# Influence of Donor–Acceptor Conjugation Between Thiophene-Phthalazinone Structures Containing Sp<sup>3</sup> C—N Bond on the Frontier Orbital Levels and Optic–Electronic Properties

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**ABSTRACT:** Herein, an electron-deficient phthalazinone unit containing a unique Sp<sup>3</sup> hybrid nitrogen atom as an acceptor to cut off the ether bond was presented and three Donor–Acceptor (D–A) conjugated fluoropolymers via Classical Aromatic Nucleophilic Displacement Polymerization (CANDP) method were successfully synthesized. These polymers exhibit excellent thermostability. The 5% weight loss temperature of PDT2TF under nitrogen atmosphere is high, up to 470 °C. This is due to that the D–A conjugation between thiophenephthalazinone units affects its resonance energy and stabilizes the thiophene-phthalazinone structures. These three fluoropolymers show strong absorptions and fluorescence in visible light region both in solution and thin film states. The band gaps ( $E_g$ ) of these polymers are narrower than that of their corresponding di-NH capped monomers, owing to the good

**INTRODUCTION** In the past decades, the intrinsic characteristics of donor-acceptor (D-A) conjugated polymers containing Sp<sup>3</sup> C–N bond have been widely studied as important organic semiconductor materials for optoelectronic applications, such as light-emitting diodes, polymer solar cells, and organic field effect transistors.<sup>1–13</sup> The classical structures, such as polyaniline and triphenylamine, are shown in Figure 1. Due to its low-cost commercial available monomer, straightforward and high-yield synthetic method, polyaniline is a star material since the very beginning in the optoelectronic research field.<sup>1-7</sup> However, the non-doped state of polyaniline, which a saturated amine is linked with two conjugated benzene rings and one hydrogen atom (Fig. 1), inhibits conjugation with large band gaps (3.6 eV).<sup>13</sup> Also, polymeric materials based on triphenylamine units have been widely used as semiconductor materials for electro-optics applications.<sup>8–12</sup> The structure feature of triphenylamine is that the electron-rich nitrogen atom links with three  $\pi$ -conjugated phenyl groups, resulting in its narrower band gaps than that

electronic communication properties of the Sp<sup>3</sup> nitrogen atom in the phthalazinone unit. The  $E_g$  value of PDT3TF is decreased to 2.03 eV. These results indicate that phthalazinone unit is an efficient acceptor and could exhibit strong D–A effect with thiophene unit. Also, the Sp<sup>3</sup> nitrogen atom in the phthalazinone shows good electronic wave function and charge transport properties. This facile CANDP synthetic method combined with Sp<sup>3</sup> C–N bond linked electron-deficient phthalazinone unit affords polymers with controllable photoelectric properties. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *00*, 000–000

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of non-doped polyaniline. Incorporating triphenylamine into polymer backbones with  $\pi$ -conjugated system could obtain excellent charge-transport, hole-transporting, and electroluminescence properties with controllable band gaps.<sup>8-10,14</sup> For the conjugated poly(4-cyanotriphenylamine), the optical band gap is determined to be approximately 2.91 eV.<sup>12</sup> However owing to the ammonia with three hydrogen atoms all replaced by aryl groups, the three phenyl substituents are non-coplanar.<sup>15,16</sup> These Sp<sup>3</sup> hybridized C-N bond could partly weaken the electron delocalization along the polymer backbone.<sup>9</sup> Besides, as a family of Sp<sup>3</sup> C-N bond linked units, the Sp<sup>3</sup> hybrid nitrogen atom in phthalazinone unit is combined into a naphthalene ring, resulting in better planarity than classical triangular pyramidal triphenylamine structure.<sup>17</sup> Furthermore, the electron-drawing C=N and C=O bond linked with electron-rich Sp<sup>3</sup> nitrogen atom exhibits better electron delocalization and charge transport properties. Generally, the conjugated effect is related to the bond length alternation (BLA) that a geometrical parameter

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The average of the difference in the length between adjacent carbon-carbon bonds



**FIGURE 1** The classical polymer structures containing  $Sp^3$  C—N bond. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

defined from the difference between the average lengths of adjacent carbon-carbon bonds in D-A polymers.<sup>18</sup> As can been seen in Figure 1, the BLA influenced by the partial charge redistribution from the conjugated effect is determined by DFT calculations.<sup>18,19</sup> The BLA of benzene ring linked with phthalazinone unit is 0.00382 Å, which is much shorter than that of benzene ring in the polyaniline (0.00961 Å) and poly(triphenylamine) (0.00751 Å). This suggests that phthalazinone could possess higher electron delocalization within the molecule compared with phenylamine and poly(triphenylamine).<sup>18,19</sup> As previously reported, the phthalazinone moiety is widely used to develop polymeric materials for high temperature-resistant resins and fibers.<sup>20-26</sup> These high-performance phthalazinone-containing polymers have exhibited good solubility and rigidity, even excellent thermalstability and mechanical properties.<sup>27-30</sup> However, there has been seldom focusing on the optoelectronic properties of the phthalazinone structure. Thus, novel building D-A conjugated polymers with phthalazinone moiety is highly desirable for investigating its optoelectronic properties deeply.

From the polymer chemistry view point, phthalazinonebased polymers are mainly synthesized by Classical Aromatic Nucleophilic Displacement Polymerization (CANDP) through the Sp<sup>3</sup> hybridized N-H reactive site. The aromatic nucleophilic displacement reactions have received considerable attention in polymer chemistry science as a promising classical polymerization method for achieving high molecular weight polymers (see Fig. 2).<sup>31-33</sup> Various kinds of polymers have been developed based on CANDP.<sup>21,34-41</sup> The CANDP is rapid, less side reactions, low-cost base catalysis (K2CO3, Cs<sub>2</sub>CO<sub>3</sub>, etc.), and yielded polymers of excellent rigid thermoplastics with high glass transitions.<sup>31</sup> Generally, the polymer synthesized by CANDP could be classified as shown in Figure 2. Polyarylether is the most important material in the family of CANDP polymers via C-O coupling polymeriza-tion.<sup>31,32,36,42</sup> And the phthalazinone-based polyarylether has been extensively studied and widely used as structural material in the aerospace and automotive industries,<sup>30,40</sup> functional membranes for the optical waveguide applications,<sup>43,44</sup> anion and proton exchange membrane materials in lithiumClassical Aromatic Nucleophilic Displacement Polymerziation



**FIGURE 2** Polymers synthesized by classical aromatic nucleophilic displacement polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ion batteries and vanadium redox flow battery fields,<sup>22,23</sup> etc. But a common drawback with the use of CANDP method is to incorporate the ether bond in the polymer main chain. This could lead to the interruption of electron delocalization in the polymer backbone.<sup>26,45-48</sup> Therefore, quite a few CANDP polymers have exhibited excellent optoelectronic properties. Developing new structure that can prolong the conjugated effect along the polymer backbone via CANDP is highly desirable for broadening the application of CANDP method into optoelectronic materials field. To address this problem, di-NH end-capped monomer containing phthalazinone structure was designed and synthesized.<sup>17</sup> This strategy is to eliminate the ether bond and enhance the electronic communication through the Sp<sup>3</sup> C–N bond. In the previous report, these C-N coupling CANDP was unique and demonstrated that the N-H group exhibited like a phenolic O-H group in the phthalazinone structure.24,25,49 Although these polymers, synthesized by C-N coupling CANDP, have been reported.<sup>21,26,37,38</sup> The optoelectronic properties, to our knowledge, have never been investigated systematically in the class of CANDP polymers containing D-A conjugated system.

Based on above considerations, two new di-NH capped monomers were successfully designed and synthesized. In order to improve D–A conjugated effect and  $\pi$ – $\pi$  stack intensity of the phthalazinone-based polymers, more thiophene units were introduced into the di-NH monomers (DT2 and DT3 in Fig. 3), not limited to our previous reported monomer (DT1). On the same principle as above, we introduced more rigid structure (decafluorobiphenyl) than that of di-



FIGURE 3 The structures of designed and synthesized di-NH capped D-A monomers.

halogenated monomers containing ketone/di-ketone/sulfone groups into the polymer main chains.<sup>17</sup> Decafluorobiphenyl has been widely used in the CANDP as a halide monomer polymerized with various bisphenol monomer to achieve high molecular polymers.<sup>27,43,44,50,51</sup> This is the first time that di-NH monomer polymerized with decafluorobiphenyl. Thus, the polymerization conditions were optimized to avoid a great degree of cross-linking and branching side reactions and obtain high molecular polymers. The structures of D-A polymers were fully characterized by relevant methods. Furthermore, the thermal stability, photophysical properties, electrochemical properties, DFT quantum chemical calculations, and morphology properties of monomers and polymers were investigated in details. Since few researchers investigated the optoelectronic properties of the CANDP polymers and phthalazinone-based polymers, a detailed study on the structure-property relationship of monomers and polymers is fundamental to understand the optoelectronic properties of the Sp<sup>3</sup> hybrid nitrogen atom in phthalazinone moiety.

#### **EXPERIMENTAL**

#### **Materials and Characterization**

Unless otherwise stated, the starting materials were commercially available and used without any further purification. Solvent and other common reagents were obtained from Shanghai Energy Chemical. Compounds 2 and DT1 were synthesized as the previous reported.<sup>17</sup> The solvents (THF, ether, and toluene) was dried from benzophenone and sodium under an inert N<sub>2</sub> atmosphere, then distilled prior to use. The NMP and DMAc were dried from CaH<sub>2</sub> and distilled before using. Compounds 4 were obtained from Dalian Polymer New Material Co., LTD. <sup>1</sup>H-NMR (400 MHz), <sup>19</sup>F-NMR (470 MHz), and <sup>13</sup>C-NMR (100 MHz) spectra were recorded on a Bruker spectrometer at 25 °C. And the NMR chemical shifts were determined relative to the residual  $CDCl_3$  (7.26 ppm in <sup>1</sup>H-NMR), DMSO-D<sub>6</sub> (2.50 ppm in <sup>1</sup>H-NMR), the <sup>13</sup>C resonance shift of CDCl<sub>3</sub> (77.16 ppm), and the <sup>19</sup>F resonance shift of trifluoroacetic acid at -76.55 ppm.<sup>52</sup> The number average molecular weight and polydispersity index (PDI) were determined on Agilent PL gel permeation chromatography (GPC) 50 by using CHCl<sub>3</sub> as eluent at 40 °C and polystyrene as standard, equipped with two Agilent PL gel 7.5  $\mu$ m MIXED-D column and one guard column. Matrix-assisted laser desorption ionization time-of-fight mass spectroscopy (MALDI-TOF-MS) analyses were collected on a Micro-mass GC-TOF CA 156 MALDI-TOF-MS. Fourier Transform Infrared Spectrometry (FT-IR) were performed on the Thermo-Nicolet Nexus 470 (KBr pellet method). Ultraviolet-visible (UV-vis) absorption spectra of polymers were determined in diluted N-methyl-2-pyrrolidinone (NMP) solutions and thin films coated on the glass slide using a PerkinElmer Lambda 700 spectrometer. Thermogravimetric analysis (TGA) was measured on a METTLER TGA/SDTA851 analyzer with a heating rate of 20 °C/min from 30 °C to 800 °C under an inert N<sub>2</sub> atmosphere. Measurements of the glass transition temperature  $(T_g)$  was performed on a METTLER DSC822 differential

scanning calorimetry (DSC) analyzer with a heating rate of 10 °C/min from 30 °C to 300 °C under an inert  $N_2$  atmosphere. The  $T_{\sigma}$  value was taken from the mid-point. Cyclic voltammetry measurements (CV) were performed on an electrochemistry (BAS100W) workstation using a three electrode cell. The polymer thin films were coated on the platinum stick working electrode. Platinum were used as the counter electrode. An Ag/Ag<sup>+</sup> electrode (containing 0.01 M silver nitrate in CH<sub>3</sub>CN) was used as a reference electrode analyzer. An anhydrous and N2-saturated dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate was used as electrolyte. The ferrocene/ferrocenium ( $Fc/Fc^+$ ) redox couple was used as an internal standard which occurs at +0.07 V under these conditions. The Lowest Unoccupied Molecular Orbital (LUMO) and Highest Occupied Molecular Orbital (HOMO) energies were determined from the onset of the first reduction peak assuming a formal potential of Fc/  $Fc^+$  of -4.80 eV relative to vacuum level (scan rate 100 mV/s). Fluorescence studies were record using a Hitachi F-4500 spectrofluorometer with a xenon lamp and 1.0 cm quartz cells. Element analysis was carried out on a Vario ELIII CHNOS Elementaranalysator from Elementaranalysesyteme GmbH. X-ray diffraction(XRD) experiments of polymer thin films were determined on the a Bruker D8 using Cu-K radiation source in the range of 2 Theta  $(1^{\circ}-40^{\circ})$  with a scanning rate of 2°. The contact angle of polymer thin films was measured on an optical contact angle measuring device DSA100. Theoretical calculation was performed by using the density functional theory (DFT) with the B3LYP/6-31G(d, p) and LC-wPBE/6-31(d, p) basis set (Gaussian 09W).<sup>53</sup>

# Synthesis of Monomers 2,2'-Bithiophene(1)

A mixture of 2-bromothiophene (1) (10 mmol, 1.63 g) and 2 mol % equivalents of NiCl<sub>2</sub>(dppp) (0.5 mmol, 271 mg) in 10 mL anhydrous THF was brought under N2 atmosphere before thiophen-2-ylmagnesium bromide (12 mmol, 2.25 g) in 10 mL THF solution was dropwise during 20 min at 0 °C. After string at 0 °C for 2 h, the mixture was then refluxed and stirred during 24 hours. After cooling to room temperature (15 min), the mixture was quenched with 1 M HCl. Then, the organic phase was extracted three more times with  $CH_2Cl_2$  (4 imes 10 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated under vacuum. After purification by flash chromatography on silica gel in petroleum ether ( $R_f = 0.7$ ). The desired product 1 was obtained in 89% yield. Light yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.31–7.19 (m, 2H), 7.07 (dt, J = 4.9, 4.5 Hz, 1H).  $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$ 137.43 (s), 127.84 (s), 124.39 (s), 123.81 (s).

# 4-(5'-(4-Oxo-3,4,4a,8a-tetrahydrophthalazin-1-yl)-[2,2'bithiophen] -5-yl)phthalazin-1(2H)-one (DT2)

DT2 were synthesized according to the reported procedure by the Friedel–Crafts reaction of isobenzofuran-1,3-dione with 2,2'-bithiophene(**1**) in the presence of anhydrous aluminum chloride.<sup>21</sup> The crude product recrystallized from acetic acid. After washed with ethanol, red solid was obtained in 81% yield. Red solid. <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  12.99 (s,



2H), 8.36 (d, J = 7.5 Hz, 2H), 8.28 (d, J = 8.2 Hz, 2H), 8.02 (t, J = 7.6 Hz, 2H), 7.95 (t, J = 7.5 Hz, 2H), 7.68 (d, J = 3.9 Hz, 2H), 7.57 (d, J = 3.9 Hz, 2H). HRMS-EI: M<sup>+</sup> Calcd. For C<sub>24</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: 454.0558; found: 454.0558. FTMS-Tof: [M + H]<sup>+</sup> Calcd. For C<sub>24</sub>H<sub>17</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: 455.0631; Found: 455.0631. Elemental analysis: Calcd. For C<sub>24</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C, 63.14; H, 3.53; N, 12.27%. Found: C, 62.61; H, 3.05; N, 11.68%. Melting Point: not detected from 30 °C to 400 °C by DSC.

# (3-Dodecylthiophene-2,5-diyl)bis(tributylstannane) (3)

To a stirred solution of 2,5-dibromo-3-dodecylthiophene (2) (20 mmol, 4.85 g) in dried ether (40 mL) at -15 °C under N<sub>2</sub> atmosphere was dropwise added n-BuLi (2.4 M, 6.07 g, 8.4 mL). The mixture was stirred for 2 h at 0 °C and subsequently tri-n-butyltin chloride (1.2 equiv, 24.0 mmol, 2.75 g, 1.9 mL) in 20 mL ether was dropwise added. The mixture was allowed to stir for 2 h at 0 °C before it was reached room temperature for 6 h. The reaction mixture was diluted with saturated sodium bicarbonate solution (40 mL) and extracted with hexanes (5  $\times$  10 mL). The combined organic layers were washed dried over MgSO4. The solvent was removed under reduced pressure. The light yellow liquid (3dodecylthiophene-2,5-diyl)bis(tributylstannane) (3) was obtained with a yield of 96%. Used immediately without further purification. Light brown liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.31 (s, 1H), 2.86–2.78 (m, 2H), 1.86–1.01 (m, 77H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  151.51 (s), 141.99 (s), 137.38 (s), 136.77 (s), 33.10-10.50 (m).

# 4-(3'-Dodecyl-5"-(4-oxo-3,4,4a,8a-tetrahydrophthalazin-1-yl)-[2,2':5',2"-terthiophen]-5-yl) phthalazin-1(2H)-one (DT3)

A mixture of (3-dodecylthiophene-2,5-diyl)bis(tributylstannane) (3) (0.2 mmol) and 2.5 equivalents of 4-(5-bromothiophen-2-yl)phthalazin-1(2H)-one (4) (0.5 mmol, 229 mg) in 10 mL anhydrous toluene/NMP(1:4) was brought under argon atmosphere before 20 mol % of PdCl<sub>2</sub>(PPh<sub>3</sub>) (0.04 mmol, 46 mg) was added in one portion. The mixture was then stirred at 110 °C during 24 h. After cooling to room temperature (45 min), the mixture was poured into cold methanol. Then the crude product was collected and dried under vacuum. The desired product was recrystallized from chloroform twice and washed with ethanol. Red yellowish solid DT3 was obtained in 23% yield. Red yellowish solid. <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  12.95 (d, I = 3.9 Hz, 2H), 8.34 (d, J = 7.8 Hz, 2H), 8.22 (d, J = 8.0 Hz, 2H), 7.98 (t, J = 7.5 Hz, 2H), 7.91 (t, J = 7.5 Hz, 2H), 7.63 (d, J = 3.8 Hz, 1H), 7.60 (d, I = 3.8 Hz, 1H), 7.42 (d, I = 3.7 Hz, 1H), 7.42 (d, I = 3.7Hz, 1H), 7.35 (s, 1H), 7.31 (d, J = 3.7 Hz, 1H), 2.76 (t, J = 7.6 Hz, 2H), 1.62 (dd, J = 14.6, 7.2 Hz, 2H), 1.42–1.02 (m, 18H), 0.76 (t, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  158.85 (s), 140.78 (s), 139.62 (s), 137.12 (d, *J* = 4.9 Hz), 136.44 (s), 136.06 (s), 134.10 (s), 133.84 (s), 131.77 (s), 129.33 (s), 128.99 (d, J = 9.6 Hz), 127.85 (dd, J = 19.5, 3.9 Hz), 126.32 (s), 125.79 (s), 124.54 (s), 79.20 (s), 31.28 (s), 29.67 (s), 29.39-28.55 (m), 22.07 (s), 13.87 (s). MALDI-TOF-MS: Calcd. For C<sub>40</sub>H<sub>41</sub>N<sub>4</sub>O<sub>2</sub>S<sub>3</sub>: 705.24; Found: 705.08. Melting Point: 211 °C by DSC.

**TABLE 1** The Synthetic Data of Fluorinated and Pi-Conjugated

 Polymers

Entry	Polymers	Temp. (°C)	<i>M</i> n <sup>a</sup> (kDa)	PDI <sup>a</sup>	Yield (%) <sup>b</sup>
				4 00	. ,
1	PDI1IF	110	11.4	1.68	88
2	PDT2TF-1	90	6.8	2.02	64
3	PDT2TF-2	110	16.8	4.22	87
4	PDT2TF-3	130	-	-	44
5	PDT2TF-4	150	-	-	32
6	PDT2TF-5	170	-	-	-
7	PDT3TF-1	90	20.6	1.86	91
8	PDT3TF-2	110	10.9	1.43	87

 $^{\rm a}$  Determined by GPC using  ${\rm CHCl}_{3}$  as eluent at 40  $^{\circ}{\rm C}$  and polystyrene for calibration.

<sup>b</sup> After Soxhlet extraction and precipitation.

# Synthesis of the Polymers General Method for CANDP

About 1.0 equiv. di-NH monomer and 1.0 equiv. decafluorobiphenyl monomer was dissolved in anhydrous DMAc. About 0.2 equiv KF and 2.0 equvi CaH<sub>2</sub> were added. Then the mixture was allowed to stir at reaction temperature. Additional solvent (DMAc) was necessary to be added when the viscosity of the mixture solution was increased to a high level. After the viscosity of the mixture solution remained almost unchanged during stirring at reaction temperature for 12 h. The reaction mixture was poured into diluted HCl solution. Then the collected solid was washed by Soxhlet extraction with acetone (12 h), ethanol (12 h), and hexane (12 h). The solid was dissolved in hot NMP and precipitated in excess ethanol to obtain resulting polymer. Then calculate the yields (Table 1). The images of final product are shown in Supporting Information Figure S9. The structures of polymers are confirmed by <sup>1</sup>H-NMR, <sup>19</sup>F-NMR, GPC, and FT-IR.

# **RESULTS AND DISCUSSION**

#### **Monomer Structures and Synthesis**

The di-NH monomers, namely, DT2 and DT3, were synthesized as illustrated in Scheme 1. DT1 were synthesized as the previous reported.<sup>17</sup> 2,2'-Bithiophene (1) were synthesized via Kumada coupling reaction of 2-bromothiophene with thiophen-2-ylmagnesium bromide. The desired product 1 was purified by flash chromatography. As 2,2'-bithiophene is an electron-rich unit, di-acid intermediate was obtained via the di-Friedel-Crafts reaction of the high activity 2,2'bithiophene with isobenzofuran-1,3-dione in the presence of anhydrous aluminum chloride.<sup>21</sup> The di-acid compound was then converted to the di-NH product DT2 by directly reacted with hydrazine hydrate in DMAc in excellent 81% yield. The 2,5-dibromo-3-dodecylthiophene (2) was distannylated and Stille coupled with 4-(5-bromothiophen-2-yl)phthalazin-1(2H)-one (4) in NMP/Toluene mixed solvent to form di-NH compound DT3. The DT2 was purified by recrystallized in NMP and washed with hot ethanol. The DT3 was purified by



SCHEME 1 Synthesis of di-NH monomers containing phthalazinone-thiophene moiety.

recrystallized in  $CHCl_3$  twice and washed with methanol. As shown in Figure 4, the assignments of proton in <sup>1</sup>H-NMR spectra are well agreement with the proposed structures. Also, the chemical structures of the synthesized di-NH monomers DT2 and DT3 were confirmed by other related technologies (see "Experimental" section).

To provide deep insight into the structural features of three di-NH monomers, Figure 5 shows their details of molecular geometries and frontier molecular orbital by DFT calculations, using the Gaussian 09w program at the B3LYP/6-31G(d, p) level.<sup>53</sup> As depicted in Figure 5, DT2 and DT3 exhibit the smaller  $\theta_2$  dihedral angle of 40.6° and 38.6° than that of 44.7° in DT1 units, respectively. The result indicates that thiophene unit exhibits better coplanarity with phthalazinone unit than that of benzene ring. Furthermore, the smallest dihedral angle ( $\theta_1 = 15.0^\circ$ ), much smaller than that of DT1 ( $\theta_1 = 24.5^\circ$ ) and DT3 ( $\theta_1 = 16.8^\circ$  and  $28.1^\circ$ ), is distinguished. Such small backbone torsion is resulted from the small steric hindrance between two unalkyl substituents thiophene rings. This better backbone coplanarity is beneficial for improving the charge transport along the polymer chains, increasing the intermolecular interaction, decreasing the band gaps and expanding absorption.<sup>54,55</sup> Additional, the LUMO level is mainly distributed on the electrondrawing phthalazinone unit. The HOMO level is mainly distributed on the electron-donor thiophene unit. The HOMO and LUMO orbitals are also calculated using long-range Hartree-Fock (HF) corrections to the DFT functionals as implemented in LC-wPBE (0%-100%) to characterize the localized charged excitations of three di-NH monomers.56,57 As shown in Figure 5, the charged excitations along the chain exhibited the similar location manners and trends, compared with calculation results at B3LYP (20% HF exchange) 6-31G(d, p) levels. The solvent effect on the localized charged excitations of di-NH monomers are investigated. As depicted in Supporting Information Figure S21, further addition of a polarizable solvent (acetonitrile) into calculation could slightly reduce the band gaps and has no substantial change in the HOMO and LUMO orbitals of di-NH monomers. Overall, the design principles of di-NH monomers should be beneficial to increasing the conjugated effect and their optoelectronic applications.

#### **Monomer Optical Properties**

The normalized UV-vis absorption and emission spectra of di-NH monomers in NMP solution are shown in Figure 6. The maximum absorption wavelength of DT1, DT2, and DT3 are 349, 377, and 398 nm, respectively. The DT1 shows larger conjugated backbone than DT2, but the maximum absorption wavelength of DT2 is red shifted relative to that of DT1. That is attributed to the stronger donor ability and better planarity (the  $\theta_1$  and  $\theta_2$  in Fig. 5) of thiophene units in DT2 (than benzene rings in DT1). As three thiophene rings are



**FIGURE 4** The <sup>1</sup>H-NMR spectra of DT2 and DT3 in DMSO-D<sub>6</sub>. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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**FIGURE 5** The calculated molecular geometries and HOMO/LUMO orbitals (vacuum) of di-NH monomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

incorporated into the di-phthalazinone monomers, DT3 exhibits the largest red shift in UV-vis absorption in NMP solution among three di-NH monomers. These suggest that the phthalazinone unit, as a new acceptor, could combine with thiophene unit (donor) to enhance the intramolecular charge transfer and expand the absorption wavelength. That's all associated with yielded the low band gap polymers for application in the optoelectronics field.<sup>58,59</sup> Additional, the maximum emission wavelength of DT1, DT2, and DT3 are 420, 477, and 498 nm, respectively. As shown in Figure 6(b), the fluorescent colors are blue, green, and yellow with high fluorescence quantum yield (53%, 84%, and 69%, respectively).<sup>17,60</sup> These results indicate that more thiophene units incorporated with phthalazinone unit could enhance the D–A effects.

## **Polymer Synthesis and Characterization**

The polymerization of bisphenol monomers with decafluorobiphenyl has been previously reported in many literatures, in which they obtained linear polymer products.<sup>28,29,43,44,50,51,61-63</sup> However, this is the first time that di-NH monomers are polymerized with decafluorobiphenyl (Scheme 2). In order to avoid forming a large degree of branched and cross-linked structures, the optimized polymerization conditions are investigated and shown in Table 1. Generally because of the high reactivity of all fluorine atoms in decafluorobiphenyl structure, the high temperature could lead to more side reactions such as branching and crosslinking. The lower temperature could result in a linear polymer with low degree of polymerization, owing to the highest selectivity of the para-position fluorine atoms. In our previous report, the reactivity of N-H in phthalazinone unit is lower than the common phenolic hydroxyl group (Ar-OH), the N-H reaction site could polymerize with the C-F bond in decafluorobiphenyl at 90°.44 In this article, the polymerization condition between DT2 with decafluorobiphenyl is performed to obtain the high molecular weight polymer. First, the polymerization proceeds under the conditions before (KF/CaH<sub>2</sub> in DMAc at 90 °C). However, the viscosity of reaction solution did not increase dramatically after 60 h. The molecular weight of PDT2TF-1 is only 6.8 kDa. We can infer that di-NH monomers show lower reactivity than 4-(4'-Hydroxyphenyl)phthalazin-1(2H)-one (both Ar-OH and NH reaction sites) in the polymerization.<sup>28,44</sup> Thus, the temperature of polymerization is increased to 110 °C. The viscosity of reaction solution gradually increases after stirring 2 h at 110 °C. After adding DMAc three times, the viscosity of solution did not increase dramatically after stirring 12 h. The molecular weight of PDT2TF-2 is 16.8 kDa. When the polymerization temperature increased to 130 °C, 150 °C, or 170 °C, the product precipitate from the reaction mixture before the viscosity of solution reach to a certain extent. This is because of forming a large degree of cross-linked product. As shown in Figure 7, due to the asymmetrical phthalazinone unit, the fluorine signal at 137 ppm split into two peaks in the <sup>19</sup>F-NMR spectra of these fluoropolymers (the



**FIGURE 6** The normalized UV–vis absorption (a) and emission (b) spectra of di-NH monomers in NMP solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

similar results can be observed in ref. 27).<sup>27</sup> And the <sup>19</sup>F-NMR spectra of PDT2TF (different entries) indicate that the most appropriate polymerization temperature is 110 °C (entry 3). The lower temperature (90 °C, entry 2) results in the low molecular weight product with unreacted terminal groups. The higher temperature (130 °C or 150 °C) results in more branched and crosslinked products with lower yield after general purification steps. When the polymerization temperature reached 170 °C, the product is precipitated from the solution in 2 h. Also, Figure 8 shows the <sup>1</sup>H-NMR spectra of PDT2TF in different entries. The proton signals are well consistent with the proposed structures. That suggests that the side reaction is occurred at the C-F bond in decafluorobiphenyl unit. Above all, even though this condition needs a long reaction time (>60 h), the optimized temperature of polymerization of DT2 and decafluorobiphenyl is 110 °C (entry 3). The polymerization of DT1 and decafluorobiphenyl is conducted under the optimized condition (entry 1, 110 °C). The molecular weight of PDT1TF is 11.4 kDa (PDI = 1.68). The <sup>1</sup>H-NMR and <sup>19</sup>F-NMR spectra are shown in Supporting Information Figure S6 and S7.

Furthermore, the PDT3TF was synthesized under two different polymerization conditions (90 °C, entry 7 and 110 °C, entry 8). As shown in Figure 9, unlike PDT2TF, the lower polymerization temperature of PDT3TF tends to achieve higher molecular weight polymers and more linear structures. As the  $T_{\rm g}$  of PDT2TF and PDT1TF are not detected from 30 °C to 300 °C, the  $T_{\rm g}$  of PDT3TF is 120 °C. We suspect that the more flexibility polymer backbone of PDT3TF lead to higher reactive end group than that of PDT2TF. Thus, the chain-propagating step could occur in low temperature (in entry 7, 90 °C). The molecular weight of PDT3TF-1 is 20.6 kDa, higher than that of PDT3TF-2 (10.9 kDa). The <sup>1</sup>H-NMR spectra is shown in Supporting Information Figure S8. Also, the images of obtained polymers in different entries are shown in Supporting Information Figure S9. Due to the large conjugated effect of polymer backbones, we can



SCHEME 2 Polycondensation of decafluorobiphenyl with di-NH monomers.

Materials



FIGURE 7 The <sup>19</sup>F-NMR spectra of PDT2TF in CDCI<sub>3</sub>.

observe that the more linear structure and higher molecular weight results in deeper color of product.

#### **FT-IR Characterization of Polymers**

The chemical structures of synthesized polymers in different entries are also verified by FT-IR (Fig. 10). The stretching FT-IR absorbing in around 1492 cm<sup>-1</sup> is detected for all obtained polymers, on the account of the stretching vibration of C=C in benzene ring (decafluorobiphenyl). The absorption peak near 978 cm<sup>-1</sup> obviously appears after polymerization. This signal is attributed to the stretching vibration of C-F in decafluorobiphenyl unit. As shown in Figure 10(c), the signal near 2800 cm<sup>-1</sup> is contributed by the stretching vibration of the alkyl side-chains in DT3 units. Hereafter, it is worth mentioning that PDT1TF, PDT2TF-2 (simply "PDT2TF" for short),



**FIGURE 8** The <sup>1</sup>H-NMR spectra of PDT2TF in CDCl<sub>3</sub>. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and PDT3TF-1(simply "PDT3TF" for short) are used for the subsequent studies.

#### **Thermal Properties of Polymers**

The thermal decomposition property and glass transition temperature of polymers are investigated by TGA and DSC measurements under N2 atmosphere. The results are summarized in Table 2 (details in Supporting Information Figs. S10 and S11). The 5% weight-loss temperature ( $T_{d5\%}$ ) of PDT1TF, PDT2TF, and PDT3TF are 460 °C, 470 °C, and 468 °C, respectively. The char yield (Cy: the weight loss at 800 °C) of polymers is PDT1TF > PDT2TF > PDT3TF. That is exactly consistent with the content of heteroatoms in polymer chains. As shown in Table 2, for PDT1TF, no glass transition behavior is observed. The  $T_{\rm g}$  of PDT2TF and PDT3TF is 288 °C and 120 °C. The results suggest that incorporating thiophene units into phthalazinone-containing polymers could decrease the glass transition temperature. Furthermore, lower  $T_{\rm g}$  indicates the polymer end groups could exhibit higher reactivity during polymerization. Not like PDT2TF, the PDT3TF in Entry 7 (synthesized at 90°) shows higher enough molecular weight than that of Entry 8. That's owing to its low  $T_{\rm g}$  value and more flexibility of the PDT3TF backbones. The polymerization condition depends on not only the activation energy of reaction functional group, but also the mobility and flexibility of the polymer chains.

The thermal decomposition property and melting point are depicted in Table 2. With incorporating more thiophene units into DT3 monomer, the melting point of DT3 (211 °C) is lower than that of DT1 and DT2 (>350 °C). The weak bond in the structures could decrease the  $T_{d5\%}$  values. Thus the polymers containing thiophene units (C—S bond) exhibit lower  $T_{d5\%}$  value than that of polymers containing fully-phenyl structure.<sup>64</sup> Also, the  $T_{d5\%}$  value of polymers containing phthalazinone moiety is higher than that of polymers containing more poor thermostability thiophene units (compared with benzene and phthalazinone units) into monomers, the order



**FIGURE 9** The <sup>19</sup>F-NMR spectra of PDT3TF in CDCl<sub>3</sub>. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



(c)

**FIGURE 10** The FT-IR spectra of polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 2 The Thermal	Data	of Synthesized	Polymers
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Polymers	<i>T</i> <sub>d5%</sub> (°C)	<i>C</i> <sub>y</sub> (%) <sup>a</sup>	<i>T</i> g (°C)
PDT1TF	460	69	>300
PDT2TF	470	67	288
PDT3TF	468	66	120
DT1 <sup>b</sup>	403	33	>350 <sup>c</sup>
DT2	407	58	$>400^{\circ}$
DT3	419	42	211 <sup>c</sup>

The char yield at 800  $^\circ C$  in  $N_2$  atmosphere.

The data of DT1 is from ref. 17.

The melting point of di-NH monomers (details see Supporting Information Figs. S12 and S13).

of  $T_{d5\%}$  values is DT3 > DT2 > DT1. We deduce that thiophene units combined with phthalazinone units could show better conjugation effect than benzene ring. This will endow the di-NH monomers with the higher resonance energy along the structures.<sup>20</sup> Although, PDT3TF contains three thiophene units and alkyl side chains, the  $T_{d5\%}$  of PDT3TF is high as 419 °C. Besides, the Cy value of monomers at 800 °C is in the range of 33%–58%, lower than that of their corresponding polymers. This result could confirm that the decafluorobiphenyl is successfully polymerized with di-NH monomers.

## **Contact Angles Measurements**

The water contact angle tests are carried out to investigate the surface tensions of obtained polymers containing decafluorobiphenyl units. The polymer thin films were casted on glass slides from NMP solutions. As shown in Figure 11, the water contact angles of synthesized polymers films are  $92.92^{\circ}$  (PDT1TF),  $91.56^{\circ}$  (PDT2TF), and  $94.80^{\circ}$  (PDT3TF). These values are higher than that of PDS ( $56.19^{\circ}$ ),<sup>17</sup>



**FIGURE 11** Contact angles of synthesized polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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**FIGURE 12** The optimized structures and front molecular orbitals (vacuum) of synthesized polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicating that hydrophobic decafluorobiphenyl unit is successfully introduced into the polymer backbones.

#### **DFT Calculations of Polymers**

To gain deep insight into the structure-electronic relationship of synthesized polymers, DFT calculations are performed using B3LYP/6-31G(d, p) and LC-wPBE/6-31(d, p) method.53,56,57 The optimized geometrical structures and front molecular orbitals of three polymers are shown in Figure 12. It is clearly observed that all LUMOs are delocalized on the strong electron deficiency phthalazinone units. As discussed in later parts, the PDT2TF and PDT3TF show boarder absorption range, larger emission wavelength and narrower band gaps. The HOMOs of PDT2TF and PDT3TF are delocalized on the electron-rich thiophene units. Thus the strong D-A effect could occur.<sup>54,59</sup> However, due to the distorted structure between benzene and phthalazinone units, the HOMOs of PDT1TF are mainly delocalized on the decafluorobiphenyl units. As shown in Figure 12, the electron transfer of PDT1TF is limited into one segment. In this case the DFT

calculated results show that the D–A effect of phthalazinone units and thiophene units in PDT1TF is rarely observed. The solvent effect on the localized charged excitations along the polymer backbones are also investigated. As shown in Supporting Information Figure S22, addition of a polarizable medium (acetonitrile) into calculation exhibits no substantial change in the HOMO and LUMO orbitals of polymers backbone and slightly reduce the band gaps corresponding with the calculation results of di-NH monomers (in Supporting Information Fig. S21).

Figure 13 shows the calculated BLA of decafluorobiphenyl units along the polymer backbones. The B3YLP exhibits the higher overall BLA compared with LC-wPBE (0%–100%). Even though, the calculation model is consisting of two repeat units. As results calculated by LC-wPBE functional model and previously reported by Nayyar,<sup>57</sup> the BLA at the middle of the chain(repeat unit size is 2, 3, 4) is lower than that at the end of the chain(repeat unit size is 1). This trend could also be observed by the inclusion of a solvent effect

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**FIGURE 13** The BLA of decafluorobiphenyl units along the polymer chains computed using B3LYP/6-31G(d, p) and LC-wPBE/6-31G(d, p) basis set. The solvent effect studies are calculated at LC-wPBE/6-31G(d, P) optimized levels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(acetonitrile) through calculations. These results could emphasize on the location of the trapping of charged excitations along the chain. $^{57,65}$ 

#### **Optical Property of Polymers**

The UV-vis absorption and photoluminescence spectra of synthesized polymers are shown in Figure 14. The maximum absorption wavelength of polymers in NMP solutions are 360 (PDT1TF), 380 (PDT2TF), and 396 nm (PDT3TF). The order of these values corresponds well with the order of the absorption values of their di-NH monomers. This is strongly suggested that the conjugated length could be expanded by the strong D-A effect between thiophene and phthalazinone units. Due to the  $\pi$ - $\pi$  stacking and the intermolecular charge transfer effect, comparing with polymers in NMP solutions, the thin films of PDT1TF and PDT2TF show bathochromic in the optical absorption spectra [Fig. 14(a)]. However, the PDT3TF film shows a hypochromatic effect. That can be attributed to the long alkyl chain weaken the  $\pi$ - $\pi$  stacking and the intermolecular aggregation in film states.

The photoluminescence spectra of obtained polymers are presented in Figure 14(b). The maximum emission wavelength of polymers in NMP solutions are 435 (PDT1TF), 470 (PDT2TF), and 525 nm (PDT3TF), with enough fluorescence quantum yield (50%, 14%, and 8%, respectively). The order of these values corresponds well with the order of the emission values of their di-NH monomers. These data also indicate the conjugated length could be efficiently extended by the strong D-A effect between thiophene and phthalazinone units. In another fact, the maximum emission wavelengths in NMP solution are both largely redshifted than that of corresponding di-NH monomers. These results demonstrate that Sp<sup>3</sup> C—N bond in the phthalazinone could expand the conjugated length and increase the intramolecular charge transfer effect. Also, the maximum emission wavelength of polymers in thin films states are moving toward long wave region, relative to that of polymers in NMP solution. Furthermore, the maximum emission wavelength of PDT2TF in film states is 543 nm, consistent with the values of PDT3TF. This is suggested that PDT2TF could form strong  $\pi$ - $\pi$  stacking and intermolecular interaction among the polymer backbone in film states.

#### **Electrochemical Property of Polymers**

To evaluate the LUMO and HOMO levels of synthesized polymer thin films, the reduction and oxidation potentials are determined by cyclic voltammetry. The CV curves are shown



**FIGURE 14** UV-vis absorption (a) and photoluminescence (b) spectra of polymers in NMP solution and thin film states. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**TABLE 3** The Electrochemical Characteristics of Synthesized

 Monomers and Polymers

-				
Polymers	HOMO (eV) <sup>a</sup>	LUMO (eV) <sup>a</sup>	$E_{\rm g}~({\rm eV})^{\rm a}$	E <sub>g</sub> (eV) <sup>b</sup>
PDT1TF	-5.76	-3.50	2.26	2.50
PDT2TF	-5.70	-3.54	2.16	2.46
PDT3TF	-5.61	-3.58	2.03	2.36
DT1 <sup>c</sup>	-5.87	-2.79	3.08	2.63
DT2	-6.06	-3.66	2.40	2.47
DT3	-5.83	-3.55	2.28	2.37

<sup>a</sup> Determined by cyclic voltammetry (CV).

<sup>b</sup> Estimated by DFT calculation at LC-wPBE/6-31G(d, p) levels.

<sup>c</sup> Ref. 17.

in Supporting Information Figures S14 and S15. The corresponding data are presented in Table 3. As can be seen from Figure 12, the LUMO orbitals of three polymers are mainly localized on the phthalazinone moiety. Thus the LUMO levels are very similar for three polymers (-3.50 to -3.58 eV). With incorporating more thiophene units into polymer backbones, the HOMO levels of polymers are increasing that the order is -5.76 eV(PDT1TF)< -5.70 eV(PDT2TF)< -5.61 eV (PDT3TF). Accordingly coplanar structure and strong D-A effect of thiophene-phthalazinone units are beneficial to intermolecular interaction,  $\pi$ - $\pi$  stacking, and charge-transfer properties. Therefore the  $E_{\rm g}$  values of polymers are 2.26 (PDT1TF), 2.16 (PDT2TF), and 2.03 eV (PDT3TF). Also, the calculated band gaps are listed in Table 3. As previous reported, the band gaps calculated by LC-wPBE/6-31G(d, p) basis set are more approach the experiment results than those calculated by B3LYP/6-31G(d, p) basis set.<sup>56</sup> The results, predicted by DFT theory, are basically consistent with the experiment ones. In another hand, the experimental and calculated  $E_{g}$  values of polymers are basically reduced relative to its corresponding monomers, confirming the Sp<sup>3</sup> C–N bond in the phthalazinone units could prolong the conjugated length via CANDP method.

#### Thin Film Morphology of Polymers

To investigate the relationship between electrical-optical properties and film microstructure, the XRD measurement is carried out on thin films. No sharp crystalline signal could be observed for the three polymers in Figure 15. However, the difference of peak intensities ( $2\theta = 20^{\circ} \sim 30^{\circ}$ ) can be distinguished, suggesting the various morphologies of polymers in thin film states. And the strength of  $\pi$ - $\pi$  stacking are PDT2TF > PDT1TF > PDT3TF. Thus, the thin film of PDT2TF shows broad absorption in UV-vis spectra (Figure 14). As we known, strong D-A effect, good coplanar structure, and better  $\pi$ - $\pi$  stacking manner could provide benefit effect on intermolecular charge transfer, widening absorption ranges, extension emission wavelength and narrowing the band gap.66-68 Furthermore, the difference of the maximum emission wavelength in thin films and in NMP solutions  $\Delta\lambda \ (\lambda^{em}_{film} - \lambda^{em}_{solution})$  for PDT1TF, PDT2TF, and PDT3TF are 58, 73, and 18 nm. These optical data coincide well with the XRD results.

## CONCLUSIONS

We have incorporated electron-deficient phthalazinone moiety into alternating D-A conjugated polymers containing thiophene and decafluorobiphenyl units via classical aromatic nucleophilic displacement C-N coupling polymerization. Remarkably, the molecular weight depends on not only the N-H activities for polymerization but also the mobility and flexibility of the polymer backbones. By optimum polymerization conditions, the  $M_{\rm n}$  of three hydrophobicity linear D-A conjugated polymers are 11.4, 16.8, and 20.6 kDa. The thermostability of di-NH monomers and polymers are increased with the increase of the resonance eneralong thiophene-phthalazinone (D-A) structures. gy Improving coplanarity of di-NH monomers by introducing thiophene unit directly connected to electron-deficient phthalazinone unit could enhance the D-A conjugated effect. Furthermore, removing ether bond in CANDP polymers affords finely mixed D-A conjugated networks, resulting in broader absorption, longer emission wavelength and narrower band gaps. The PDT2TF exhibits strong bathochromic shift effect both in UV-vis absorption and PL spectra. However, the PDT3TF shows the blue shift from solution states to film states in UV-vis absorption spectrum. The XRD results suggest that introducing the long alky side chain could significantly change the morphology of polymers in film states.

Summarizing, most of classical aromatic nucleophilic displacement polymerization contains C—O linkage along the polymer backbones. In general, ether bond limits the delocalization of the electronic wave function and charge transport properties. Herein, the di-NH monomers, derived from phthalazinone structure, exhibit outstanding D–A conjugated effect. The Sp<sup>3</sup> C—N linkage shows fine delocalization of the electronic wave function along the chains. Future works mainly progress with phthalazinone-based new materials (not just decafluorobiphenyl as di-halide monomer) and its applications in the organic electronic fields.



**FIGURE 15** XRD patterns of polymer thin films coated from NMP solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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