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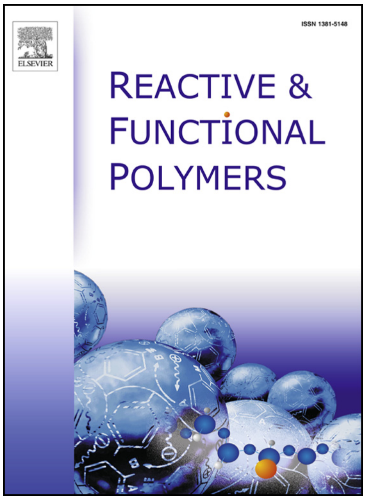

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Synthesis and characterization of a main-chain donor-acceptor type low-bandgap polymer by post-functionalization of a poly(arylene ethynylene)**

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ABSTRACT

I report a facile synthetic route for synthesizing a main-chain donor-acceptor type polymercontaining strong electron donating dialkylamino groups and strong electron accepting 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) units. To accomplish this, an electron donating monomer 4,6-diethynyl-N,N,N,N-tetrahexylbenzene-1,3-diamine was successfully synthesized by converting two carbaldehyde groups in the corresponding monomer into acetylene groups using lithium trimethylsilyldiazomethane via Colvin rearrangement. This electron donating monomer was then polymerized with a carbonyl-activated diiodide monomer to afford an electron-donating π-conjugated precursor polymer with a reasonably high molecular weight, which was further reacted with TCNE via cycloaddition/retroelectrocyclization reaction under mild conditions to afford the target polymer with a low bandgap energy (E_g^{opt} = 1.40 eV and E_g^{CV} = 1.10 eV) arising from strong intramolecular charge-transfer interactions between electron donors and acceptors in the polymer.

Keywords: Low bandgap polymers; Intramolecular charge-transfer interactions; π–Conjugated polymers; Poly(arenylene ethynylene); Cycloaddition/retroelectrocyclization reaction.

1. Introduction

The low bandgap energy of π-conjugated polymers is critical for their applications in many emerging areas such as organic photovoltaic devices, light emitting diodes, and nonlinear optical devices [1-3]. The intramolecular charge-transfer interactions between electron donor and electron acceptor represent one of the most effective pathways toward lowering the bandgap energy of π-conjugated polymers. The enhancement in the strength of electron donors and/or acceptors can further reduce the bandgap energy of the polymer [1, 2, 4-9]. This prompted me to designing and synthesizing π-conjugated polymers with a lower bandgap energy by integrating stronger electron donor and acceptor moieties into the macromolecules.

It is fundamentally difficult to directly incorporate strong electron acceptors like tetracyanoethylene (TCNE) into the π-conjugated macromolecular chains. Instead, post-functionalization via the "click" type cycloaddition/retroelectrocyclization reaction of TCNE with activated alkynes has proven to be an effective approach to attain novel donor-acceptor type polymers. This was first confirmed by Michinobu [10] for aromatic polyamines with electron-rich alkyne side chains. Very recently, Huang et al. have demonstrated the feasibility of achieving a low-bandgap poly(arylene ethynylene) through the selective reaction of tetracyanoethylene (TCNE) with dialkylanilino–activated alkynes in the side chains of the polymer via the same reaction mechanism to afford donor-acceptor type chromophores while maintaining the important features of alternating aromatic ring and ethynylene bonds in the main chain of the polymer [11].

However, it is much more difficult to successfully implement the post-functionalization of main-chain ethynyl groups along the chain in a complete manner if the chemical structure of the polymer is not properly designed, because the alkynes must be activated by strong electron donating groups for the cycloaddition/retroelectrocyclization reaction with TCNE [12]. Dialkylanilino group has been recognized as a strong electron donor for many systems, especially for the activation of alkynes [13-15]. In particular, dialkylanilino group in the *para*-position gives the strongest electron donating effect on alkynes, and thus it is desirable to integrate this structure into the precursor polymer in order to obtain the highest reactivity between TCNE and main-chain alkynes [16, 17]. However, to the best of our knowledge, there is not such a report in the literature regarding the synthesis of one benzene molecule bearing a pair of alkylanilino group and alkynyl group in the *para*-position (chemical structure of **3** shown in Scheme 1).

Herein I reported a facile method to achieve 4,6-N,N,N',N'-tetrahexyl-benzene-1,3-diamine monomer, which was then polymerized with activated *p*-benzenediiodide monomer to give an electron donating π-conjugated polymer. The activation of alkynes in this precursor polymer facilitated the cycloaddition/retroelectrocyclization reaction of main-chain alkynes with TCNE, thus affording a main-chain donor-acceptor type polymer with a low bandgap energy.

2. Experimental part

2.1. Materials

All of the chemicals, otherwise stated, were purchased from Aldrich and used as received. N,N-dimethylformamide (DMF) and diisopropylamine were distilled from sodium hydride under an argon atmosphere. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under an argon atmosphere. All of the chemical reactions were performed under an inert atmosphere by applying a positive pressure under an argon atmosphere. Synthesis of 4,6-diethynyl-N,N,N',N'-tetrahexyl-benzene-1,3-diamine (**3**) was schematically represented in Scheme 1. 2,5-Diiodo-1,4-dibutyl terephthalate (**4**) was synthesized according to the procedure described in a previous paper [11].

2.2. Characterizations

^{1}H and ^{13}C NMR spectra were obtained on a Varian Mercury 300 spectrometer at 298 K. Chemical shifts (δ) are reported in ppm relative to the signal of tetramethylsilane (TMS). Residual solvent signals in the ^{1}H and ^{13}C NMR spectra were used as an internal reference. Coupling constants (J) are given in Hz. The apparent resonance multiplicity is described as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). FTIR spectra were recorded on a Thermo Nicolet 380 FTIR spectrometer (Thermo Fisher Scientific) with a diamond attenuated total reflectance (ATR) accessory. Thin-layer chromatography was conducted on aluminum sheets coated with silica gel having fluorescent indicator 254 nm, which was visualized with a UV lamp (254 or 366 nm). GPC analyses were carried out using a Waters 510 HPLC pump and a Waters 410 differential refractometer with THF as an eluent at a flow rate of 1.0 mL/min at 30°C, using polystyrene standards. The thermal degradation temperature of the polymers synthesized was determined using a thermogravimetric analyzer (TGA 2050, TA Instrument) at a heating rate of 10^{o}C/min under a nitrogen atmosphere. UV−vis spectra were obtained at Hewlett-Packard 8435 UV–visible spectrophotometer. The spectra were measured in CH_2Cl_2 in a quartz cuvette (1 cm) at 298 K. Cyclic voltammetry (CV) experiments were conducted on an Epsilon^{TM} BAS potentiostat-galvanostat coupled with a typical three-electrode cell. The electrochemical cell consisted of a conical vial fitted with a glassy carbon working electrode, a reference electrode of $Ag/Ag^+/CH_3CN/(n\text{-}C_4H_9)_4NPF_6$, and a platinum wire as the counter electrode. All CV measurements were conducted at 20^{o}C in CH_2Cl_2 containing 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ as the supporting electrolyte at a scanning rate of 0.1 V/s. Dry argon gas was bubbled carefully through the electroactive solution for at least 10 min before each measurement to deoxygenate the solution.

2.3. Monomer Synthesis

*2.3.1. Synthesis of N,N,N',N'-tetrahexyl-benzene-1,3-diamine (**1**)*

1,3-Phenylenediamine (1.1 g, 10 mmol) was dissolved in 60 mL anhydrous tetrahydrofuran in a 250 mL round bottom flask with a magnetic stir bar and a reflux condenser. To this solution was added 1-iodohexane (9 mL, 60 mmol) and 15-crown-5 (0.2 mL, 1 mmol). This was followed by slow addition of sodium hydride (60% dispersion in mineral oil, 2.4 g, 60 mmol). The reaction mixture was then allowed to reflux at 65^{o}C for 2 days. After cooling down to room temperature, the reaction mixture was poured into 100 g ice, and then extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over magnesium sulfate and filtered. Removal of solvent under the reduced pressure gave the crude product, which was purified over a silica gel column using hexane as an eluent to give 3.6 g light yellowish liquid. Yield: 81%. TLC: R_f = 0.73 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.90 (t, J = 6.6 Hz, 12H, $-CH_3$), 1.31 (s, 24H, $-CH_2-$), 1.59 (s, 8H, $-CH_2-$), 3.23 (t, J = 8.1 Hz, 8H, $-NCH_2-$), 5.90 (d, J = 2.1 Hz, 1H, Ar–H), 6.00 (dd, J_1 = 8.2 Hz, J_2 = 2.3 Hz, 2H, Ar–H), 7.03 (t, J = 8.2 Hz, 1H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 14.2 ($-CH_3$), 22.9 ($-CH_2-$), 27.1 ($-CH_2-$), 27.7 ($-CH_2-$), 32.0 ($-CH_2-$), 51.5 ($-CH_2-$), 95.3 (Ar–C), 100.0 (Ar–C), 129.7 (Ar–C), 149.3 (Ar–C). FTIR (v, cm^{-1}): 2952, 2924, 2854, 1601 (–phenyl), 1570, 1503, 1461, 1365, 1289, 1248, 1219, 1176, 1138, 1110, 989, 887, 801, 733, 687, 633, 586, 550. Anal. Calcd for $C_{30}H_{56}N_2$ (444.79): C, 81.01; H, 12.69; N, 6.30. Found: C, 81.07; H, 12.71; N, 6.22.

*2.3.2. Synthesis of 4,6-dicarbaldehyde-N,N,N', N'-tetrahexyl-benzene-1,3-diamine (**2**)*

Phosphorus(V) oxychloride (2.4 mL, 25 mmol) was slowly added to a solution of N,N,N', N'-tetrahexyl-benzene-1,3-diamine (2.2 g, 5 mmol) in 15 mL DMF at 0°C and then stirred for 24 hours at room temperature. After the completion of reaction, 1 N sodium hydroxide aqueous solution was added to neutralize the solution at 0°C and the product was extracted with ethyl acetate (50 mL x 3). The combined organic layers were washed with saturated sodium bicarbonate and dried over magnesium sulfate, and the solvent was removed under the reduced pressure. The residue was purified over silica gel column using hexane/ethyl acetate (10/1, v/v) as an eluent to give 1.5 g yellow liquid. Yield: 58%. TLC: $R_f = 0.54$ (hexane/ethyl acetate = 10/1, v/v). ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.86 (t, J = 6.6 Hz, 12H, $-CH_3$), 1.25 (s, 24H, $-CH_2-$), 1.57 (s, 8H, $-CH_2-$), 3.28 (t, J = 7.2 Hz, 8H, $-NCH_2-$), 6.33 (s, 1H, Ar–H), 8.18 (s, 1H, Ar–H), 9.88 (s, 2H, –CHO). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 13.9 ($-CH_3$), 22.5 ($-CH_2-$), 26.6 ($-CH_2-$), 27.2 ($-CH_2-$), 31.5 ($-CH_2-$), 53.5 ($-CH_2-$), 107.3 (Ar–C), 120.2 (Ar–C), 139.6 (Ar–C), 157.4 (Ar–C), 188.3 (–CHO). FTIR (v, cm^{-1}): 2952, 2924, 2853, 1673 (–CHO), 1576 (–phenyl), 1517, 1489, 1460, 1374, 1342, 1254, 1150, 1101, 1024, 926, 841, 778, 724, 681, 609, 558. Anal. Calcd for $C_{32}H_{56}N_2O_2$ (500.81): C, 76.75; H, 11.27; N, 5.59; O, 6.39. Found: C, 76.73; H, 11.26; N, 5.60; O, 6.41.

2.3.3. Synthesis of 4,6-diethynyl-N,N,N',N'-tetrahexyl-benzene-1,3-diamine (3)

n-Butyllithium (1.6 M in hexane, 9.4 mL, 15 mmol) was added to a solution of diisopropylamine (2.1 mL, 15 mmol) in 20 mL dry tetrahydrofuran at –78°C and stirred for 1 hr. Trimethylsilyldiazomethane (2.0 M in hexane, 7.5 mL, 15 mmol) was added dropwise at –78°C, and then stirred for 60 min. After that, a solution of 4,6-dicarbaldehyde-N,N,N', N'-tetrahexyl-benzene-1,3-diamine (2.5 g, 5 mmol) in 10 mL dry THF was added and the mixture was stirred at –78°C for 2 hours and then heated to reflux at 65°C for 3 hours. Upon the completion of reaction, the mixture was cooled down to room temperature and stirred overnight. Consequently, the reaction solution was poured into 50 g crushed ice. The solution was extracted with ethyl acetate (100 mL x 3). The combined organic layers were washed with water (100 mL x 3), brine

(50 mL) and dried ($MgSO_4$). The solvent was removed under the reduced pressure, and then the crude product was dissolved in a mixed solvent of 15 mL anhydrous tetrahydrofuran and 10 mL methanol, followed by the addition of potassium carbonate (5.6 g, 40 mmol). After stirring at room temperature for 10 hours, the solid was filtered off and the solvent was removed under the reduced pressure. The residue was purified over silica gel column using hexane/ethyl acetate (50/1, v/v) as an eluent to afford 1.0 g yellowish liquid. Yield: 41%. TLC: R_f = 0.57 (hexane/ethyl acetate = 50/1, v/v). ^1H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.89 (m, 12H, $-CH_3$), 1.29 (s, 24H, $-CH_2-$), 1.56 (s, 8H, $-CH_2-$), 3.21 (s, 2H, −acetylene), 3.30 (t, J = 7.5 Hz, 8H, $-NCH_2-$), 6.27 (s, 1H, Ar−H), 7.51 (s, 1H, Ar−H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 14.0 ($-CH_3$), 22.7 ($-CH_2-$), 26.8 ($-CH_2-$), 27.5 ($-CH_2-$), 31.8 ($-CH_2-$), 52.3 ($-NCH_2-$), 79.6 (−acetylene), 83.3 (−acetylene), 104.9 (Ar−C), 108.0 (Ar−C), 142.7 (Ar−C), 153.5 (Ar−C). FTIR (v, cm^{-1}): 3310 (−acetylene), 2954, 2923, 2854, 2096 (−ethynyl), 1589 (−phenyl), 1498, 1460, 1371, 1258, 1167, 1153, 1095, 1016, 901, 799, 748, 722, 640, 568. Anal. Calcd for $C_{34}H_{56}N_2$ (492.83): C, 82.86; H, 11.45; N, 5.68. Found: C, 82.89; H, 11.41; N, 5.70.

2.4. *Polymerization of PBBmN*

As shown in Scheme 4, 4,6-diethynyl-N,N,N',N'-tetrahexyl-benzene-1,3-diamine (2.5 g, 5 mmol) and 2,5-diiodo-1,4-dibutyl terephthalate (2.7 g, 5 mmol) were dissolved in a mixed solvent of 40 mL anhydrous tetrahydrofuran and 20 mL triethylamine, which was thoroughly degassed through freeze-pump-thaw procedures. Under argon gas atmosphere, copper(I) iodide (49 mg, 0.25 mmol) and $Pd(PPh_3)_4$ (0.29 g, 0.25 mmol) were added to the solution. Then, the reaction mixture was degassed once again using freeze-pump-thaw procedures. The reaction solution was stirred at 50°C for 2 days. Upon completion of the reaction, the mixture was passed through a short silica gel plug using THF as an eluent. The solvent in the collected solution was removed under the reduced pressure. The crude product was dissolved in chloroform and precipitated in methanol, and after filtration, the product was redissolved in chloroform and precipitated in hexane to give 2.4 g red powder. Yield: 63 %. ^1H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.84 (s, 12H, $-CH_3$), 0.91 (s, 6H, $-CH_3$), 1.25 (s, 24H, $-CH_2-$), 1.44 (s, 4H, $-CH_2-$), 1.59 (s, 8H, $-CH_2-$), 1.77 (s, 4H, $-CH_2-$), 3.42 (s, 8H, $-NCH_2-$), 4.38 (s, 4H, $-OCH_2-$), 6.24 (s, 1H, Ar−H), 7.64 (s, 1H, Ar−H), 8.09 (s, 2H, Ar−H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 13.7 ($-CH_3$), 14.0 ($-CH_3$), 19.3 ($-CH_2-$), 22.7 ($-CH_2-$), 26.9 ($-CH_2-$), 27.6 ($-CH_2-$), 30.8 ($-CH_2-$), 31.8 (–CH_2–), 52.3 (–NCH_2–), 65.4 (–OCH_2–), 90.7 (–ethynyl), 97.0 (–ethynyl), 104.7 (Ar–C), 107.0 (Ar–C), 123.0 (Ar–C), 133.5 (Ar–C), 135.2 (Ar–C), 142.1 (Ar–C), 153.2 (Ar–C), 165.4 (–C=O). FTIR (v, cm^{-1}): 2954 (–CH_2–), 2924 (–CH_2–), 2854 (–CH_2–), 2185 (–ethynyl), 1726 (–COO–), 1583 (–phenyl), 1504, 1460, 1427, 1371, 1280, 1221, 1147, 1091, 1022, 956, 916, 806, 786, 727, 694, 605. UV-vis (λ_{max}, nm, $\varepsilon = 5.7 \times 10^4$ mol^{-1} •L•cm^{-1} calculated based on the molecular weight of each repeat unit): 248, 277, 351, 458. Anal. Calcd for $(C_{50}H_{74}N_2O_4)_n$ (767.15 for each repeat unit): C, 78.28; H, 9.72; N, 3.65; O, 8.34. Found: C, 78.23; H, 9.76; N, 3.61; O, 8.40.

2.5. Synthesis of PBBmN-TCBD

As shown in Scheme 4, to a solution of PBBmN (3.8 g, 5 mmol) in 50 mL dichloromethane was added a solution of tetracyanoethylene (1.3 g, 10.1 mmol) in 50 mL dichloromethane under the atmosphere of argon gas at 0°C. The reaction mixture was allowed to stir overnight. The polymer solution was concentrated under reduced pressure and then precipitated in hexanes. The obtained product was redissolved in dichloromethane and precipitated in hexane for three times to give 1.15 g red powder. Yield: 88%. ^1H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.89 (s, 18H, –CH_3), 1.31 (s, 28H, –CH_2–), 1.57 (s, 8H, –CH_2–), 1.80 (s, 4H, –CH_2–), 3.13 (s, 8H, –NCH_2–), 4.45 (s, 4H, –OCH_2–), 6.87 (s, 1H, Ar–H), 8.10 (s, 1H, Ar–H), 8.41 (s, 2H, Ar–H). FTIR (v, cm^{-1}): 2959 (–CH_2–), 2927 (–CH_2–), 2858 (–CH_2–), 2217 (–CN), 1716 (–COO–), 1585 (–phenyl), 1493, 1461, 1430, 1373, 1288, 1227, 1153, 1096, 1015, 931, 836, 803,767, 727, 692, 603. UV-vis (λ_{max}, nm, $\varepsilon = 3.9 \times 10^4$ mol^{-1} •L•cm^{-1} calculated based on the molecular weight of each repeat unit): 230, 308, 578. Anal. Calcd for $(C_{62}H_{74}N_{10}O_4)_n$ (1023.33 for each repeat unit): C, 72.77; H, 7.29; N, 13.69; O, 6.25. Found: C, 72.82; H, 7.25; N, 13.74; O,6.19.

3. Results and discussion

To date, the synthetic strategy for the phenylacetylene derivatives has relied heavily on the Sonogashira cross-coupling protocol [18], which was not applicable for the synthesis of 4,6-diethynyl-N,N,N,N-tetrahexylbenzene-1,3-diamine (**3**) in Scheme 1. Initially, attempt has been made to synthesize **3** by standard method of Sonogashira coupling with acetylene derivatives, but failed as illustrated in Schemes 2 and 3. In Scheme 2, it was easy to introduce diiodide groups into 1,3-phenylenediamine by oxidative iodination using potassium iodide and hydrogen peroxide in the presence of methanol and sulfuric acid at ambient temperature to afford **5** in a high yield [19]. However, the diiodide group in **5** cannot survive in the alkylation reaction conditions when synthesizing **6**. Another attempt was made to couple trimethylsilylacetylene with **5** using $PdCl_2(PPh_3)_2$, CuI, and PPh_3 as the catalyst in a mixed solvent of THF and diisopropylamine to give **7** in a good yield, as indicated in Scheme 3. Unfortunately, it was ofgreat difficulty to obtain **8** in Scheme 3, because trimethylsilyl group was replaced by hexyl group.

Consequently, a new strategy was developed to successfully synthesize the target monomer **3** by the reaction scheme given in Scheme 1. Specifically, tetraalkylation with 1,3-phenylenediamine with 1-iodohexane in the presence of sodium hydride and 15-crown-5 gave the desired tetrahexyldiamine monomer precursor **1** [20]. The use of Na_2CO_3/N,N-dimethylformamide reaction system [13] for an extended period only afforded di- or tri-alkylated monomers. Direct iodization based on **1** was unsuccessful using a couple of methods [21, 22]. Therefore, this problem was circumvented by reacting **1** with $POCl_3$ and N,N-dimethylformamide [23] to give **2** having two carbaldehyde groups. Subsequently, **2** was further reacted with lithium trimethylsilyldiazomethane to afford dialkyne monomer **3** via Colvin rearrangement [24] in a good yield.

Referring to Scheme 4, the obtained dialkyne monomer **3** was then polymerized with diiodide monomer **4** by Sonogashira cross-coupling reaction with tetrakis(triphenylphosphine) palladium and copper iodide as the catalysts in a mixed solvent of tetrahydrofuran and triethylamine at 50^{o}C. The strong electron donating property of dihexylamino groups in **3** has a negative effect on the palladium-catalyzed cross-coupling reactions [11, 22], and thus electron withdrawing (carbonyl) groups are introduced into **4** for improving the reactivity of this coupling reaction. As a consequence, PBBmN has a reasonably high molecular weight with an M_w of 82,044 and a polydispersity (M_w/M_n) of 3.2 as determined by GPC using polystyrenes as standards and THF as the eluent, and it shows good solubility in THF, chloroform, and dichloromethane. In contrast, if diiodide monomer **4** was replaced by 1,4-benzenediiodide, where the iodide groups were not activated, I only obtained oligomers with M_n = 1,854 and M_w = 3,719.

The alkynes activated by electron-rich groups will react with electron withdrawing TCNE via thermal [2+2] cycloaddition first to form cyclobutenes and the subsequent spontaneous electrocyclic ring opening to afford 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) [25, 26]. By this mechanism, the main-chain akynes in PBBmN were able to react with TCNE due to the activating effect of dialkylanilino groups in the *para*-position. This reaction proceeded smoothly under mild conditions in the absence of any catalyst. Upon the addition of TCNE, I observed the immediate color change of reaction mixture from light yellow to reddish color.

NMR spectroscopy was investigated to understand the chemical structures of PBBmN and PBBmN-TCBD, as illustrated in Fig. 1. Upon the completion of reaction with TCNE, the chemical shift for proton at 1 position of PBBmN has shifted from 6.24 ppm to 6.87 ppm for that at 1' position of PBBmN-TCBD. Similarly, the chemical shift for proton at 2 position of PBBmN has also shifted from 7.64 ppm to 8.10 ppm for that at 2' position of PBBmN-TCBD. The large increase in chemical shifts for these two protons may be attributed to the strong influence of electron withdrawing effect of TCBD units in PBBmN-TCBD. Further, I observe the same trend for protons at 3 and 4 positions for PBBmN, which shifts from 8.09 ppm to 8.41 ppm for those at 3' and 4' positions for PBBmN-TCBD. Besides these, there are no additional peaks appearing in the range of 6 ppm to 9 ppm in the ^{1}H NMR spectrum of PBBmN-TCBD that can be assigned to other chemical structures. This means that the extent of cycloaddition/retroelectrocyclization reaction of main-chain alkynes in PBBmN with TCNE should be extremely high, if not completely. I also observe the variation of chemical shifts of flexible side chains in PBBmN-TCBD, as compared with those in PBBmN. For example, the chemical shift at 3.42 ppm for $-NCH_2-$ groups in PBBmN has reduced to 3.13 ppm for those in PBBmN-TCBD, arising from the electron delocalization from electron donating dialkylamino groups to electron accepting TCBD groups. In contrast, the chemical shift at 4.38 ppm for $-OCH_2-$ groups in PBBmN has increased to 4.45 ppm because of the presence of stronger electron withdrawing TCBD groups in PBBmN-TCBD. The broader peaks for $-NCH_2-$ and $-OCH_2-$ groups in PBBmN-TCBD can be interpreted by the conformation change of side chains due to the intramolecular charge-transfer interactions between the dialkylamino groups and TCBD units.

The chemical structure of PBBmN-TCBD can be further confirmed by the FTIR spectra given in Fig. 2. It can be seen from Fig. 2 that the absorption peak appearing at 2185 cm^{-1} for main-chain alkynes in PBBmN has shifted to 2217 cm^{-1} for cyano groups of TCBD units in PBBmN-TCBD, indicative of the successful cycloaddition/retroelectrocyclization reaction of alkynes in PBBmN with TCNE [11]. Correspondingly, I oberved the shift of absoprtion peak for carbonyl groups from 1726 cm^{-1} for PBBmN to 1716 cm^{-1} for PBBmN-TCBD, as a consequence of the electron withdrawing effect of TCBDs in PBBmN-TCBD. TGA data in Fig. 3 show that the thermal degradation temperatures, which were defined as the heating temperature at 5% weight loss, for PBBmN and PBBmN-TCBD are 162°C and 198°C, respectively. The improvement of thermal stability in PBBmN-TCBD may be associated with the intramolecular charge-transfer interactions along the macromolecular chains [10, 11], which will be elaborated on by UV-vis spectroscopy and cyclic voltammetry.

Fig. 4 gives plots of UV-vis spectra versus (a) wavelength and (b) energy for PBBmN and PBBmN-TCBD. Here, the bandgap energy, $E_g = 1242/\lambda$ (eV), is originated from the equation, $E_g = hC/\lambda$ with h being Planck's constant (6.626×10^{-34} J·s), C being the speed of light (3.0×10^{8} m/s), λ_{onset} being the onset wavelength (nm x 10^{-9} m), and 1 eV being equal to 1.6×10^{-19} J [11]. It can be observed from Fig. 4a that PBBmN exhibits a broad band with a maximum absorption peak at 458 nm in the visible absorption region due to the strong electron donating effect of dihexylamino groups in the polymer. The onset wavelength (λ_{onset}) of PBBmN is about 583 nm, and correspondingly the optical bandgap energy of PBBmN is about 2.13 eV, as illustrated in Fig. 4b. In the UV region of Fig. 4a, I also observe strong absorption bands at a wavelength of 248, 277, and 351 nm, which are equal to 5.0, 4.5, and 3.5 eV, respectively, and thus assigned to the $\pi-\pi^*$ transitions located on the phenyl and ethynyl subunits. In the case of PBBmN-TCBD (Fig. 4b), I observe a very broad absorption band with a maximum absorption peak at 578 nm, which is attributed to the intramolecular charge-transfer interactions between dihexylamino groups and TCBD units in PBBmN-TCBD. The onset wavelength (λ_{onset}) of PBBmN-TCBD is about 890 nm, affording an optical bandgap (E_g^{opt}) of 1.4 eV, as confirmed by Fig. 4b. The strong charge-transfer interactions between dihexylamino groups and TCBD units in PBBmN-TCBD result in such a low bandgap energy. Similarly, I observe strong absorption bands at a wavelength of 230 nm and 308 nm, which are equal to 5.4 and 4.0 eV respectively, and thus assigned to the $\pi-\pi^*$ transitions located on the phenyl units of PBBmN-TCBD.

The electrochemical behaviors of PBBmN and PBBmN-TCBD were also investigated by cyclic voltammograms with an internal reference to ferricinium/ferrocene (Fc/Fc^+) couple. As displayed in Fig. 5a and Table 1, PBBmN shows a one-electron oxidation step at a half-wave oxidation ($E_{1/2}^{ox}$) of 0.30 V vs Fc/Fc$^+$ as a consequence of the redox between amine and amine cation, and the other oxidation step at $E_{1/2}^{ox}$ of 0.89 V vs Fc/Fc$^+$, indicative of the subsequent oxidation from amine cation to bication. As shown in Fig. 5b and Table 1, PBBmN-TCBD shows an irreversible anondic peak at E_{pa}^{ox} = 0.99 V and a half-wave oxidation potential of ($E_{1/2}^{ox}$) of 1.19 V vs. Fc/Fc$^+$, which are ascribed to the amino groups in PBBmN-TCBD. Also, two additional quasi-reversible half-wave reduction potentials ($E_{1/2}^{red}$) of –0.91 V and –1.76 V vs. Fc/Fc$^+$ are observed in Fig. 5b, which are assigned to the electron accepting TCBD units in PBBmN-TCBD. Since PBBmN-TCBD exhibits an onset oxidation potential (Φ_{ox} = 0.48 V) and an onset reduction potential (Φ_{red} = –0.62 V) as given in Fig. 5b, the the highest occupied molecular orbital energy and the lowest unoccupied molecular orbital energy of PBBmN-TCBD are determined to be E_{HOMO} = –5.42 eV and E_{LUMO} = –4.32 eV, respectively. These are calculated based on the assumption that the energy level of Fc/Fc$^+$ is 4.80 eV below the vacuum level [27]. Thus, PBBmN-TCBD has a low bandgap energy (E_g^{CV}) of 1.10 eV, arising from the strong intramolecular charge-transfer interactions between dihexylamino groups and TCBD units within the molecule.

4. Conclusions

In summary, a facile synthetic route was developed to achieve 4,6-diethynyl-N,N,N',N'-tetrahexyl-benzene-1,3-diamine by introducing carbaldehyde intermediates, which was then converted into acetylene groups via Colvin rearrangement, while the procedures based on palladium-catalyzed coupling reaction was unsuccessful. This unique strong electron-donating monomer was then polymerized with a carbonyl-activated diiodide monomer to afford a strong electron donating π-conjugated polymer having a reasonably high molecular weight. This precursor polymer was then reacted with TCNE via cycloaddition/retroelectrocyclization reaction to afford the main-chain donor-acceptor type polymer, which exhibited a very low bandgap energy due to the strong intramolecular charge-transfer interactions between electron donors and acceptors along the macromolceular chains.

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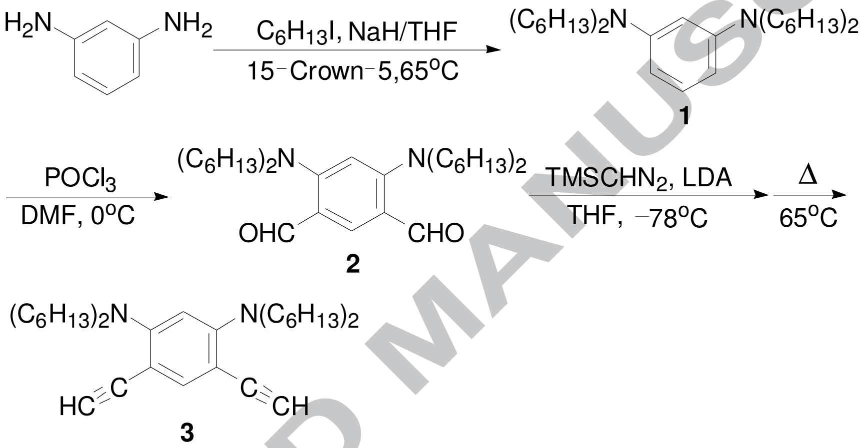
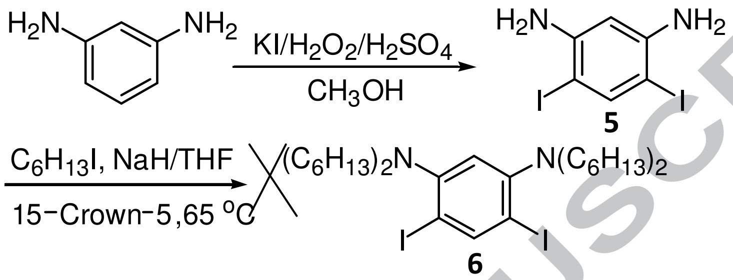
Table 1. Electrochemical properties of PBBmN and PBBmN-TCBD obtained from cyclic voltammetry measured in CH_2Cl_2 versus Ag/Ag^+ as a reference electrode and calibrated versus Fc/Fc^+

Polymers	Oxidation Potential (V)				Reduction Potential (V)			
	E_{pa}	E_{pc}	ΔE	$E_{1/2}^{ox}$	E_{pa}	E_{pc}	ΔE	$E_{1/2}^{red}$
PBBmN	0.39	0.21	0.18	0.3				
	1.02	0.76	0.26	0.89				
PBBmN-TCBD	0.99	Irreversible			-1.53	-1.98	0.45	-1.76
	1.23	1.14	0.09	1.19	-0.73	-1.08	0.35	-0.91

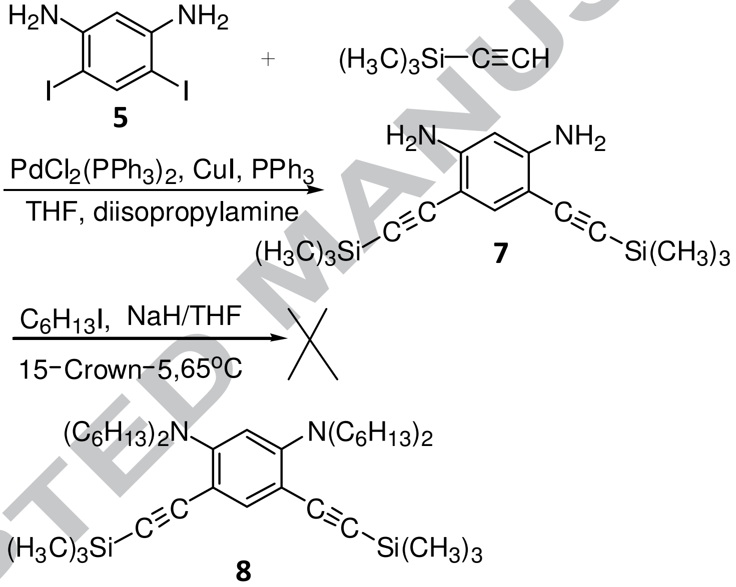
Note: $\Delta E = E_{pa} - E_{pc}$; $E_{1/2} = (E_{pa} + E_{pc})/2$. E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively, with *ox* denoting oxidation and *red* denoting reduction.



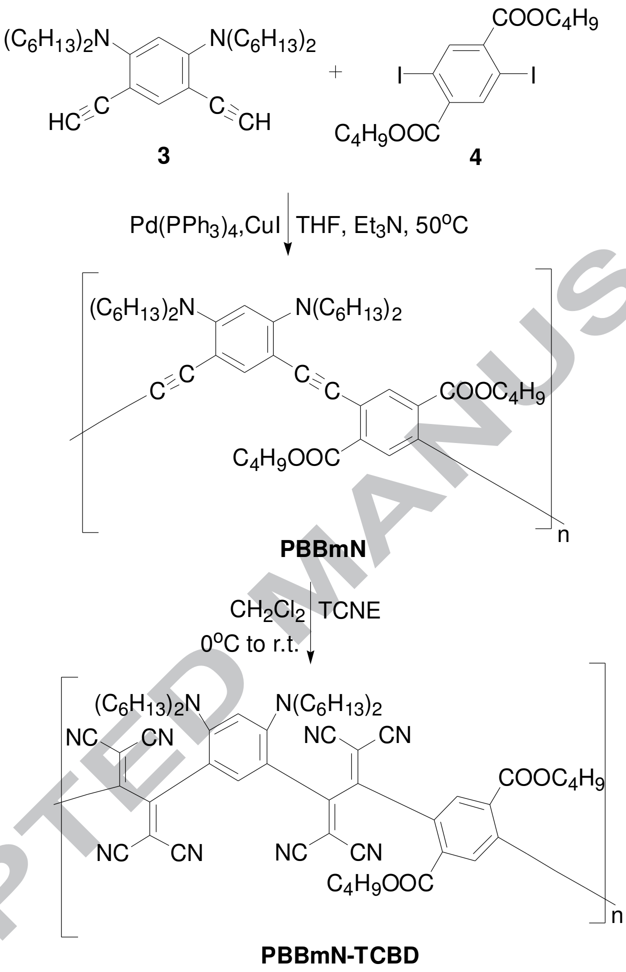
Scheme 1. Synthesis of 4,6-diethynyl-N,N,N', N'-tetrahexyl-benzene-1,3-diamine (**3**).



Scheme 2. Unsuccessful attempt to synthesize 4,6-diethynyl-N,N,N', N'-tetrahexyl-benzene-1,3-diamine (**3**).



Scheme 3. Unsuccessful attempt to synthesize 4,6-diethynyl-N,N,N', N'-tetrahexyl-benzene-1,3-diamine (**3**).



Scheme 4. Synthesis of the precursor π-conjugated poly(arylene ethynylene) (PBBmN) and main-chain donor-acceptor type polymer (PBBmN-TCBD).

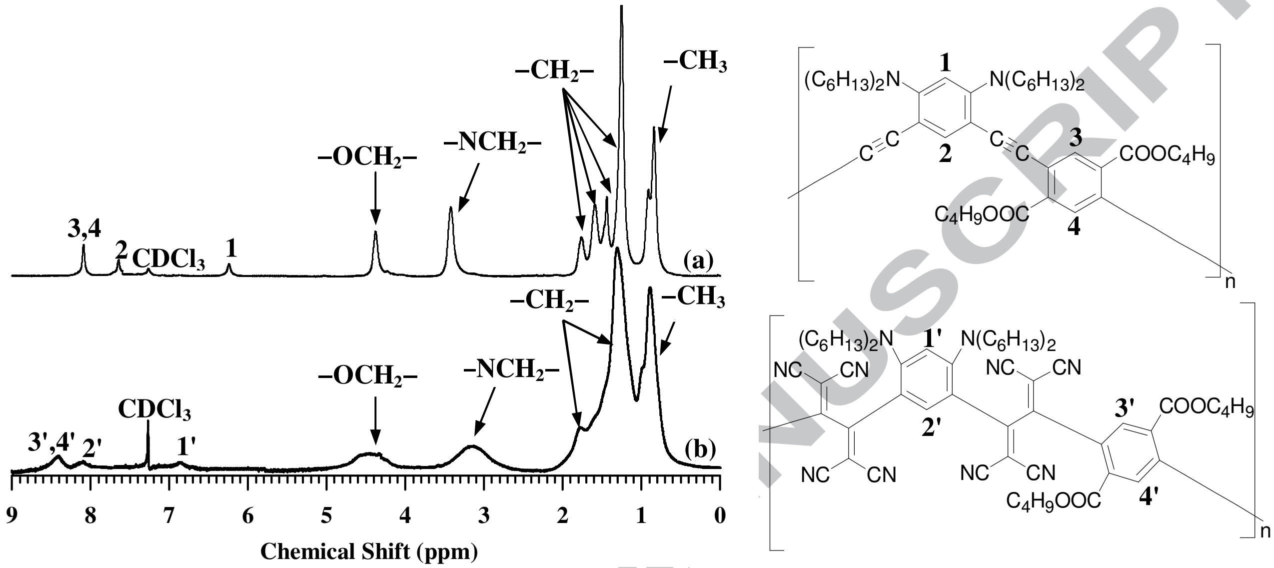


Fig. 1. ^{1}H NMR spectra of (a) PBBmN and (b) PBBmN-TCBD in CDCl$_3$.

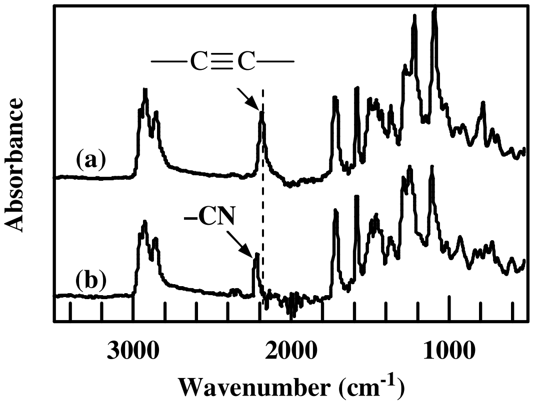


Fig. 2. FTIR spectra of (a) PBBmN and (b) PBBmN-TCBD.

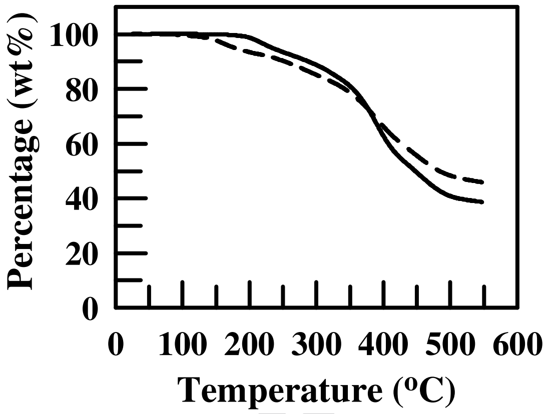


Fig. 3. TGA data for PBBmN (dashed line) and PBBmN-TCBD (solid line).

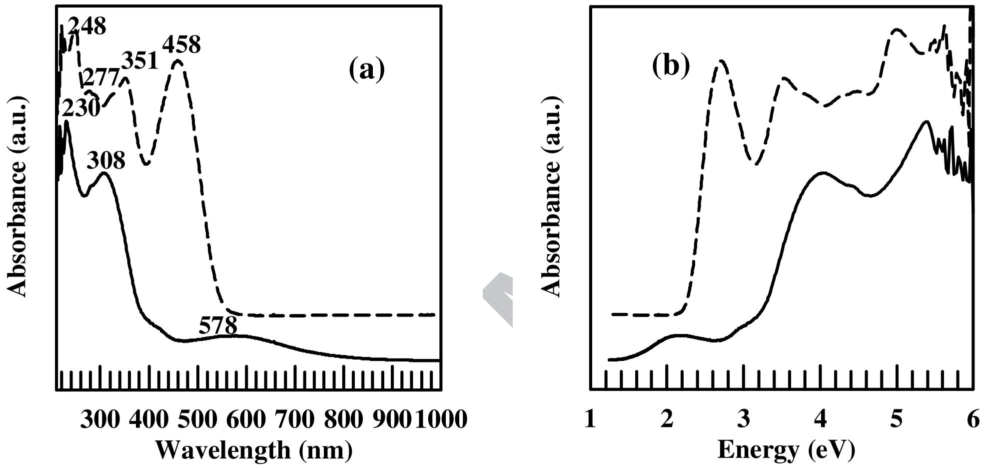


Fig. 4. Plots of UV-vis spectra versus (a) wavelength and (b) energy for PBBmN (dash line) and (b) PBBmN-TCBD (solid line) in dichloromethane.

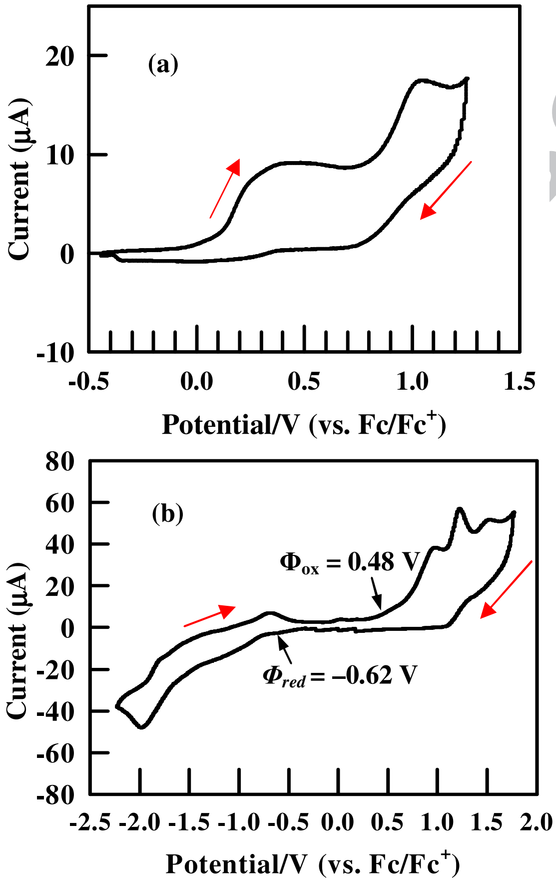


Fig. 5. Cyclic voltammograms of (a) PBBmN and (b) PBBmN-TCBD in dichloromethane solution containing 0.1 M nBu_4NPF_6. Φ_{ox} and Φ_{red} are the onset oxidation and reduction potentials, respectively. Red arrows describe the directions of scans.