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Synthesis, optical and electrochemical properties of novel D-π-A type conjugated polymers based on benzo[*c*][1,2,5]selenadiazole unit *via* alkyne module

Duanqin Li, Hui Li, Miaochang Liu, Jiuxi Chen, Jinchang Ding, Xiaobo Huang*, Huayue Wu*

College of Chemistry & Materials Engineering, Wenzhou University, Wenzhou 325035, PR China

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ABSTRACT

Three novel donor-π-acceptor (D-π-A) type conjugated polymers **P-1**, **P-2**, and **P-3** based on benzo[*c*][1,2,5]selenadiazole moiety and phenyl or naphthyl group *via* alkyne module were firstly prepared by Sonogashira–Hagihara reaction of various diiodo aryl compounds with the key monomer 4,7-diethynylbenzo[c] [1,2,5]selenadiazole (**M-1**), which was synthesized by a strategy of firstly introducing the trimethylsilylacetylene flexible group, and then introducing the selenium atom. The polymers displayed obvious absorption peaks at the region from 503 to 510 nm and narrow orange-red or red fluorescence in the range of 576–595 nm because benzo[*c*][1,2,5]selenadiazole unit can effectively reduce the lowest unoccupied molecular orbital (LUMO) energy levels of these polymers. The band gaps of these polymers can be tuned in the range of 1.37–1.76 eV by using different aryl donor groups. These findings indicate that these benzo[*c*][1,2,5]selenadiazole-based conjugated polymers can be developed for excellent fluorescent materials.

1. Introduction

In the past few decades, conjugated polymers with excellent photoelectric properties have made great progress in a number of materials science fields, including light-emitting diodes [1,2], field effect transistors [3,4], solar cells devices [5–10] and fluorescent sensors [11–13], etc. Among the diverse classes of organic π-systems, donor-π-acceptor (D-π-A) type conjugated polymers have attracted an increasing interest due to low band gaps in recent years, they can show a high tendency for absorbing visible wavelength photons as well as enhancing the intramolecular charge transfer (ICT), leading to good charge carrier mobilities [14,15]. A very common strategy for the design of low-band gap polymers is based on alternating electron-rich donor (D) and electron-poor acceptor (A) fragments along the π-conjugated backbone. This derives from the fact that D groups raise the HOMO energy and A groups lower the LUMO energy, which led to the decrease of the polymer band gap energy [16].

Recently, the acceptor benzothiadiazole (BT) ring has received great attention since its electron-withdrawing ability can be applied for the construction of low band gap conjugated polymers [17–20]. 2,1,3-Benzoselenadiazole (BSe) has a similar chemical structure as BT. But compared with BT, BSe can exhibit more effective in lowering the band gaps of the conjugated polymers because the selenium atom has a much larger size and is more electron rich than the sulfur atom, which leads to the absorption and emission red shift of BSe-based polymers [21–23]. The BSe-based conjugated polymers can also exhibit interesting photoelectric properties in their applications as light-emitting diodes and solar cells [24–28].

Among the D-π-A systems, poly(aryleneethynylene)s (PAEs) are a class of conjugated polymers, in which aromatic or heteroaromatic groups are linked by alkyne modules. The triple bonds in the polymer main chain provide extended conjugation and rigidified backbones for pronounced interchain interactions [5]. They reportedly show better photostability than poly(arylene vinylene)s (PAVs) [29], and are widely used in the fields of fluorescent sensors [11,13] and organic electronics [1,5]. As a further extension of our research on PAE type of fluorescent materials [30–32], a series of D-π-A conjugated polymers based on BSe moiety and aryl unit *via* alkyne module are designed to gain narrow band gap conjugated polymers with long absorption and emission wavelength, and for fluorescent material applications. But to the best of our knowledge, these kinds of conjugated polymers have not been reported. This is likely because dihalo compounds of benzoselenadiazole, such as

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* Corresponding authors.
E-mail addresses: xiaobhuang@wzu.edu.cn, xiaobhuang@hotmail.com (X. Huang), huayuewu@wzu.edu.cn (H. Wu).

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4,7-dibromobenzoselenadiazole (**4**) and 4,7-diiodo-benzoselenadiazole (**5**) are hard to participate in the Sonogashira-Hagashira coupling reaction due to the poor reactivity and solubility influenced by the selenium atom, and a similar unsuccessful example has recently been reported [33].

To solve the problems of synthesizing conjugated polymers containing BSe, the key monomer diethynylbenzoselenadiazole (**M-1**) was synthesized by a strategy of firstly introducing the trimethylsilylacetylene flexible group, and then introducing the selenium atom. In this way, a series of D-π-A conjugated polymers incorporating BSe moiety as an acceptor and aryl group as a donor, such as phenyl and naphthyl group in the main chain backbone were successfully synthesized by Sonogashira–Hagihara coupling reaction. Optical and electrochemical properties of these polymers were investigated by UV–vis absorption, fluorescence spectra and cyclic voltammetry (CV) analyses. These polymers displayed obvious absorption peaks at the region from 503 to 510 nm and narrow orange–red or red fluorescence in the range of 576–595 nm. And the resulting polymers show tunable band gaps in the range of 1.37–1.76 eV. The results show that the optical and electrochemical properties of the copolymers can be easily tuned by introducing different electron rich groups, which is beneficial for preparation of good fluorescent materials.

2. Experimental part

2.1. Materials

All solvents and reagents were commercially available and analytical-reagent-grade. THF and Et_3N were purified by distillation from sodium in the presence of benzophenone. 4,7-Dibromobenzo[*c*] [1,2,5]-thiadiazole (**2**), 3,6-dibromobenzene-1,2-diamine (**3**), 4,7-dibromobenzo[*c*] [1,2,5]selenadiazole (**4**) and 4,7-diiodobenzo[*c*] [1,2,5]selenadiazole (**5**) could be prepared from 2,1,3-benzothiadiazole (**1**) according to the literature reported by Myashi and co-workers [34]. 1,4-Dibutoxy-2,5-diiodobenzene (**M-2**) [35], 1,2-dibutoxy-4,5-diiodobenzene (**M-3**) [36] and 1,4-dibromo-2,3-dibutoxy-naphthalene [37] could be prepared according to reported literature from corresponding starting materials.

2.2. Measurements

The ^{1}H NMR and ^{13}C NMR spectra were recorded in solution of $CDCl_3$ on Bruker DPX 300 or DRX 500 NMR spectrometer with tetramethylsilane (TMS) as the internal standard. The chemical shift was recorded in ppm and the following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, m = multiplet, br = broad. FT-IR spectra were taken on a Nexus 870 FT-IR spectrometer. EI mass spectra were recorded on Agilent 5975C DIP/MS mass spectrometer. C, H and N of elemental analyses were performed on an Elementar Vario MICRO analyzer. UV–vis absorption was recorded on Shimadzu UV-1700 spectrometer and fluorescence spectra were recorded on a RF-5301PC fluorometer. TGA was performed on a Perkin–Elmer Pyris-1 instrument under N_2 atmosphere. Molecular weight was determined by GPC with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards. The electrochemical measurements were carried out in anhydrous CH_2Cl_2 with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte at a scan rate of 0.02 V/s at room temperature under the protection of nitrogen. A gold disk was used as working electrode, platinum wire was used as counter electrode, and Ag/AgCl (3 M KCl solution) was used as reference electrode.

2.3. Preparation of compound *M-1* (Scheme 1)

A mixture of 3,6-dibromobenzene-1,2-diamine (**3**) (266 mg, 1.0 mmol), $Pd(PPh_3)_2Cl_2$ (70.1 mg, 0.10 mmol), CuI (19.1 mg, 0.10 mmol), PPh_3 (26.2 mg, 0.10 mmol) and trimethyl silyl acetylene (0.86 mL, 6.00 mmol) was dissolved in 10 mL of Et_3N and 10 mL of THF. The reaction mixture was stirred at 80 °C for 12 h under N_2 atmosphere. The solution was cooled to room temperature and then the solvent was removed under reduced pressure, and the residue was extracted with $CHCl_3$. The organic layer was washed with water and then brine, dried over anhydrous Na_2SO_4, and then evaporated in vacuum to dryness. The residue was purified by silica gel column chromatography (petroleumether/ethyl acetate) (30:1, v/v) to give compound **6** as yellow solids in 45% yield. MS (EI): m/z: 300 [M^+]. Compound **6** was unstable in air and need be used immediately for the synthesis of compound **7**.

To a solution of compound **6** (56.1 mg, 0.19 mmol) in refluxing ethanol (20 mL) was added a solution of SeO_2 (21.6 mg, 0.2 mmol) in hot water (8 mL). The mixture was heated under reflux for 2 h. The solvent was evaporated and the residues were extracted with $CHCl_3$. The organic layer was washed with water and then brine, dried over anhydrous Na_2SO_4, and then evaporated in vacuum to dryness. The residues were purified by silica gel column chromatography with petroleum ether as an eluant to give compound **7** as yellow solids in 80% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (s, 2H); 0.33 (s, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 158.0, 132.8, 118.2, 102.3, 99.5, −1.2; Anal. calcd for $C_{16}H_{20}N_2SeSi_2$: C, 51.18; H, 5.37; N, 7.46. Found: C, 51.10; H, 5.43; N, 7.38.

A solution of compound **7** (50 mg, 0.13 mmol) was dissolved in THF (10 mL) and MeOH (10 mL), and then K_2CO_3 (18 mg, 0.133 mmol) was added to the reaction mixture. After being stirred at room temperature for 1 h, the solvent was evaporated and the residues were extracted with $CHCl_3$. The organic layer was washed with water and then brine, dried over anhydrous Na_2SO_4, and then evaporated in vacuum to dryness to give yellow solids **M-1** in 85% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.68 (s, 2H); 3.68 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.1, 133.5, 118.5, 85.2, 79.4; Anal. calcd for $C_{10}H_4N_2Se$: C, 51.97; H, 1.74; N, 12.12. Found: C, 51.90; H, 1.71; N, 12.06.

2.4. Preparation of compound *M-2* (Scheme 1)

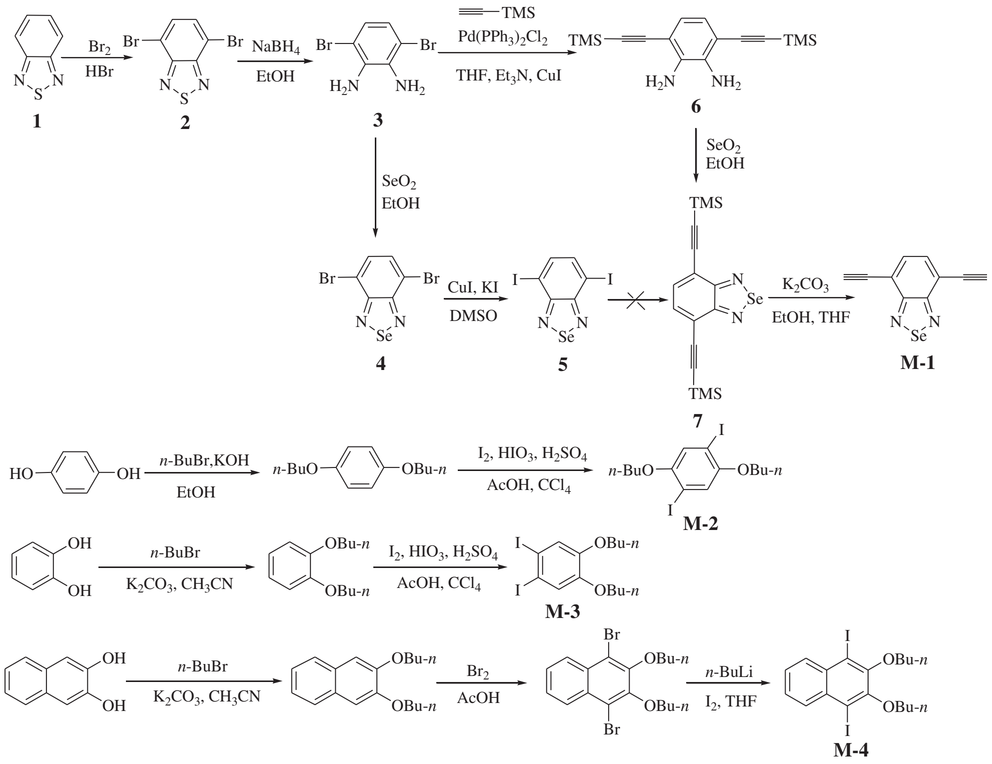
M-2 was prepared according to reported literature [35]. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.17 (s, 2H), 3.93 (t, *J* = 6.5 Hz, 4H), 1.81–1.76 (m, 4H), 1.57–1.51 (m, 4H), 0.98 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.9, 122.8, 86.3, 70.1, 31.3, 19.3, 13.9.

2.5. Preparation of compound *M-3* (Scheme 1)

M-3 was prepared according to reported literature [36]. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25 (s, 2H), 3.93 (t, *J* = 7.0 Hz, 4H), 1.80–1.75 (m, 4H), 1.52–1.44 (m, 4H), 0.97 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 149.7, 123.5, 95.8, 69.2, 31.1, 19.2, 13.8.

2.6. Preparation of compound *M-4* (Scheme 1)

1,4-Dibromo-2,3-dibutoxy-naphthalene was synthesized according to previous reports [37]. 1,4-Dibromo-2,3-dibutoxy-naphthalene (4.0 g, 9.3 mmol) was dissolved in anhydrous THF (50 mL), *n*-BuLi (11.2 mL, 2.5 mol L^{-1} in hexanes, 28.0 mmol) was added by syringe injection at room temperature under N_2 atmosphere. After the reaction mixture was stirred for 5 h, I_2 (7.12 g, 28.0 mmol in 40 mL of THF) was added to the above solution at −78 °C under N_2 atmosphere. The reaction mixture was gradually warmed to room temperature and stirred overnight. The reaction was quenched



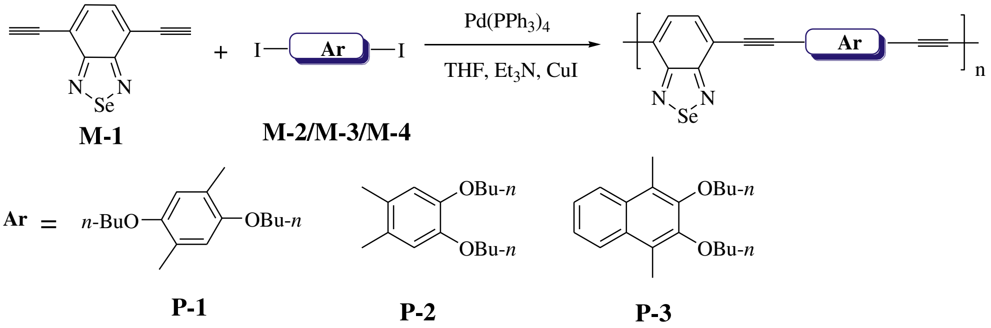
Scheme 1. Synthetic procedures of **M-1**, **M-2**, **M-3** and **M-4**.

with saturated $Na_2S_2O_3$ solution (45 mL). After removal of the solvent under reduced pressure, the residue was extracted with ethyl acetate (2 × 50 mL). The combined organic layers were washed with water and brine, and then dried over anhydrous Na_2SO_4. After removal of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/ethylacetate) (50:1, v/v) to afford pale yellow solids **M-4** (2.29 g) in 47% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.15–8.11 (m, 2H), 7.51–7.48 (m, 2H), 4.11 (t, $J = 6.5$ Hz, 4H), 1.94–1.88 (m, 4H), 1.64–1.56 (m, 4H), 1.03 (t, $J = 7.5$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.2, 132.6, 132.5, 127.3, 97.8, 73.9, 32.5, 19.5, 14.1.

2.7. *Preparation of **P-1**, **P-2** and **P-3** (Scheme 2)*

A mixture of **M-1** (57.8 mg, 0.25 mmol), **M-2** (118.3 mg, 0.25 mmol), 10 mol% $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) and 20 mol% CuI (10.0 mg, 0.05 mmol) was dissolved in the mixed solvents of 30 mL THF and 15 mL Et_3N. The solution was stirred at reflux for 2 days under N_2. The mixture was cooled to room temperature, and then was filtered through a short silica gel column eluted with THF. The polymer solution is concentrated by evaporation of the solvents under reduced pressure, and the polymer is precipitated in methanol (30 mL). The resulting polymer was filtered and washed with methanol several times. Further purification could be conducted by dissolving the polymer in THF to precipitate in methanol again. The polymer was dried in vacuum to give 65.0 mg as red solids in 65% yield. **P-1** spectroscopic data: ^{1}H NMR (500 Hz, $CDCl_3$): δ 7.76–7.64 (m, 2H), 7.17–7.02 (m, 2H), 4.12–3.97 (m, 4H), 1.88–1.80 (m, 4H), 1.62–1.49 (m, 4H), 1.01–0.98 (m, 6H); FT-IR (KBr, cm^{-1}): 2914, 2352, 1554, 1368, 1215, 1096; Anal. calcd for $C_{24}H_{22}N_2O_2Se$: C, 64.14; H, 4.93; N, 6.23. Found: C, 62.78; H, 4.85; N, 6.07.

By using the same procedure as for the preparation of **P-1**, polymer **P-2** was obtained as red solids in 60% yield from **M-1** and **M-3**. P-2 spectroscopic data: ^{1}H NMR (500 Hz, $CDCl_3$): δ 7.77–7.65 (m, 2H), 7.16–7.03 (m, 2H), 4.03–3.97 (m, 4H), 1.83–1.80 (m, 4H),



Scheme 2. Synthetic procedures of **P-1**, **P-2** and **P-3**.

1.53–1.50 (m, 4H), 1.01–0.96 (m, 6H); FT-IR (KBr, cm^{-1}): 2968, 2365, 1558, 1374, 1232, 1086; Anal. calcd for $C_{24}H_{22}N_2O_2Se$: C, 64.14; H, 4.93; N, 6.23. Found: C, 62.43; H, 5.02; N, 6.38.

By using the same procedure as for the preparation of **P-1**, polymer **P-3** was obtained as red solids in 70% yield from **M-1** and **M-4**. **P-3** spectroscopic data: ^1H NMR (500 Hz, $CDCl_3$): δ 7.75–7.70 (m, 2H), 7.55–7.50 (m, 2H), 7.47–7.43 (m, 2H), 4.39–4.09 (m, 4H), 2.04–1.91 (m, 4H), 1.68–1.60 (m, 4H), 1.05–1.00 (m, 6H); FT-IR (KBr, cm^{-1}): 2954, 2358, 1550, 1398, 1222, 1096; Anal. calcd for $C_{28}H_{24}N_2O_2Se$: C, 67.33; H, 4.84; N, 5.61. Found: C, 65.16; H, 4.75; N, 5.37.

3. Results and discussion

3.1. Synthesis and feature of the conjugated polymers

The synthetic procedures of **M-1**, **M-2**, **M-3**, **M-4** and **P-1**, **P-2**, **P-3** are outlined in Schemes 1 and 2, respectively. We first designed key intermediate compound 4,7-bis(2-(trimethylsilyl)ethynyl)-benzo[*c*][1,2,5]selenadiazole (**7**) for the synthesis of the monomer 4,7-diethynylbenzo[*c*] [1,2,5]selenadiazole (**M-1**). Theoretically compound **7** could be synthesized from 4,7-dibromobenzoselenadiazole (**4**) with trimethylsilylacetylene *via* Sonogashira–Hagihara coupling reaction, but we failed and found that a similar unsuccessful example has recently been reported [33]. The coupling reaction could not be carried out between diiodo compound **5** and trimethylsilylacetylene, which may be due to the reason that the selenium atom reduces the reactivity and solubility of dihalo compounds. Therefore we chose the second synthesis procedure as shown in Scheme 1. Compound **7** could be obtained by the treatment of 3,6-bis(2-(trimethylsilyl)ethynyl)benzene-1,2-diamine (**6**) using SeO_2 in hot ethanol. Herein, compound **6** synthesized by the Sonogashira–Hagihara coupling reaction of 3,6-dibromobenzene-1,2-diamine (**3**) with trimethylsilylacetylene was unstable in air and need be used immediately for the synthesis of compound **7**. **M-1** could be obtained in 85% yield by deprotection of compound **7** using K_2CO_3 in the mixed solvent of THF and methanol. 1,4-Dibromo-2,3-dibutoxy-naphthalene synthesized according to previous reports [37] was first lithiated with *n*-BuLi at room temperature, and then followed by I_2 at -78 °C to afford 2,3-dibutoxy-1,4-diiodonaphthalene (**M-4**) in 47% yield.

M-1, **M-2**, **M-3** and **M-4** could be served as the monomers for the synthesis of the target polymers. In this paper, a typical Sonogashira–Hagihara reaction condition was applied to the synthesis of these polymers. The polymerization was easily carried out by the diiodo monomers with **M-1** in the presence of a catalytic amount of $Pd(PPh_3)_4$ and CuI with Et_3N under N_2. The molecular weight and polydispersity index (PDI) of the polymers measured by gel permeation chromatography (GPC) were $Mn = 5610$, $Mw = 8580$ and PDI = 1.53 for **P-1**, $Mn = 4420$, $Mw = 5850$ and PDI = 1.32 for **P-2**, and $Mn = 4250$, $Mw = 5320$ and PDI = 1.25 for **P-3**. The GPC results of three polymers show the moderate molecular weight. The D-π-A conjugated polymers show good solubility in some common solvents, such as toluene, THF, $CHCl_3$, and CH_2Cl_2, which can be attributed to the flexible *n*-butyl group substituents on aryl units as side chains of the polymers. Thermogravimetric analyses (TGA) of these polymers were carried out under a N_2 atmosphere at a heating rate of 10 °C/min. As shown in Fig. 1, although the repeating units of **P-1**, **P-2** and **P-3** are the similar polymer composition and backbone chain structure, their TGA plots are different. The TGA curves reveal that the degradation temperature (T_d) of 5% weight loss of **P-1**, **P-2** and **P-3** was 270 °C, 310 °C and 290 °C, respectively, which indicates an excellent thermal stability of these materials. There is a total loss of about 75.4%, 46.0% and 60.0% for **P-1**, **P-2** and **P-3** when heated to 700 °C, respectively. Therefore, three resulting polymers can provide a desirable thermal property for photoelectric materials.

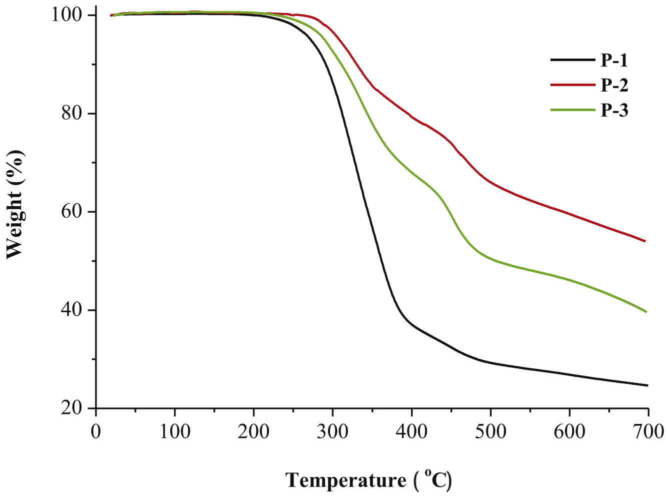


Fig. 1. TGA curves of **P-1**, **P-2** and **P-3**.

3.2. Photophysical properties

The UV–vis absorption and fluorescence spectra of the resulting polymers were recorded in $CHCl_3$ as shown in Figs. 2 and 3, respectively, and the data are collected in Table 1. As is evident from Fig. 2, three polymers exhibit two distinct bands and have well-resolved absorption peaks with large molar absorption coefficients in the range of 300 nm–520 nm, which may be attributed that the low band gaps of these conjugated polymers promote the tendency for absorbing visible wavelength photons. One band situated at a shorter wavelength 341–350 nm region is assigned to the localized π–π^* transition, and the other band at a longer wavelength around 503–510 nm can be regarded as the absorption of the conjugated structure arisen from the intramolecular charge transfer (ICT) band between electron-rich donors and electron-deficient acceptors [38]. Herein, the BSe unit acts as an electron acceptor and aryl group as an electron donor. The optical band gaps (E_g^{opt}, Table 1) of three polymers estimated from the UV–vis onset absorptions are 2.10 eV, 2.12 eV and 2.15 eV for **P-1**, **P-2** and **P-3**, respectively. It can be found that incorporating BSe unit into the poly(phenylene ethynylene) (PPE) main chain (**P-1**) results in obvious absorption red shift (about 20 nm) in comparison with its sulfur analog (483 nm) reported by Yang and co-workers [39].

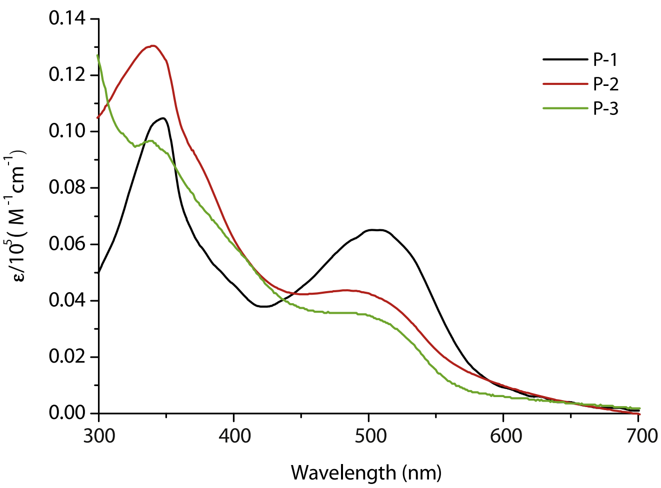


Fig. 2. UV–vis absorption spectra of **P-1**, **P-2** and **P-3** (1×10^{-5} mol/L in $CHCl_3$).

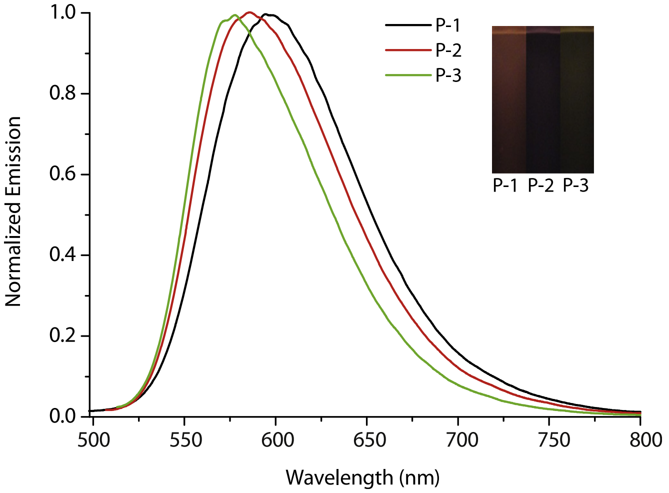


Fig. 3. Fluorescence spectra of **P-1**, **P-2** and **P-3** in $CHCl_3$. Inset: fluorescence photos of three polymers in $CHCl_3$ under a 365 nm UV lamp.

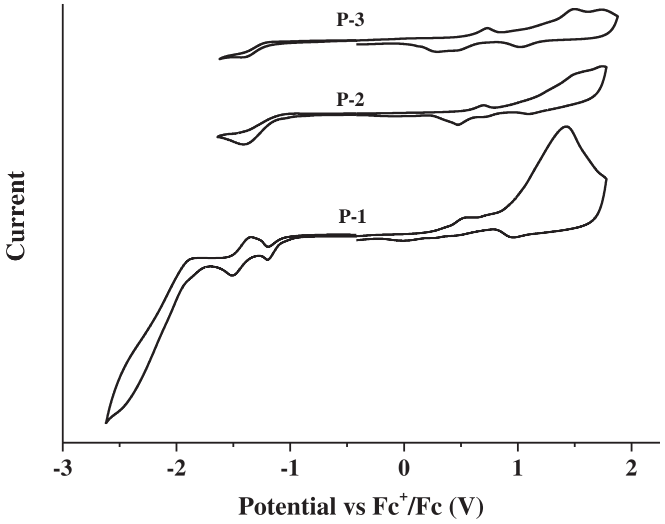


Fig. 4. Cyclic voltammograms of **P-1**, **P-2** and **P-3**.

In this paper three BSe-based polymers also show longer absorption wavelength than the corresponding BT polymers due to the larger size and the weaker electron-withdrawing character of selenium, which is also consistent with Cao and co-workers' reports [23,24]. The UV absorptions of these polymers in thin films (Fig. S1) show red shifts more than 30 nm relative to those measured in $CHCl_3$ solution, respectively. It can be attributed to a higher conjugated structure stacking of the repeating unit in the solid than in the solution [40]. These polymers display red fluorescence centered at 596 nm, 586 nm, and 578 nm (Table 1), respectively by using a commercially available UV lamp (365 nm) (Insert of Fig. 3), which have about 35 nm red shift than the corresponding BT polymer (561 nm) [39]. But these red polymers have low fluorescence quantum yields ($\Phi_{PL} = 0.04–0.11$) compared with BT polymer using Rhodamine B as the fluorescence reference, which could be due to the fact that the narrow energy band gap may increase the probability of singlet excitons decaying to the ground state in a non-radiative way [41].

3.3. Electrochemical properties

Cyclic voltammetry (CV) analyses of three polymers were performed to examine their electrochemical behavior and measure their energy levels (Fig. 4, Table 1). Three-electrode electrochemical cell was used with a gold disc electrode as working electrode, a platinum wire as counter electrode and an AgCl/Ag (in 3 M aq. KCl) as reference electrode. The electrochemical measurements were carried out in anhydrous DCM with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte at a scan rate of 0.05 V/s at room temperature under the protection of nitrogen. The redox potentials were calibrated using a ferrocene–ferrocenium ($Fc–Fc^+$) couple as the internal potential standard, and under our experimental conditions, E (Fc^+/Fc) = 0.42 V versus Ag/AgCl. The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels of these polymers can be estimated according to the equations of HOMO = $-(4.8 + E_{ox}^{onset})$, LUMO = $-(4.8 + E_{red}^{onset})$. On the basis of these onset potentials, the HOMO energy levels of **P-1**, **P-2** and **P-3** were determined to be −5.10 eV, −5.33 eV and −5.36 eV, and the LUMO energy levels were −3.73 eV, −3.67 eV and −3.60 eV, respectively. The electrochemical band gaps (E_g) of **P-1**, **P-2** and **P-3** are 1.37 eV, 1.66 eV and 1.76 eV, respectively. It can be observed that the LUMO energy levels of **P-1**, **P-2** and **P-3** are little difference because they have the same electron-deficient acceptor, whereas donors have much effect on their HOMO levels, such as 2,5-dialkoxyphenyl group (**P-1**) with strong electron-donating ability and small steric hindrance results in an obvious negative shift of the onset potential of the oxidation wave compared with 3,4-dialkoxyphenyl group (**P-2**) and 2,3-dialkoxynaphthyl group (**P-3**), and thus an increase in the HOMO level. Among the three polymers, **P-1** has the lowest band gap (1.37 eV) due to its most extended π-conjugation as demonstrated from its UV–vis absorption spectra, which is also identical to the result of density functional theory (DFT) calculations (Fig. 5). The band gaps of these BSe-based polymers can be effectively tuned by the modification of the different substituted moieties at the well-defined molecular level, which can change and control the internal charge transfer from an electron-rich moiety to an electron-deficient moiety.

Table 1
Optical and electrochemical data of **P-1**, **P-2** and **P-3**.

	UV–vis [nm]	λ_{em} (λ_{ex}) [nm]	$E_{ox}^{onset\,a}$ [eV]	HOMO[b] [eV]	$E_{red}^{onset\,a}$ [eV]	LUMO[b] [eV]	E_g[b] [eV]	HOMO[c] [eV]	LUMO[c] [eV]	E_g[c] [eV]	E_g[d] [eV]	Φ_{PL}[e]
P-1	350, 510	595 (468)	0.30	−5.10	−1.07	−3.73	1.37	−5.48	−3.10	2.38	2.10	0.08
P-2	341, 505	586 (497)	0.53	−5.33	−1.13	−3.67	1.66	−5.80	−3.15	2.65	2.12	0.04
P-3	343, 503	578 (503)	0.56	−5.36	−1.20	−3.60	1.76	−5.82	−3.06	2.76	2.15	0.11

[a] E_{ox}^{set} and E_{red}^{set} were determined from the onset potentials of the oxidation and reduction waves.

[b] HOMO energy level was calculated from the onset of oxidation wave; LUMO energy level was calculated from the onset of the first reduction wave; the energy levels were calculated by using the following equations: HOMO = $-(4.8 + E_{ox}^{onset})$, LUMO = $-(4.8 + E_{red}^{onset})$, E_g = LUMO-HOMO.

[c] DFT quantum mechanical calculations (B3LYP/6-31 + G**).

[d] E_g was calculated from the absorption of UV–vis spectra in $CHCl_3$ solution: band gap energy [eV] = 1240/wavelength [nm].

[e] Quantum yields were determined with Rhodamine B as the fluorescence reference in ethanol ($\Phi = 0.97$).

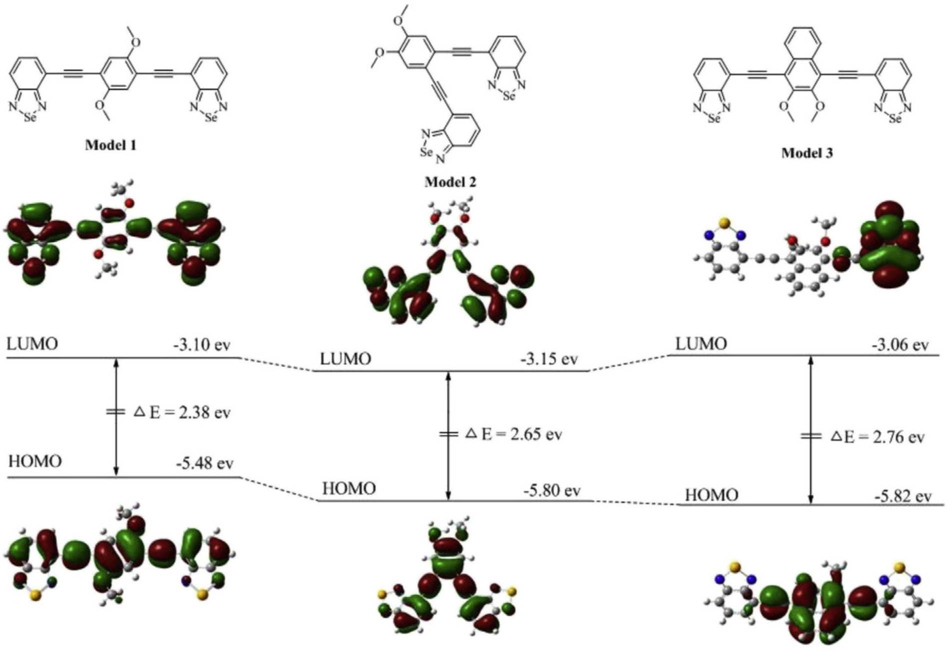


Fig. 5. Structures and molecular orbital diagrams for the LUMO and HOMO of the designed model compounds **1**, **2** and **3** from DFT calculations.

3.4. *Molecular orbital calculations*

To gain a better insight into the geometric and electronic structure, we performed theoretical calculation analysis on the model molecules **1**, **2** and **3** constituting the corresponding repeat units. All calculations were carried out with the Gaussian 03, Revision C. 02 program [42], using the B3LYP method and 6-31 + G** basis set. Herein, all the alkyl chains were replaced by methyl groups in the calculation for simplicity. Fig. 5 displays the LUMO and the HOMO of model **1**, model **2** and model **3**, and the calculated HOMO, LUMO and E_g are listed in Table 1. As shown in Fig. 5, the LUMO of the model compounds is mainly centered on the BSe core because it is an electron acceptor. In comparison with model **1** and model **2**, model **3** shows a lower HOMO level, which should be attributed to the steric effects of naphthyl group and the HOMO isosurfaces are well spread over the whole of the conjugated backbones except model **3**. Because of the strong donor–acceptor interaction between 2,5-dialkoxyphenyl and BSe unit, the HOMO-LUMO band gaps of model **1** is smaller than those of model **2** with 3,4-dialkoxyphenyl moiety and model **3** with a naphthyl segment. Further, the order of the absorption maxima of **P-1**, **P-2** and **P-3** was identical to that of the band gaps of the designed model compounds, that is, the λ_{abs} is in the order of **P-1** > **P-2** > **P-3** and the band gaps are in the order model **1** < model **2** < model **3**.

4. Conclusion

Three novel D-π-A conjugated polymers containing BSe unit and phenyl or naphthyl group *via* alkyne module were firstly synthesized by Sonogashira–Hagihara reaction. These polymers show obvious absorption peaks at the region from 503 to 510 nm due to the intramolecular charge transfer band between electron-rich aryl donors and electron-deficient BSe acceptors. These polymers can also exhibit narrow orange–red or red fluorescence (576–595 nm). The band gaps of these polymers can be tuned in the range 1.37–1.76 eV by using different aryl donor groups. These optical and electrochemical properties indicate that these polymers can be developed for excellent fluorescent materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.09.017.

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