed to the great co-planar conformation of adjacent thiophene rings induced by the hexyl side chains at the  $\beta$ , $\beta'$ -positions on the thiophene rings in the polymer backbone that increase the effective conjugation length. Similar behaviors were observed in the UV-Vis absorption spectra of similar polymers.<sup>[22]</sup>

## 2.4 | Electrochemical properties

The electrochemical properties of the synthesized copolymers are measured by cyclic voltammetry (CV) in CH<sub>3</sub>CN solutions by using ferrocene as reference. The CV curves of copolymers **P1-P8** are presented in Figure 6, and the corresponding data are listed in Table 2. The highest occupied molecular orbital and the lowest unoccupied molecular orbital energy levels ( $E_{\rm HOMO}$  and  $E_{\rm LUMO}$ , respectively) of the copolymers were determined from their cast films on ITO glass substrates. They were calculated according to the empirical formulas<sup>17b, 26, 27</sup>: $E_{\rm HOMO} = -(E_{\rm ox}+4.40)$  eV and  $E_{\rm LUMO} =$  $-(E_{\rm re}+4.40)$  eV, where  $E_{\rm ox}$  and  $E_{\rm re}$  are the onset oxidation and reduction potentials of the polymers, respectively, vs. SCE.  $E_{\rm LUMO}$  values of polymers lie in the range of −4.91 to −5.66/−3.25 to −3.53 eV, respectively. Interestingly, the  $E_{\rm LUMO}$  values of all polymers are higher than that of PC<sub>61</sub>BM (≈ −3.90 eV), which may guarantee the efficient photoinduced charge separation between the polymer donor and PC<sub>61</sub>BM.<sup>[28]</sup>

As shown in Table 2, the estimated electrochemical bandgaps  $(E_{\sigma}^{ec})$  for all polymers are lower than that of PBTHT. Incorporating different donor units in the polymer chains has a direct impact on the  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ of the resulting copolymers. Increasing the electrondonating moieties in the polymer backbones lowers the bandgap and oxidation potentials.<sup>[29]</sup> Because the  $E_{HOMO}$ of copolymers P2, P3, and P8 are below the air oxidation threshold (approximately -5.27 eV),<sup>[30]</sup> these polymers may show good stabilities toward air and oxygen. This is one of the prerequisites for the polymer used in electronic device applications.<sup>[30]</sup> The estimated electrochemical bandgaps  $(E_{q}^{ec})$  of all of the polymers were found to be somewhat higher than the corresponding optical bandgaps  $(E_{\sigma}^{op})$ , which might be originated from the interface energy barriers present between the polymer films and the electrode surfaces.<sup>26c, 31</sup>



FIGURE 6 Cyclic voltammograms of copolymers P1-P8



FIGURE 7 Optimized structures of the studied comonomer

### 2.5 | Theoretical study

DFT at wB97XD/6-31+G(d,p)<sup>[32]</sup> level using Gaussian 09<sup>[33]</sup> was used to investigate the optimal geometric structure and the electronic configuration of **PBTHT**, **P1**, **P3**, **P5**, and **P7**. Copolymers **P2**, **P4**, **P6**, and **P8** gave very similar results to those of **P1**, **P3**, **P5**, and **P7**, respectively, because of the similar effect between ethylhexyl and hexyl groups of **DTSi** or **DTP** units in polymer chains, and therefore, the former polymers were not modeled. The alkyl side chains were replaced by methyl groups to reduce the computational load. It was reported that this replacement does not affect the frontier orbitals but affects the torsion angles to some extent.<sup>[34]</sup> The geometrically optimized structures are shown in Figure 7, and the torsion angles ( $\varphi_1$ ,  $\varphi_2$ , and  $\varphi_3$ ) between every two

**TABLE 3**Torsion angles in degrees along the conjugatedbackbone of the optimized molecular geometries

Polymer	φ1	φ <sub>2</sub>	φ <sub>3</sub>
PBTHT	1.92	0.10	-
P1	-23.49	0.23	-
P3	-28.47	0.38	-
P5	-65.31	-9.60	-14.04
P7	-58.90	-5.44	-9.84

adjacent subunits of the comonomers are listed in Table 3.

The findings showed that **PBTHT** is coplanar, where the torsion angles range from -0.04 to  $1.92^{\circ}$ . Upon replacement of benzothiadiazole moiety of **PBTHT** by **DTP** (**P1**) or **DTSi** species (**P3**), only a remarked increase of  $\varphi_1$  by 25 and 30°, respectively, was observed. To verify the validity of comonomers modeling as the correct



**FIGURE 8** Experimental and simulated ultraviolet-visible spectra of copolymer **P7** 



FIGURE 9 The contour plots of HOMO and LUMO orbitals of the studied compounds

representative for polymers, we simulated the UV-Vis spectra using time-dependent density functional theory (TD-DFT) at wB97XD/6-31+G(d,p) level.<sup>[32]</sup>

The experimental and simulated UV-Vis spectra of **P7** as representative examples are shown in Figure 8. There is a good match between the positions of the three peaks of both spectra, where the experimental peaks located at 561, 425, and 342 nm, while the simulated ones located at very close values, 578, 403, and 324 nm. The area under a peak is not consistent with the experimental one because of the difference in conditions where our calculations are performed at zero Kelvin against 298° for the experimental measurements. Also, we used implicit solvation for simulation compared with the explicit solvent effect in the real condition.

The frontier molecular orbitals (FMO) of the tested comonomers were shown in Figure 9. Three kinds of observations were found as a result of the structural changes. The HOMO and LUMO of **PBTHT** are distributed over the whole molecular selection because of the absence of **D**-**A** character. On the other hand, the electron density of the HOMO electron is delocalized over the molecular backbone of **P1** and **P5**, while the LUMO is primarily located on the acceptor moiety. The replacement of **DTSi** moiety by a stronger donor, **DTP** as in **P3** and **P7**, has a definite impact on the FMO topology, where the HOMO is predominantly located on the donor moiety, while the LUMO is primarily located mainly on the acceptor moiety. As a result, polymer **P3** and **P7** had a clear charge separation when compared with the other polymers. This is also supported by the



**FIGURE 10** Experimental (cyclic voltammetry) and calculated HOMO and LUMO energy levels

**TABLE 4** Excited-state vertical transition energies (Cal  $\lambda_{max}$ , nm), oscillator strengths (*f*, arbitrary units), and main electronic configuration of the first excited state and their percentage contribution (C%) of the polymers, as calculated for the monomers using TD-DFT at the B3LYP/6-31+G\* level of theory

Polymer	Cal $\lambda_{max}$ , nm	<i>f</i> , au	Main configuration	<b>C</b> %	Exp $\lambda_{max}$ , nm
PBTHT	522	1.06	$H \to L$	0.96	513
	437	0.13	$H \to L\text{+}1$	0.90	
	333	0.26	$H \to L\text{+}2$	0.86	
P1	541	1.07	$H \to L$	0.94	519
	413	0.56	$H \to L\text{+}1$	0.79	
	380	0.28	$\text{H-1} \rightarrow \text{L}$	0.81	319
P3	561	0.93	$H \to L$	0.94	545
	368	0.86	$H \to L\text{+}1$	0.86	419
	299	0.38	$\text{H-3} \rightarrow \text{L}$	0.60	314
P5	528	0.94	$H \to L$	0.92	564
	398	0.17	$\text{H-1} \rightarrow \text{L}$	0.64	425
	372	0.77	$H \to L\text{+}1$	0.77	325
P7	578	0.94	$H \to L$	0.92	561
	403	0.60	$\text{H-1}{\rightarrow}\text{L}$	0.68	425
	324	0.31	$H \to L\text{+}1$	0.84	342

Abbreviation: TD-DFT: time-dependent density functional theory.

clear intramolecular charge transfer seen in the absorbance spectra, as described earlier.

The predicted average HOMO and LUMO energy levels are -6.07 and -3.58 eV giving an average bandgap of 2.49 eV. This bandgap is higher to some extent than the crossponding experimentally determined by optical technique (1.99 eV), the CV (1.91 eV). The calculated FMO energies are consistently underestimated compared with the experimental values (Figure 10). This could produce overestimated bandgaps compared with those of the experimental values. The systematic difference between both results are originated from differences in conditions between experiments and calculations with respect to, e.g., finite temperature and explicit solvent effects, as well as the shortcomings in standard hybrid DFT functionals. TD-DFT calculations were performed to gain insights into the excited state properties of the polymers. The calculated excited-state vertical transition energies by nanometer, oscillator strengths, and transition electronic configurations are given in Table 4.

It can be seen that the calculations well reproduce experimental absorption peaks. For all polymer systems, the  $S_0 \rightarrow S_1$  transition is primarily a HOMO $\rightarrow$ LUMO transition (92-96%). All the copolymers show three optical transitions, one in the range of 320 to 377 nm, arising from a delocalized  $\pi \rightarrow \pi^*$  transition in the main chain, and the other two peaks occur in the range between 348 to 437 and 435 to 578 nm, originating from a charge transfer state in the **D**-**A** segment. After examining the predominant component of the molecular orbitals involved in the pertinent transitions, one can see that the lowest singlet  $S_0 \rightarrow S_1$  excited state with high-oscillator strength (between 0.93 and 1.86) corresponds predominantly to HOMO $\rightarrow$ LUMO transition. Other single excitations that contribute to the total excited state wave function involve mainly HOMO $\rightarrow$ LUMO+1 and HOM-O $\rightarrow$ LUMO+2 transitions.

# 2.6 | Conclusions

A series of low bandgap conjugated copolymers based on comonomers 4,7-bis(3,3'/4,4'-hexylthiophene-2-yl)benzo[c][2,1,3]thiadiazoles (HT-BT-HT) with two different donor units were synthesized and fully characterized. The nature and position of alkyl side-chain on the thiophene bridge were also deeply investigated. Due to the similar structure between the examined polymers and the well-studied polymer PBTHT, a comparative study was performed in this respect. Based on the experimental and theoretical findings, we have concluded the following: (a) All copolymers showed good solubility in most organic solvents. (b) Compared with PBTHT, all copolymers exhibited high thermal stability. (c) The position of alkyl-side chain on thiophene could significantly lead to variation in the photophysical and electrochemical properties of the copolymers. (d) Interestingly, incorporating DTP within the polymer backbone extends the absorption beyond 804 nm and creates an optical bandgap that is much smaller than any of the other polymers. (e) The findings shed light on the role of the position of alkyl side chain on the thiophene bridge and the power of donor moiety on the improvement of the light-harvesting properties of the title copolymers as seen from the remarked reduction of both optical and electrochemical bandgap and the significant bathochromic shifts in  $\lambda_{onset}$  and  $\lambda_{max}$ .

## **3** | EXPERIMENTAL SECTION

### 3.1 | Reagents and materials

Unless otherwise noted, all manipulations and reactions involving air-sensitive reagents were performed under a dry oxygen-free nitrogen atmosphere. All reagents and solvents were obtained from commercial sources and dried using standard procedures. Thin-layer chromatography (TLC) was used for monitoring all reactions for completion. 3,3'-5,5'-Tetrabromo-2,2'-bithiophene (**6**), 3,3'-dibromo-2,2'-bithiophene (**10**) were prepared according to the literature procedures.<sup>[35]</sup> <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of the synthesized comonomers and polymers are provided in the supporting information.

## 3.2 | Instrumentation and methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Varian spectrometer (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C) in CDCl<sub>3</sub> at 25°C with TMS as the internal standard, and chemical shifts were recorded in ppm units. The coupling constants (J) are given in Hz. Flash column chromatography was performed with Merck silica gel 60 (particle size 230-400 mesh ASTM). Neutralized silica gel was prepared by adding triethylamine to the silica gel in the same eluent used for column chromatography. Analytical TLC was conducted with Merck 0.25-mm 60F silica gel precoated aluminum plates and UV-254 fluorescent indicators. The UV-Vis absorption spectra were obtained using a Varian Cary UV-Vis-NIR-5000 spectrophotometer on the pure polymer samples. The thermal degradation temperature was measured using TGA (TGA-TA instrument Q-50) under a nitrogen atmosphere. DSC was performed on a TA instrument (DSC-TA instrument Q-20) under a nitrogen atmosphere at a heating rate of 10°C/min. CV measurements were performed on B-class solar simulator: Potentiostate/Galvanostate (SP-150 OMA company). The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in acetonitrile (0.1 M) at a scan rate of 50 mV/s<sup>-1</sup>. A three-electrode cell was used. A Pt wire and silver/silver chloride [Ag in 0.1 M KCl] were used as the counter and reference electrodes, respectively. The polymer films for electrochemical measurements were spin-coated from polymerа chlorobenzene solution on ITO glass slides, approximately 10 mg/mL. The gel permeation chromatographic analysis was carried with a Shimadzu (LC-20A Prominence Series) instrument. Chloroform was used as a carrier solvent (flow rate: 1 mL/min, at 30°C), and calibration curves were made with standard polystyrene samples. Microwave-assisted polymerizations were performed in a focused microwave synthesis system<sup>CEM</sup> (Discover S-Class System). The low-temperature reactions were essentially performed in a low-temperature bath (PSL1810-SHANGHA EYELA). A syringe pump KD Scientific (KDS-100) was used for delivering accurate and precise amounts of reagents during the dropwise addition processes.

## 3.3 | Synthesis of comonomers

# 3.3.1 | Synthesis of 3,3'-dibromo-5,5'-bis (trimethylsilyl)-2,2'-bithiophene (7)<sup>18c</sup>

3,3'-5,5'-Tetrabromo-2,2'-bithiophene (**6**, 4.78 g, 10 mmol) was dissolved in 150-mL dry THF, and the solution was cooled down to -90°C by a methanol/liquid nitrogen bath. Then, 8-mL n-butyllithium solution in hexane (2.5mol/L) was added drowsily throughout 1 hour after the addition of *n*-butyllithium; the reactant was stirred for 30 minutes. Subsequently, chlorotrimethylsilane (2.7 g, 25 mmol) was added in one portion, and the temperature of the reactant was raised to ambient temperature by removal cooling bath. Then, the reactant was poured into water and extracted by diethyl ether several times. The volatiles were removed under vacuum. The residue was purified by silica gel chromatography using hexane as eluent to give a white solid of 7 (3.42 g, 73%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 7.15 (s, 2H, 2X CH-CBr), 0.33 (s, 18H, 2X -Si (CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, δ/ ppm): 143.23, 137.35, 134.22, 113.25, 0. C<sub>14</sub>H<sub>20</sub>Br<sub>2</sub>S<sub>2</sub>Si<sub>2</sub> (468.42): calcd. C 35.90, H 4.30, Br 34.12, S 13.69, Si, 11.99; found C 36.12, H 4.39, Br 33.96, S 13.72.

## 3.3.2 | Synthesis of 4,4-dihexyl-5,5'-bis (trimethylsilyl)-dithieno[3,2-b:2',3'-d]silole (8)<sup>18c</sup>

Compound 7 (5 mmol) and 40-mL THF were put into a flask and cooled down to  $-80^{\circ}$ C by a lowtemperature bath. Then, *n*-butyllithium solution in hexane (2.5mol/L) was added dropwise in 5 minutes, and the reactant was stirred for another 30 minutes at that temperature. Subsequently, dichlorodihexylsilane (6 mmol) was added in one portion, and the cooling bath was removed, and the reactant was stirred for 2 hours under ambient temperature. Then, the reactant was poured into water and extracted by diethyl ether several times. The volatiles were removed under vacuum. The residue was purified by silica gel chromatography using hexane as eluent to give a colorless oil of **8** in a 55% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ /ppm): 7.12 (s, 2H, 2X CH-Si-), 1.42-1.40 (t, J = 8.00 Hz, 4H, 2X Si-CH<sub>2</sub>-), 1.23-1.20 (m, 16H, 2X Si-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>4</sub>), 0.9-0.85 (m, 6H, 2X CH<sub>3</sub>), 0.33 (s, 18H, 2X -Si (CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz,  $\delta$ /ppm): 154.31, 143.72, 140.81, 136.46, 32.37, 31.28, 24.07, 22.46, 13.99, 11.7, 0. C<sub>26</sub>H<sub>46</sub>S<sub>2</sub>Si<sub>3</sub> (507.03): calcd. C 61.59, H 9.14, S 12.65, Si 16.62; found C 61.51, H 9.19, S12.55.

## 3.3.3 | Synthesis of 4,4-dialkyl-5,5'dibromo-dithieno[3,2-b:2',3'-d]silole (9a,b)<sup>18c</sup>

Compound **8a,b** (2.56 mmol) was dissolved in 20-mL THF, and *N*-bromosuccinamide (5.12 mmol) was added in one portion at  $0^{\circ}$ C. The reactant was stirred at ambient temperature for 4 hours and then extracted by diethyl ether. The volatiles was removed under vacuum, and the residue was purified by silica gel chromatography using hexane as eluent to give a sticky yellowish green oil of **9a,b** in a 94% and 91% yield, respectively.

# 4,4-Dihexyl-5,5'-dibromo-dithieno[3,2-b:2',3'-d]silole (9a)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 6.98 (s, 2H, 2X CH-Si-), 1.35-1.22 (m, 16H, 2X Si-(CH<sub>2</sub>)<sub>4</sub>), 0.86-0.83 (m, 10H, 2X -CH<sub>2</sub>-CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, δ/ppm): 148.85, 140.91, 132.10, 111.36, 32.80, 31.35, 23.95, 22.53, 14.08, 11.58. C<sub>20</sub>H<sub>28</sub>Br<sub>2</sub>S<sub>2</sub>Si (520.46): calcd. C 46.15, H 5.42, Br 30.71, S 12.32, Si 5.40; found C 46.49, H 5.52, Br 30.28, S 12.41.

# 4,4-Bis(2-ethylhexyl)-5,5'-dibromo-dithieno[3,2-b:2',3'-d] silole (9b)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 6.97 (s, 2H, 2X CH-Si-), 1.39-1.35 (m, 2H, 2X Si-CH<sub>2</sub>-CH-), 1.25-1.13 (m, 16H, 2X Si-CH<sub>2</sub>-CH-(CH<sub>2</sub>)<sub>3</sub>), 0.95-0.90 (m, 4H, 2X CH-CH<sub>2</sub>-), 0.83-0.78 (m, 6H, 2X CH-CH<sub>2</sub>-CH<sub>3</sub>), 0.76-0.74 (m, 6H, 2X CH<sub>2</sub>-CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, δ/ppm): 148.56, 141.95, 132.27, 111.31, 35.78, 35.56, 28.84, 28.80, 22.93, 17.45, 14.09, 10.75. C<sub>24</sub>H<sub>36</sub>Br<sub>2</sub>S<sub>2</sub>Si (576.57): calcd. C 50.00,

H 6.29, Br 27.72, S 11.12, Si 4.87; found C 49.83, H 6.31, Br 27.54, S 11.18.

# 3.3.4 | Synthesis of *N*-alkyldithieno[3,2b:2',3'-d]pyrrole (11a,b)<sup>18f</sup>

A solution of **10** (3.09 mmol), *t*-NaOBu (7.4 mmol), Pd<sub>2</sub>dba<sub>3</sub> (0.077 mmol) and BINAP (0.31 mmol) in dry toluene (10 mL) was purged with nitrogen for 20 minutes. Alkylamine (3.09 mmol) was added via a syringe, and the mixture was refluxed under nitrogen for 7 hours. After cooling to room temperature, water was added to the solution, and the reaction mixture was extracted by diethyl ether. After the organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, the solvents were removed using a rotary evaporator. The crude product was purified by column chromatography, and the desired products of **11a,b** were obtained in a 92% and 90% yield, respectively.

#### N-Hexyldithieno[3,2-b:2',3'-d]pyrrole (11a)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ /ppm): 7.09-7.08 (d, *J* = 4.00 Hz, 2H, CH-C-N), 6.98-6.97 (d, *J* = 4.00 Hz, 2H, CH-C-S), 4.16-4.12 (t, *J* = 16.00 Hz, 2H, N-CH<sub>2</sub>-), 1.84-1.80 (t, *J* = 16.00 Hz, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-), 1.27-1.24 (m, 6H, N-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-), 0.86-0.84 (t, *J* = 8.00 Hz, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz,  $\delta$ /ppm): 144.87, 122.67, 114.53, 110.90, 47.34, 31.36, 30.28, 26.60, 22.45, 14.16, 13.97. C<sub>14</sub>H<sub>17</sub>NS<sub>2</sub> (263.42): calcd. C 63.83, H 6.50, N 5.32, S 24.35; found C 64.01, H 6.62, N 5.25, S 24.44.

#### N-2-Ethylhexyldithieno[3,2-b:2',3'-d]pyrrole (11b)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ /ppm): 7.13-7.12 (d, *J* = 4.00 Hz, 2H, CH-C-N), 7.00-6.99 (d, *J* = 4.00 Hz, 2H, CH-C-S), 4.05-4.02 (t, *J* = 12.00 Hz, 2H, N-CH<sub>2</sub>), 1.98 (t, 1H, N-CH<sub>2</sub>-CH-), 1.35 (m, 8H, N-CH<sub>2</sub>-CH (CH<sub>2</sub>)-(CH<sub>2</sub>)<sub>3</sub>), 0.95-0.92 (t, 6H, 2X CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz,  $\delta$ /ppm): 145.06, 122.40, 114.31, 110.87, 40.22, 30.41, 30.11, 28.45, 25.41, 22.79, 13.86, 10.47. C<sub>16</sub>H<sub>21</sub>NS<sub>2</sub> (291.47): calcd. C 65.93, H 7.26, N 4.81, S 22.00; found C 65.85, H 7.40, N 4.72, S 21.89.

## 3.3.5 | Synthesis of 2,6-dibromo-*N*alkyldithieno[3,2-b:2',3'-d]pyrrole (12a,b)

Compound **11a,b** (3.49 mmol) was dissolved in THF (50 mL), and *N*-bromosuccinamide (NBS) (8.37 mmol) was added in one portion. The reactant was stirred at room temperature for 4 hours and then extracted by diethyl ether. The volatiles were removed under vacuum, and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>. The residue was purified by column chromatography,

and the desired products **12a,b** were obtained in a 75% and 70% yield, respectively.

# 2,6-Dibromo-N-hexyldithieno[3,2-b:2',3'-d]pyrrole (12a)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 7.02 (s, 2H, CH-N), 4.09-4.05 (t, J = 16.00 Hz, 2H, N-CH<sub>2</sub>-), 1.81-1.78 (t, J =12.00 Hz 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-), 1.28-1.25 (m, 6H, N-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>), 0.88-0.85 (t, J = 12.00 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, δ/ppm): 141.42, 114.21, 109.70, 47.55, 31.34, 30.30, 26.56, 22.46, 13.97. C<sub>14</sub>H<sub>15</sub>Br<sub>2</sub>NS<sub>2</sub> (421.21): calcd. C 39.92, H 3.59, Br 37.94, N 3.33, S, 15.23; found C 39.81, H 3.64, Br 37.90, N 3.40, S 15.20.

# 2,6-Dibromo-N-2-ethylhexyldithieno[3,2-b:2',3'-d]pyrrole (12b)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 6.92 (s, 2H, CH-N) 3.84-3.80 (t, J = 16.00 Hz, 2H, N-CH<sub>2</sub>-), 1.80 (t, 1H, N-CH<sub>2</sub>-CH-), 1.25-1.21 (m, 8H, N-CH<sub>2</sub>-CH (CH<sub>2</sub>)-(CH<sub>2</sub>)<sub>3</sub>), 0.86-0.82 (t, J = 16.00 Hz, 6H, 2X CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, δ/ppm): 141.58, 114.42, 114.16, 109.51, 40.43, 30.40, 28.48, 23.84, 22.87, 13.93, 10.54. C<sub>16</sub>H<sub>19</sub>Br<sub>2</sub>NS<sub>2</sub> (449.27): calcd. C 42.77, H 4.26, Br 35.57, N 3.12, S 14.27; found C 42.71, H 4.33, Br 35.63, N 3.02, S 14.39.

# 3.3.6 | Synthesis of 2,6-di (tributyltin)-*N*-hexyldithieno[3,2-b:2',3'-d]pyrrole (13)<sup>24f</sup>

By the modification of the reported method: Under nitrogen atmosphere, compound 11a (1.22 g, 4.63 mmol) was dissolved in dry THF (50 mL), was cooled to  $-80^{\circ}$ C with a cooling reactor-acetone bath and *n*-butyllithium (1.6 M in hexane, 8.6 mL, 18.5 mmol), and was added dropwise over 1 hour. The reaction mixture was stirred at  $-80^{\circ}C$ for 1 hour and then brought to room temperature. The stirring was continued for 20 minutes, and the reaction mixture was cooled again to -80°C. A solution of tributylstannyl chloride (6.02 g, 18.5 mmol) in dry THF (7 mL) was added dropwise over 30 minutes. The mixture was slowly brought to room temperature and stirred another 2 hours. Subsequently, water was added to the reaction mixture, and the aqueous phase extracted with diethyl ether twice. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>. Afterward, the column chromatography technique was utilized to purify the crude product to obtain the desired product 13 as a yellow oil (3.35 g, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 6.95 (s, 2H, CH-N), 4.20-4.17 (t, J = 12.00 Hz, 2H, N-CH<sub>2</sub>-), 1.90 (t, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-), 1.59-1.50 (m, 12H, 6X Sn-CH<sub>2</sub>), 1.36-1.32 (m, 18H, 6X Sn-CH<sub>2</sub>-CH<sub>2</sub>- + (CH<sub>2</sub>)<sub>3</sub>-hexyl), 1.14-1.10 (m, 12H, 6X Sn (CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-), 0.91-0.88 (m, 21H, 2X (CH<sub>3</sub>)<sub>3</sub>-butyl + CH<sub>3</sub>-hexyl). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 147.90, 134.66, 120.13, 118.02, 47.34,

## 3.4 | Synthesis of polymers

## 3.4.1 | General procedure for microwave-assisted Stille cross-coupling polymerization

Equimolar amounts (0.5 mmol) from the desired dibromo and di (tributylstannyl) derivatives were dissolved in dry DMF and degassed with N2 atmosphere for at least 30 minutes followed by adding Pd (PPh)<sub>4</sub> (5 mol% relative to Br) and degassed again with nitrogen for 30 minutes. The screw-capped glass tube was then irradiated by microwave under the following conditions: 5 minutes at 100°C, 5 minutes at 120°C, and 30 minutes at 150°C. The end-capping process was performed in separated two steps: A solution of phenylboronic acid pinacol ester (5 mol%) in 0.5-mL DMF was first added, followed by irradiating the reaction mixture by microwave under the following condition: 2 minutes at 100°C, 2 minutes at 120°C, and 5 minutes at 150°C. The same process was repeated by adding a solution of bromobenzene (5 mol%) in 0.5-mL DMF. After the second end-capping process, the screw capped glass tube was allowed to return to room temperature, and the reaction mixture was poured into methanol. The crude copolymer was collected by filtration and washed consecutively with MeOH. The residual solid was loaded into an extraction thimble and washed successively with MeOH (24 h) followed by acetone (24 h).

Poly[(4,4-di (hexyl)dithieno[3,2-b:2',3'-d]silole-2,6-diyl)alt-(4,7-bis(3-hexylthiophen-2-yl) benzo[c][2,1,3] thiadiazole)-5,5-diyl] (P1)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 7.69 (br. s, 2H, 2X CH (Ph)), 7.22 (s, 2H, 2X CH-C-Si), 7.19 (s, 2H, 2X CH-C-hexyl), 2.7-2.68 (br. m, 4H, 2X C-CH<sub>2</sub>-hexyl), 1.75-1.56 (br. m, 4H, 2X C-CH<sub>2</sub>-CH<sub>2</sub>-), 1.50-1.20 (br. m, 32H, 2X Si (CH<sub>2</sub>)<sub>5</sub> + 2X (CH<sub>2</sub>)<sub>3</sub>), 0.87-0.83 (br. m, 12H, 2X CH<sub>3</sub> (DTSi) + 2X CH<sub>3</sub> (HT)). (C<sub>46</sub>H<sub>58</sub>N<sub>2</sub>S<sub>5</sub>Si)<sub>n</sub> (827.38)<sub>n</sub>: calcd. C 66.78, H 7.07, N 3.39, S 19.38, Si 3.39; found C 66.91, H 7.01, N 3.44, S 19.29.

## Poly[(4,4-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole-2,6-diyl)-alt-(4,7-bis(3-hexylthiophen-2-yl)benzo[c][2,1,3] thiadiazole)-5,5-diyl] (P2)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 7.65 (br. s, 2H, 2X CH (Ph)), 7.17 (s, 2H, 2X CH-C-Si), 7.15 (s, 2H, 2X CH-C-hexyl), 2.59-2.56 (br. m, 4H, 2X C-CH<sub>2</sub>-hexyl), 1.65-1.55

(br. m, 4H, 2X C-CH<sub>2</sub>-CH<sub>2</sub>-), 1.34-1.32 (br. s, 2H, 2X Si-CH<sub>2</sub>-CH-), 1.25-1.08 (br. m, 32H, 2X Si-CH<sub>2</sub>-CH (CH<sub>2</sub>)-(CH<sub>2</sub>)<sub>3</sub> + 2X (CH<sub>2</sub>)<sub>3</sub>), 0.74-0.70 (br. m, 18H, 2X (CH<sub>2</sub>-CH<sub>3</sub>) + CH (CH<sub>2</sub>-CH<sub>3</sub>)) (DTSi) + 2X CH<sub>3</sub> (HT)). (C<sub>50</sub>H<sub>66</sub>N<sub>2</sub>S<sub>5</sub>Si)<sub>n</sub> (883.48)<sub>n</sub>: calcd. C 67.97, H 7.53, N 3.17, S 18.15, Si 3.18; found C 68.09, H 7.49, N 3.03, S 18.22.

### Poly[(N-hexyl-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)-alt-(4,7-bis(3-hexylthiophen-2-yl)benzo[c][2,1,3] thiadiazole)-5,5-diyl] (P3)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 7.69 (br. s, 2H, 2X CH (Ph)), 7.21 (s, 2H, 2X CH-C-N), 7.15 (s, 2H, 2X CH-C-hexyl), 4.18 (br. s, 2H, N-CH<sub>2</sub>), 2.71-2.69 (br. m, 4H, 2X C-CH<sub>2</sub>), 1.90-1.85 (br. m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-), 1.71-1.69 (br. m, 4H, C-CH<sub>2</sub>-CH<sub>2</sub>-), 1.33-1.25 (br. m, 18H, -(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub> (DTP) + 2X -(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub> (HT)), 0.87-0.84 (br. m, 9H, CH<sub>3</sub> (DTP) + 2X CH<sub>3</sub> (HT)). (C<sub>40</sub>H<sub>45</sub>N<sub>3</sub>S<sub>5</sub>)<sub>n</sub> (728.13)<sub>n</sub>: calcd. C 65.98, H 6.23, N 5.77, S 22.02; found C 65.82, H 6.41, N 5.86, S 21.89.

### Poly[(N-2-ethylhexyl-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)-alt-(4,7-bis(3-hexylthiophen-2-yl)benzo[c][2,1,3] thiadiazole)-5,5-diyl] (P4)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ /ppm): 7.69-7.65 (br. s, 2H, 2X CH (Ph)), 7.21 (s, 2H, 2X CH-C-N), 7.15 (s, 2H, 2X CH-C-hexyl), 4.04 (br. s, 2H, N-CH<sub>2</sub>), 2.71-2.65 (br. s, 4H, 2X C-CH<sub>2</sub>), 1.99 (br. s, 1H, N-CH<sub>2</sub>-CH-), 1.75-1.65 (br. m, 4H, C-CH<sub>2</sub>-CH<sub>2</sub>-), 1.32-1.25 (br. m, 20H, -CH (CH<sub>2</sub>)-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub> (DTP) + 2X -(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub> (HT)), 0.92-0.83 (br. m, 12H, (-CH<sub>2</sub>-CH<sub>3</sub> + CH (CH<sub>2</sub>-CH<sub>3</sub>) (DTP) + 2X CH<sub>3</sub> (HT)). (C<sub>42</sub>H<sub>49</sub>N<sub>3</sub>S<sub>5</sub>)<sub>n</sub> (756.18)<sub>n</sub>: calcd. C 66.71, H 6.53, N 5.56, S 21.20; found C 66.63, H 6.61, N 5.60, S 21.02.

## Poly[(4,4-di (hexyl)dithieno[3,2-b:2',3'-d]silole-2,6-diyl)alt-(4,7-bis(4-hexylthiophen-2-yl) benzo[c][2,1,3] thiadiazole)-5,5-diyl] (P5)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 7.98 (s, 2H, 2X CH (Ph)), 7.83 (s, 2H, 2X CH-C-Ph), 7.23 (s, 2H, 2X CH-C-Si), 2.69 (br. m, 4H, 2X C-CH<sub>2</sub>-hexyl), 1.85-1.65 (br. m, 4H, 2X C-CH<sub>2</sub>-CH<sub>2</sub>-), 1.36-1.28 (br. m, 32H, 2X Si (CH<sub>2</sub>)<sub>5</sub> + 2X (CH<sub>2</sub>)<sub>3</sub>), 092-0.88 (br. m, 12H, 2X CH<sub>3</sub> (DTSi) + 2X CH<sub>3</sub> (HT)). (C<sub>46</sub>H<sub>58</sub>N<sub>2</sub>S<sub>5</sub>Si)<sub>n</sub> (827.38)<sub>n</sub>: calcd. C 66.78, H 7.07, N 3.39, S 19.38, Si 3.39; found C 66.89, H 7.19, N 3.30, S 19.22.

## Poly[(4,4-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole-2,6-diyl)-alt-(4,7-bis(4-hexylthiophen-2-yl)benzo[c][2,1,3] thiadiazole)-5,5-diyl] (P6)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 7.88-7.87 (br. s, 2H, 2X CH (Ph)), 7.69 (s, 2H, 2X CH-C-Ph), 7.15 (s, 2H, 2X CH-C-Si), 2.61-2.57 (br. m, 4H, 2X C-CH<sub>2</sub>-hexyl), 1.70-1.55 (br. m, 4H, 2X C-CH<sub>2</sub>-CH<sub>2</sub>-), 1.45-1.40 (br. s,

2H, 2X Si-CH<sub>2</sub>-CH-), 1.28-1.16 (br. m, 32H, 2X Si-CH<sub>2</sub>-CH (CH<sub>2</sub>)-(CH<sub>2</sub>)<sub>3</sub> + 2X (CH<sub>2</sub>)<sub>3</sub>), 0.81-0.76 (br. m, 18H, 2X (CH<sub>2</sub>-CH<sub>3</sub> + CH (CH<sub>2</sub>-CH<sub>3</sub>)) (DTSi) + 2X CH<sub>3</sub> (HT)). (C<sub>50</sub>H<sub>66</sub>N<sub>2</sub>S<sub>5</sub>Si)<sub>n</sub> (883.48)<sub>n</sub>: calcd. C 67.97, H 7.53, N 3.17, S 18.15, Si 3.18; found C 67.84, H 7.63, N 3.09, S 18.07.

## Poly[(N-hexyl-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)-alt-(4,7-bis(4-hexylthiophen-2-yl) benzo[c][2,1,3] thiadiazole)-5,5-diyl] (P7)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ/ppm): 8.00 (br. s, 2H, 2X CH (Ph)), 7.87 (s, 2H, 2X CH-C-Ph), 7.12 (s, 2H, 2X CH-C-N), 4.20 (br. s, 2H, N-CH<sub>2</sub>), 3.02-2.92 (br. s, 4H, 2X C-CH<sub>2</sub>), 2.15 (br. m, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-), 1.82-1.79 (br. m, 4H, C-CH<sub>2</sub>-CH<sub>2</sub>-), 1.33-1.24 (br. m, 18H, -(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub> (DTP) + 2X -(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub> (HT)), 0.90-0.80 (br. m, 9H, CH<sub>3</sub> (DTP) + 2X CH<sub>3</sub> (HT)). (C<sub>40</sub>H<sub>45</sub>N<sub>3</sub>S<sub>5</sub>)<sub>n</sub> (728.13)<sub>n</sub>: calcd. C 65.98, H 6.23, N 5.77, S 22.02; found C 66.07, H 6.39, N 5.82, S 21.89.

### Poly[(N-2-ethylhexyl-dithieno[3,2-b:2',3'-d]pyrrole-

2,6-diyl)-alt-(4,7-bis(4-hexylthiophen-2-yl)benzo[c][2,1,3] thiadiazole)-5,5-diyl] (P8). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ / ppm): 7.99 (br. s, 2H, 2X CH (Ph)), 7.83 (s, 2H, 2X CH-C-Ph), 7.12 (s, 2H, 2X CH-C-N), 4.07 (br. s, 2H, N-CH<sub>2</sub>), 2.92 (br. s, 4H, 2X C-CH<sub>2</sub>), 1.99 (br. s, 1H, N-CH<sub>2</sub>-CH-), 1.79-1.69 (br. m, 4H, C-CH<sub>2</sub>-CH<sub>2</sub>-), 1.37-1.25 (br. m, 20H, -CH (CH<sub>2</sub>)-(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub> (DTP) + 2X -(CH<sub>2</sub>)<sub>3</sub>-CH<sub>3</sub> (HT)), 0.92-0.86 (br. m, 12H, (-CH<sub>2</sub>-CH<sub>3</sub> + CH (CH<sub>2</sub>-CH<sub>3</sub>) (DTP) + 2X CH<sub>3</sub> (HT)). (C<sub>42</sub>H<sub>49</sub>N<sub>3</sub>S<sub>5</sub>)<sub>n</sub> (756.18)<sub>n</sub>: calcd. C 66.71, H 6.53, N 5.56, S 21.20; found C 66.89, H 6.51, N 5.63, S 21.11.

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#### REFERENCES

 (a)T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds (Eds), Handbook of Conductive Polymers, New York, Marcel Dekker 1998. (b)Z. V. Vardeny, A. J. Heeger, A. Dodabalapur (Eds), Summary of the Fundamental Research Needs in Organic Electronic Materials, Amsterdam, Elsevier 2005. (c)S. Ahmad, J. Polym, Engineering 2014, 34(4), 279. (d)A. Marrocchi, A. Facchetti, D. Lanari, C. Petruccia, L. Vaccaro, Energy *Environ Forensic Sci* **2016**, *9*, 763. (e)G. H. Roche, D. Thuau, P. Valvin, S. Clevers, T. Tjoutis, S. Chambon, D. Flot, Y. H. Geerts, J. J. E. Moreau, G. Wantz, O. J. Dautel, 1700218*Adv Electron Mater* **2017**, (1–12), 3.

- [2] (a)H. E. Katz, *Chem. Mater.* 2004, *16*(23), 4748. (b)R. Ponce Ortiz, M. C. Ruiz Delgado, J. Casado, V. Hernandez, O.-K. Kim, H. Y. Woo, J. T. Lopez Navarrete, J. Am, *Chem Soc* 2004, *126*(41), 13363; (c)A. M. Fraind, J. D. Tovar, *J. Phys, Chem B* 2010, *114*(9), 3104. (d)R. Szűcs, P.-A. Bouit, L. Nyulászi, M. Hissler, *ChemPhysChem*, Wiley-VCH Verlag 2017, *18*(19), 2618.
- [3] (a)J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, *Chem Commun* 2001, 1740. (b)H. Y. Chen, J. W. Y. Lam, J. D. Luo, Y. L. Ho, B. Z. Tang, D. Zhu, M. Wong, H. S. Kwok, *Appl. Phys. Lett.* 2002, *81*, 574. (c)J. Chen, Z. Xie, J. W. Y. Lam, C. C. W. Law, B. Z. Tang, *Macromolecules* 2003, *36*, 1108.
- [4] (a)J. Chen, Y. Cao, Macromol Rapid Commun 2007, 28, 1714.
  (b)L. Liao, L. Dai, A. Smith, M. Durstock, J. Lu, J. Ding, Y. Tao, Macromolecules 2007, 40(26), 9406. (c)P. Shen, Z. Zhuang, Z. Zhao, B. Z. Tang, J. Mater, Chem C 2018, 6, 11835.
- [5] Y. F. Geng, A. L. Tang, K. Tajima, Q. D. Zeng, E. J. Zhoug, J. Mater, Chem A 2019, 7, 64.
- [6] (a)J.-S. Wu, Y.-J. Cheng, T.-Y. Lin, C.-Y. Chang, P.-I. Shih, C.-S. Hsu, *Adv. Funct. Mater.* 2012, *22*, 1711. (b)C. Gu, Q. Zhu, X. Bao, S. Wen, M. Qiu, L. Han, W. Huang, D. Zhua, R. Yang, *Polym. Chem.* 2015, *6*, 6219.
- [7] (a)K. Ogawa, S. C. Rasmussen, J. Org Chem 2003, 68(7), 2921.
  (b)K. Ogawa, J. A. Stafford, S. D. Rothstein, D. E. Tallman, S. C. Rasmussen, Synth. Met. 2005, 152, 137.
- [8] (a)G. Koeckelberghs, C. Samyn, *Macromolecules* 2005, *38*, 4545. (b)K. Ogawa, S. C. Rasmussen, *Macromolecules* 2006, *39*, 1771.
- [9] K. Ogawa, S. C. Rasmussen, Macromolecules 2006, 39, 1771.
- [10] Q. Fan, H. Jiang, Y. Liu, W. Su, H. Tan, Y. Wang, R. Yang, W. Zhu, J. Mater. Chem. C 2016, 4, 2606.
- [11] C. Gao, L. Wang, X. Li, H. Wang, Polym. Chem. 2014, 5, 5200.
- [12] (a)W. J. Belcher, S. C. Rasmussen, P. C. Dastoor, *Polym Prepr* 2007, 48, 11. (b)J. Liu, R. Zhang, G. Sauvé, T. Kowalewki, R. D. McCullough, *J. Am. Chem. Soc.* 2008, 130, 13167. (c) W. Zhang, J. Li, B. Zhang, J. Qin, Z. Lu, P. Y. Mary, B. Chan-Park, C. M. Li, *Macromolecules* 2008, 41(23), 8953. (d) T. T. Steckler, X. Zhang, J. Hwang, R. Honeyager, S. Ohira, X.-H. Zhang, A. Grant, S. Ellinger, S. A. Odom, D. Sweat, D. B. Tanner, A. G. Rinzler, S. Barlow, J. L. Brédas, B. Kippelen, S. R. Marder, J. R. Reynolds, *J. Am, Chem Soc* 2009, 131(8), 2824. (e) C. Li, Z. Bo, *RSC Polymer Chemistry* 2016, 17, Chapter(1), 1.
- [13] G. Dennler, M. C. Scharber, C. J. Brabec, Adv. Mater. 2009, 21, 1323.
- [14] (a)F. C. Krebs, Sol. Energy Mater. Sol. Cells 2009, 93, 394. (b)
   W. Cai, X. Gong, Y. Cao, Sol. Energy Mater. Sol. Cells 2010, 94, 114.
- [15] (a)H. A. M. van Mullekom, J. Vekemans, E. E. Havinga,
  E. W. Meijer, *Mater Sci Eng Res* 2001, 32, 1. (b)W. C. Wu,
  W. Y. Lee, W. C. Chen, *Macromol. Chem. Phys.* 2006, 207, 1131. (c)W. C. Wu, C. L. Liu, W. C. Chen, *Polymer* 2006, 47, 527. (d)W. C. Wu, W. Y. Lee, C. L. Pai, W. C. Chen,

C. S. Tuan, J. L. Lin, *J Polym Sci Polym Phys* **2007**, *45*, 67. (e) W. Y. Lee, K. F. Cheng, T. F. Wang, C. C. Chueh, W. C. Chen, C. S. Tuan, J. L. Lin, *Macromol. Chem. Phys.* **2007**, *208*, 1919.

- [16] (a)M. C. Scharber, D. Wuhlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. L. Brabec, Adv. Mater. 2006, 18, 789. (b)F. L. Zhang, K. G. Jespersen, C. Bjorstrom, M. R. Andersson, M. Svensson, V. Sundstrom. K. Magnusson, E. Moons, A. Yartsev, O. Inganas, Adv. Funct. Mater. 2006, 16, 667. (c)A. Gadisa, W. Mammo, L. M. Andersson, S. Admassie, F. Zhang, M. R. Andersson, O. Inganas, Adv. Funct. Mater. 2007, 17, 3836. (d)M. A. Loi, S. Toffanin, M. Muccini, M. Forster, U. Scherf, M. Scharber, Adv. Funct. Mater. 2007, 17, 2111. (e)J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, G. C. Bazan, Nat. Mater. 2007, 6, 497. (f)N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletete, G. Durocher, Y. Tao, M. Leclerc, J. Am. Chem. Soc. 2008, 130, 732. (g)G. Dennler, M. C. Scharber, T. Ameri, P. Denk, K. Forberich, C. Waldauf, C. J. Brabec, Adv. Mater. 2008, 20, 579.
- [17] (a)P. Herguth, X. Jiang, M. S. Liu, A. K. Y. Jen, Macromolecules 2002, 35, 6094. (b)E. Wang, M. Wang, L. Wang, C. Duan, J. Zhang, W. Cai, C. He, H. Wu, Y. Cao, Macromolecules 2009, 42, 4410. (c)J.-Y. Lee, M.-H. Choi, H.-J. Song, D.-K. Moon, J. Polym. Sci., Part a: Polym. Chem. 2010, 48, 4875. (d) S. C. Price, A. C. Stuart, W. You, Macromolecules 2010, 43, 4609.
- [18] (a)L. Liao, L. Dai, A. Smith, M. D. J. Lu, J. Ding, Y. Tao, *Macromolecules* 2007, 40, 9406. (b)P. Anant, N. T. Lucas, J. Jacob, Org. Lett. 2008, 10, 5533. (c)J. Hou, H.-Y. Chen, S. Zhang, G. Li, Y. Yang, J. Am. Chem. Soc. 2008, 130, 16144. (d) J. Zhang, Y. Yang, C. He, Y. H. G. Zhao, Y. Li, *Macromolecules* 2009, 42, 7619. (e)R. C. Coffin, J. Peet, J. Rogers, G. C. Bazan, Nat. Chem. 2009, 1, 657. (f)Y. Lua, H. Chena, X. Houa, X. Hub, S.-C. Nga, Synth. Met. 2010, 160, 1438.
- [19] (a)S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, A. J. Heeger, *Nat Photon* 2009, *3*, 297. (b)Y. Geng, J. Cong, K. Tajima, Q. Zeng, E. Zhou, *Polym. Chem.* 2014, *5*, 6797. (c)G. P. Kini, Q. V. Hoang, C. E. Song, S. K. Lee, W. S. Shin, W.-W. So, M. A. Uddin, H. Y. Woo, J.-C. Lee, *Polym. Chem.* 2017, *8*, 3622. (d)J. Lee, J. Kim, T. L. Nguyen, M. Kim, J. Park, Y. Lee, S. Hwang, Y.-W. Kwon, J. Kwak, H. Y. Woo, *Macromolecules* 2018, *51*(9), 3360.
- [20] (a)A. A. El-Shehawy, N. I. Abdo, A. A. El-Barbary, J.-S. Lee, *Eur. J. Org. Chem.* 2011, 4841. (b)N. I. Abdo, A. A. El-Shehawy, A. A. El-Barbary, J.-S. Lee, *Eur. J. Org. Chem.* 2012, 5540. (c) N. I. Abdo, J. Ku, A. A. El-Shehawy, H.-S. Shim, J.-K. Min, A. A. El-Barbary, Y. H. Jang, J.-S. Lee, *J. Mater. Chem.* 2013, *A1*, 10306. (d) A. A. El-Shehawy, N. I. Abdo, A. A. El-Barbary, J. W. Choi, H. S. El-Sheshtawy, J.-S. Lee, *J. Mater Sci Nano Mater* 2018, *2*(1), 1.
- [21] (a)W. Elsawy, C.-L. Lee, S. Cho, S.-H. Oh, S.-H. Moon, A. El-Barbary, J.-S. Lee, *Phys. Chem. Chem. Phys.* 2013, *15*, 15193.
  (b)W. Elsawy, H. Kang, K. Yu, A. Elbarbary, K. Lee, J.-S. Lee, *J Polym Sci A Polymer Chem* 2014, *52*, 2926. (c)W. Elsawy, M. Son, J. Jang, M.-J. Kim, Y. Ji, T.-W. Kim, H.-C. Ko, A. El-Barbary, M.-H. Ham, J.-S. Lee, *ACS Macro Lett.* 2015, *4*, 322.
  (d) M. Shaker, J.-H. Lee, C.-K. Trinh, W. Kim, K. Lee, J.-

S. Lee, *RSC Adv.* **2015**, *5*, 66005. (e)M. Shaker, C.-K. Trinh, W. Kim, H. Kim, K. Lee, J.-S. Lee, *New J, Chem* **2015**, *39*, 4957.

- [22] L. Biniek, S. Fall, C. L. Chochos, D. V. Anokhin, D. A. Ivanov, N. Leclerc, P. Lévêque, T. Heiser, *Macromolecules* 2010, 43, 9779.
- [23] (a)Z.-G. Zhang, J. Min, S. Zhang, J. Zhang, M. Zhang, Y. Li, *Communique* 2011, 47, 9474. (b)H. Zhou, L. Yang, S. C. Price, K. J. Knight, W. You, *Angew Chem Int Ed* 2010, 49, 7992. (c) H. Zhou, L. Yang, S. Xiao, S. Liu, W. You, *Macromolecules* 2009, 43, 811.
- [24] C.-H. Liu, S.-H. Chen, Y. Chen, J. Polym. Sci., Part a: Polym. Chem. 2006, 44, 3882.
- [25] P. Wûrfel, In Physics of Solar Cells, Weinheim, Wiley-VCH 2005.
- [26] (a)J. L. Bredas, R. Silbey, D. S. Boudreux, R. R. Chance, J. Am. Chem. Soc. 1983, 105, 6555. (b)D. M. Deleeuw, M. M. Simeonon, E. B. Brown, R. E. F. Einerhand, Synth. Met. 1997, 87, 53. (c)T. Johansson, W. Mammo, M. Svensson, M. R. Andersson, O. J. Inganas, Mater Chem 2003, 13, 1316. (d)S. Admassie, O. Inganas, W. Mammo, E. Perzon, M. R. Andersson, Synth. Met. 2006, 156, 614. (e)H. Usta, C. Risko, Z. Wang, H. Huang, M. K. Deliomeroglu, A. Zhukhovitskiy, A. Facchetti, T. J. Marks, J. Am. Chem. Soc. 2009, 131, 5586.
- [27] Y. Li, Y. Cao, J. Gao, D. Wang, G. Yu, A. J. Heeger, Synth. Met. 1999, 99, 243.
- [28] Z. Li, K. Feng, J. Liu, J. Mei, Y. Li, Q. Peng, J. Mater. Chem. A 2016, 4, 7372.
- [29] H. Roncali, Chem. Rev. 1997, 97, 173.
- [30] C. R. McNeill, J. J. M. Halls, R. Wilson, G. L. Whiting, S. Berkebile, M. G. Ramsey, R. H. Friend, N. C. Greenham, *Adv. Funct. Mater.* 2008, 18, 2309.

- [31] (a)D. A. M. Egbe, L. H. Nguyen, H. Hoppe, D. Mühlbacher, N. S. Saricigtci, *Macromol. Rapid Commun.* 2005, 26, 1389. (b) J. Hou, Z. Tan, Y. Yan, Y. He, C. Yang, Y. Li, *J. Am, Chem Soc* 2006, 128, 4911. (c)H. Shang, H. Fan, Q. S. S. Li, Y. Li, X. Zhan, *Sol Ener Mater Sol Cells* 2010, 94, 457.
- [32] J.-D. Chai, M. Head-Gordon, Phys. Chem. Chem. Phys. 2008, 10, 6615.
- [33] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. Gaussian, Inc., Wallingford CT, 2009.
- [34] R. Stalder, C. Grand, J. Subbiah, F. So, J. R. Reynolds, *Polym. Chem.* 2012, 3, 89.
- [35] H. Usta, G. Lu, A. Facchetti, T. J. Marks, J. Am. Chem. Soc. 2006, 128, 9034.

#### SUPPORTING INFORMATION

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