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Novel luminescent materials based on linear-shaped polycyclic aromatic hydrocarbons

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A series of novel linear-shaped polycyclic aromatic hydrocarbons containing thiophene heterocyclic structure had been synthesized by Suzuki reaction as fluorescent materials. These novel compounds were symmetric and a certain degree of twisted structure. The molecules exhibited good thermal stabilities, fluorescence properties and good electronic transmission abilities. The compounds of 1, 4-bis(2, 5-diphenylthiophen-3-yl)benzene (BPTB) and 1, 4-bis(2, 5-di(thiophen-3-yl)thiophen-3-yl)benzene (BTTB) showed a higher decomposition temperature (T_d), but the compounds of 1, 4-bis(2, 5-diphenylthiophen-3-yl)-2-nitrobenzene (BPTNB) and 1, 4-bis(2, 5-di(thiophen-3-yl)thiophen-3-yl)-2-nitrobenzene (BTTNB) exhibited the better fluorescence properties and electronic transmission capacities.

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Keywords: Linear-shaped, Fluorescent material, Suzuki reaction, Twisted structure

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted attention due to the advantages of a high luminous efficiency, low driving voltage, fast response, wide viewing angle and so on [1-5]. OLEDs technology has been successfully used in business, for example, lighting applications and full-color displays, but designing and discovering novel emitting materials with thermal stability and excellent color for a full-color organic electroluminescent display remain a hot research direction. Compared with red or green emitting materials, the blue emitting materials still needs to be improved in many areas [6-10]. It is much more difficult to produce a blue emitter because of its intrinsic band gap and inferior blue electroluminescent.

In the past decade, although many blue electroluminescent emitter materials have been developed for OLEDs, there are still needs to being further improved. In addition, compared with polymer emitters, small molecule emitters have been paid more attention, as their simple synthesis methods and well solubility. Many small molecule emitters, including anthracene [11-13], fluorine [14, 15], pyrene [16, 17], carbazole derivatives [18-20], were reported for application in blue OLED devices.

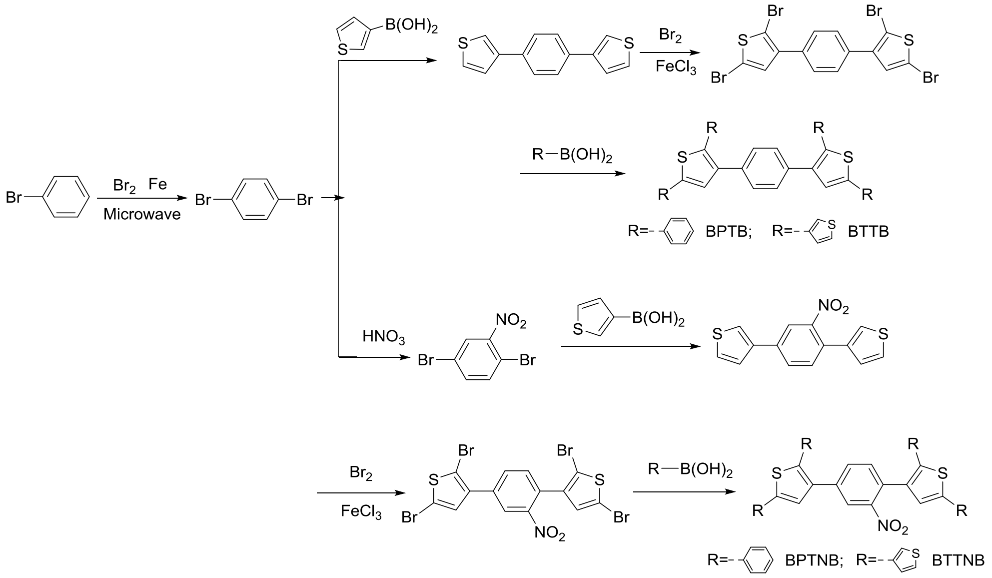
In this work, we synthesized a series of new linear-shaped Polycyclic Aromatic Hydrocarbons (PAHs) containing thiophene heterocyclic structure. These compounds owning symmetric and twisted structure exhibited strong π-electron delocalization characteristics. These small molecules exhibited high stable thermal properties and potential as host materials for blue or green luminescent emitters. Compared with the compounds of 1, 4-bis(2, 5-diphenylthiophen-3-yl)benzene (BPTB), 1, 4-bis(2, 5-di(thiophen-3-yl)thiophen-3-yl)benzene (BTTB), 1, 4-bis(2, 5-diphenylthiophen-3-yl)-2-nitrobenzene (BPTNB) and 1, 4-bis(2, 5-di(thiophen-3-yl)thiophen-3-yl)-2-nitrobenzene (BTTNB), the compounds of BPTB and BTTB showed a higher decomposition temperature (T_d), but the compounds of BPTNB and BTTNB exhibited the better fluorescence properties and electronic transmission capacities.

2. Experimental

2.1. Materials and characterization

All starting materials were purchased from TCI; the reagents were obtained from J&K Chemical Company and used without further purification. ^1H, ^{13}C NMR spectra were determined in $CDCl_3$ with a Bruker DRX 400 MHz spectrometer. Chemical shifts (d) were given relative to tetramethylsilane (TMS). The coupling constants (J) were reported in Hz. Experiment course was monitored by TLC. Column chromatography was carried out on silica gel (200

~ 300 mesh). The main synthetic routes to the PAHs are shown in Scheme 1.



Scheme 1. Synthetic route of PAHs.

2.2 Synthesis

1, 4-dibromobenzene. Bromobenzene (10.0 mL, 95.53 mmol) was poured into a 50 mL four-necked flask. Iron powders (106.7 mg, 1.91 mmol) as a catalyst was added, and the exhaust gas absorption apparatus was connected. Under a condition of microwave radiation, liquid bromine was slowly dropped. After this reaction was completed, a mixture of the reaction was poured into a dilute sodium bisulfite solution to wash away the unreacted liquid bromine; and the solid mixtures were collected by a suction filtration. The obtained solids were dissolved in hot ethanol, and iron powders in the mixtures were removed by hot filtering. After the filtrate was cooled, 1, 4-dibromobenzene (20.3 g, 90%) as white powder was afforded by filtration.

1, 4-bis(thiophen-3-yl)benzene. A mixture of 1, 4-dibromobenzene (2.0 g, 8.48 mmol), thiophen-3-yl-boronic acid (2.7 g, 21.20 mmol), Na_2PdCl_4 (49.9 mg, 169.56 μmol), K_2CO_3 (3.5 g, 25.43 mmol) and polyethylene glycol 400 (PEG400) (14.0 mL) was stirred at 80 ^{o}C for 10 h. After cooling to room temperature, the mixture was poured into water and extracted with ethyl acetate. A combined organic phase was washed with water and dried over Na_2SO_4. The subjection of the crude mixture to silica gel chromatography (eluent: petroleum ether and ethyl acetate) afforded 1, 4-di(thiophen-3-yl) benzene (1.5 g, 73%) as pale yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.64 (s, 4H), 7.48 (d, J = 1.5 Hz, 2H), 7.44–7.39 (m, 4H).

1, 4-bis(2, 5-dibromothiophen-3-yl)benzene. A mixture of 1, 4-di(thiophen-3-yl)benzene (1.5 g, 6.19 mmol), $FeCl_3{\cdot}6H_2O$ (501.7 mg, 1.86 mmol) and $CHCl_3$ (100.0 mL), CH_3COOH (50.0 mL) was well stirred and cooled to 0 ^{o}C. Then the liquid bromine (1.9 mL, 37.73 mmol) was slowly dropped and the reaction temperature was controlled under 10 ^{o}C. The reaction was monitored by TLC. After the reaction completed, the cooled mixture was poured into water and then filtered, the solid was collected and washed by the solution of $NaHSO_3$, water and ethanol in turn. 1, 4-bis(2, 5-dibromothiophen-3-yl) benzene (3.2 g, 93%) as pale yellow powder was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.57 (s, 4H), 7.06 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.34, 133.69, 131.57, 128.58, 111.48, 107.98.

1, 4-bis(2, 5-diphenylthiophen-3-yl)benzene (BPTB). A mix of 1, 4-bis(2, 5-dibromothiophen-3-yl)benzene (139.5 mg, 0.25 mmol), phenylboronic acid (182.9 mg, 1.50 mmol), Na_2PdCl_4 (1.5 mg, 5.00 μmol), K_2CO_3 (276.4 mg, 2.00 mmol) and PEG400 (4.0 mL) was stirred at 80 ^{o}C for 48 h. After cooling to room temperature, the mixture was poured into water and extracted with ethyl acetate. A combined organic phase was washed with water and dried over Na_2SO_4. The subjection of the crude mixture to silica gel chromatography (eluent: petroleum ether and ethyl acetate) afforded 1, 4-bis(2, 5-diphenyl- thiophen-3-yl) benzene (84.7 mg, 62%) as pale yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.66 (d, J = 7.3 Hz, 4H), 7.44 – 7.38 (m, 6H), 7.35 (d, J = 1.5 Hz, 4H), 7.34 – 7.27 (m, 6H), 7.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.67, 138.59, 138.09, 135.22, 134.25, 134.11, 129.18, 129.08, 128.97, 128.47, 127.66, 127.51, 126.29, 125.63.

1, 4-bis(2, 5-di(thiophen-3-yl)thiophen-3-yl) benzene (BTTB). BTTB was synthesized in a manner similar to that of BPTB. Yield: 56%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.44 – 7.41 (m, 2H), 7.37 (d, J = 2.9 Hz, 2H), 7.35 (d, J =

2.4 Hz, 6H), 7.24 (dd, J = 5.1, 2.7 Hz, 4H), 7.21 – 7.17 (m, 2H), 6.96 (dd, J = 4.9, 0.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.33, 136.80, 135.61, 135.23, 134.47, 131.90, 129.06, 127.95, 126.50, 126.24, 125.86, 125.57, 122.58, 119.66.

1, 4-dibromo-2-nitrobenzene. A mixture of 1, 4-dibromobenzene (3.0 g, 12.72 mmol), concentrated sulphuric acid (6.0 mL) with mechanical agitation was cooled at 0 °C. Then a mixture of sulphuric acid and nitric acid was dropped, the reaction temperature was maintained at 0 ~ 10 °C. After the addition, the reaction temperature was maintained at 55 °C. The reaction was monitored by TLC and stopped after the raw material was completed. The reaction mixture was poured into water, and the solids were collected by filtering. The crude products were purified by recrystallization in ethanol, and afforded 1, 4-dibromo-2-nitrobenzene (3.3 g, 92%).

1, 4-bis(thiophen-3-yl)-2-nitrobenzene. A mixture of 1, 4-dibromo-2-nitrobenzene (2.0 g, 7.12 mmol), thiophen-3-ylboronic acid (2.3 g, 17.80 mmol), Na_2PdCl_4 (41.9 mg, 142.40 μmol), K_2CO_3 (3.0 g, 21.36 mmol) and PEG400 (14.0 mL) was stirred at 80 °C for 10 h. After being cooled to room temperature, the mixture was poured into water and extracted with ethyl acetate. A combined organic phase was washed with water and dried over Na_2SO_4. The subjection of the crude mixture to silica gel chromatography (eluent: petroleum ether and ethyl acetate) afforded 1, 4-bis(thiophen-3-yl)-2-nitrobenzene (1.6 g, 78%) as pale yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.99 (s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 1.2 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.49 – 7.38 (m, 3H), 7.36 (s, 1H), 7.11 (d, J = 4.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.52, 139.47, 136.71, 136.15, 132.11, 129.65, 128.99, 127.37, 127.22, 126.26, 125.85, 123.48, 122.04, 121.52.

1, 4-bis(2, 5-dibromothiophen-3-yl)2-nitrobenzene. A mixture of 1, 4-bis(thiophen-3-yl)-2-nitrobenzene (1.6 g, 5.57 mmol), $FeCl_3 \cdot 6H_2O$ (451.4 mg, 1.67 mmol) and $CHCl_3$ (100.0 mL), CH_3COOH (50.0 mL) was well stirred and cooled to 0 °C. Then liquid bromine (1.7 mL, 33.41 mmol) was slowly dropped and the reaction temperature was controlled under 10 °C. After the raw material was almost completed by TLC monitoring, the cooled mixture was poured into water and filtered, and the solids were collected and washed by the solution of $NaHSO_3$, water and ethanol in turn. 1, 4-bis(2, 5-dibromothiophen-3-yl) 2-nitrobenzene (3.0 g, 89%) as pale yellow powder was achieved. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.20 (d, J = 1.7 Hz, 1H), 7.82 (dd, J = 8.0, 1.7 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.11 (s, 1H), 6.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.66, 138.85, 137.70, 135.56, 132.69, 132.59, 130.98, 130.84, 128.51, 124.58, 112.55, 111.89, 110.39, 109.66.

1, 4-bis(2, 5-diphenylthiophen-3-yl)-2-nitrobenzene (BPTNB). A mixture of 1, 4-bis(2, 5-dibromothiophen-3-yl)2-nitrobenzene (150.7 mg, 0.25 mmol), phenylboronic acid (182.9 mg, 1.50 mmol), Na_2PdCl_4 (1.5 mg, 5.00 μmol), K_2CO_3 (276.4 mg, 2.00 mmol) and PEG400 (4.0 mL) was stirred at 80 °C for 48 h. After being cooled to room temperature, the mixture was poured into water and extracted with ethyl acetate. A combined organic phase was washed with water and dried over Na_2SO_4. The subjection of the crude mixture to silica gel chromatography (eluent: petroleum ether and ethyl acetate) afforded 1, 4-bis(2, 5-diphenylthiophen-3-yl)-2-nitrobenzene (89.0 mg, 61%) as pale yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.89 (d, J = 1.5 Hz, 1H), 7.65 (dd, J = 13.9, 7.5 Hz, 5H), 7.48 – 7.35 (m, 9H), 7.34 – 7.30 (m, 7H), 7.24 – 7.17 (m, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 149.64, 143.62, 143.16, 139.88, 139.69, 137.06, 135.83, 133.74, 133.64, 133.52, 133.34, 133.31, 133.00, 132.86, 129.94, 129.20, 129.07, 128.96, 128.82, 128.78, 128.61, 128.17, 128.02, 127.86, 127.79, 125.71, 125.69, 125.37, 125.10, 124.38.

1, 4-bis-(2, 5-di(thiophen-3-yl)thiophen-3-yl)-2-nitro benzene (BTTNB). TBTNB was synthesized in a manner similar to that of PBTNB. Yield: 58%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.92 (d, J = 1.6 Hz, 1H), 7.51 (dd, J = 7.9, 1.7 Hz, 1H), 7.45 (d, J = 1.6 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.33 (dtd, J = 9.5, 5.0, 3.1 Hz, 5H), 7.27 (s, 1H), 7.25 – 7.20 (m, 2H), 7.10 (s, 1H), 7.01 (d, J = 1.7 Hz, 1H), 6.96 – 6.91 (m, 1H), 6.90 – 6.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.56, 137.85, 137.42, 137.25, 135.54, 134.87, 134.74, 133.63, 133.53, 133.34, 133.01, 132.96, 132.75, 130.16, 127.71, 127.39, 126.77, 126.56, 126.45, 126.02, 125.85, 125.78, 125.27, 125.11, 124.40, 123.45, 122.56, 120.14, 120.00.

3. Results and discussion

3.1. Thermal stability

The thermal properties of BPTB, BTTB, BPTNB and BTTNB were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. 1). The decomposition temperature (T_d), glass transition (T_g) and melting transition (T_m) were summarized in Table 1. The T_d is defined by a 5%-weight-loss temperature under a nitrogen atmosphere.

All of the synthesized linear-shaped symmetric PAHs were found to exhibit stable thermal properties. TGA studies showed that all the compounds exhibited good of thermal stabilities with decomposition temperatures in the range of 340 ~ 423 °C, glass transition temperature in the range of 136 ~ 236 °C. The introduction of nitro substituent resulted in a slight reduce of T_d, when being compared the compounds BPTB and BTTB with their nitro substituted compounds BPTNB and BTTNB. The reason is that the introduction of nitro substituent increased dihedral angles of the compounds, so that twisting extent of the molecules were increased, and stabilities had a slight decrease.

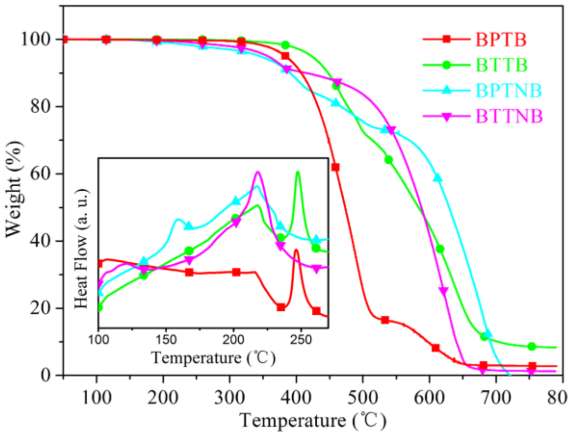


Fig. 1. TGA graphs of linear-shaped PAHs recorded at a heating rate of 10 ℃/min.

Table 1. UV absorption, PL, energy levels and thermal properties of synthesized PAHs.

compound	λ_{max} Abs (nm)	λ_{max} PL (nm)	HOMO (eV)	LUMO (eV)	E_g (eV)	T_d (^oC)	T_m (^oC)	T_g (^oC)	CIE (x, y)
BPTB	290	420	-5.27	-1.92	3.35	384	246	175	0.161, 0.082
BTTB	290	465	-5.26	-1.42	3.84	423	247	236	0.169, 0.208
BPTNB	290	529	-5.46	-2.08	3.38	344	217	171	0.282, 0.509
BTTNB	285	531	-5.47	-2.25	3.22	358	218	136	0.284, 0.529

3.2. Optical and photoluminescent characteristics

The photophysical properties of linear-shaped polyarylates were investigated by UV-vis and photoluminescence (PL) for dilute solutions as shown in Fig. 2. The UV-vis spectra of the four compounds in CH_2Cl_2 showed an almost identical absorption in 290 nm (Fig. 2 (a)), which are assigned to the π-π* absorption band of conjugated aromatic rings. The compound BPTNB and BTTNB had the wider absorption peak because of nitro substituent. As seen from Fig. 2 (b) and Fig. 3, the PL spectra in solution of the BPTB and BTTB showed the emission peak in the blue region of 420 nm and 465 nm, with CIE coordinates are (0.161, 0.082) and (0.169, 0.208) respectively. The BPTB emitted deep-blue color with CIE coordinates of x = 0.161 and y = 0.082, which is close to the National Television System Committee (NTSC) deep-blue (CIE coordinates of x = 0.14 and y = 0.08) standard [21]. And the PL spectra of the BPTNB and BTTNB in solution showed an almost identical fluorescent emission peak in the green region of 529 nm and 531 nm, with CIE coordinates are (0.282, 0.509) and (0.284, 0.529) respectively. Compared with BPTB, the emission spectra of BPTNB showed red shifts of 109 nm; compared with compounds BTTB, the emission spectra of BTTNB showed red shifts of 66 nm. The main reason may be due to the introduction of a nitro substituent which possesses strong electron withdrawing effect, improve the molecular polarity and the intramolecular electron transfer.

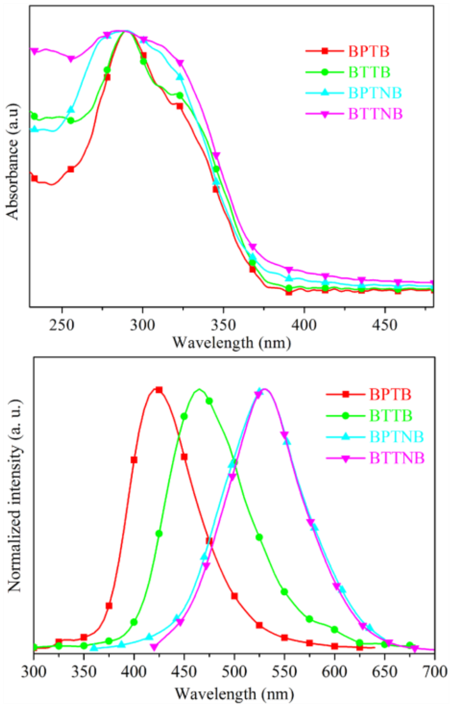


Fig. 2. (a) Room temperature UV-vis absorption spectra in CH_2Cl_2, (b) PL spectra in CH_2Cl_2 solution.

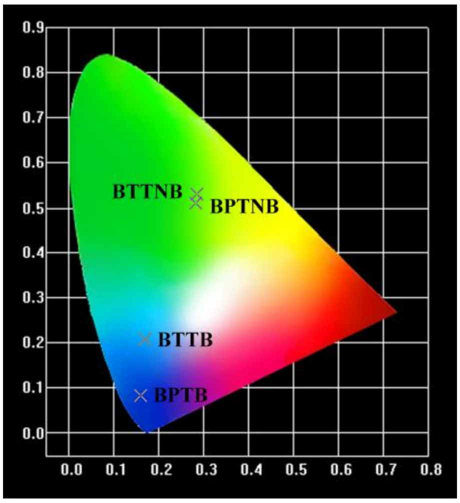


Fig. 3. The CIE coordinates of linear-shaped PAHs.

3.3. Quantum chemistry calculation

Molecular simulation of four compounds was carried out to understand the orbital distributions and energy levels at the molecular scale. The geometric and electronic properties of the compounds were obtained using the Gaussian 03 program package, shown in Fig. 4. The calculation was optimized by means of the B3LYP with the 6-31G (d) basis set. Fig. 4 showed the spatial distribution of the calculated HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital) levels of these four compounds. The HOMO and LUMO levels were all uniform distributed on the molecular BPTB and BTTB. After the introduction of nitro substituent, the HOMO was distributed on the branch of near the nitro substituent; the LUMO was distributed on the center benzene core. The reason of this phenomenon was the electron properties of the nitro substituent. The effect of the spatial distribution improved the electron transport ability of the compound. As seen from Table 1, all HOMO energies of the aryl derivatives were at about 5.26 ~ 5.47 eV, all LUMO energies were at about 1.42 ~ 2.25 eV. The HOMO-LUMO energy gaps (E_g) were at about 3.22 ~ 3.84 eV. It was found that introduction of nitro substituent resulted in increased both of HOMO and LUMO, when compared within the compound BPTB, BTTB and their nitro substituted compounds BPTNB, BTTNB. Especially the LUMO of BTTNB was obviously increased. At the same time, a higher twisting conformation might effectively suppress the more strong intermolecular interactions of their π systems and crystallinity.

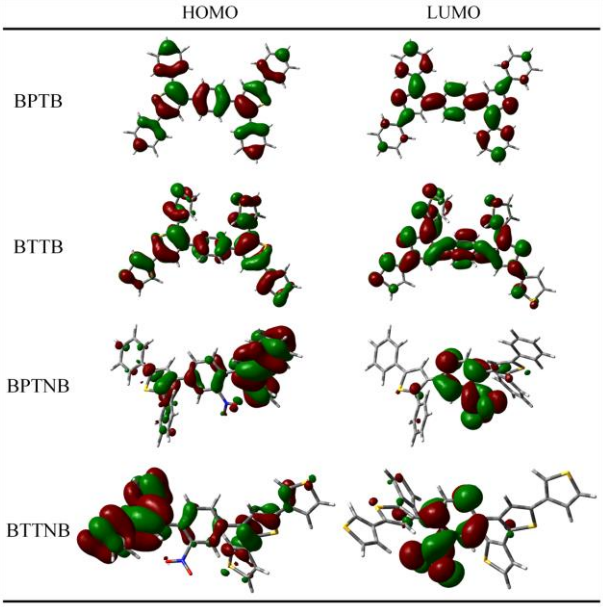


Fig. 4. HOMO and LUMO electronic density distributions of linear-shaped PAHs.

4. Conclusion

In conclusion, we synthesized four PAHs containing thiophene heterocyclic structure by Suzuki reaction, all of the synthesized linear-shaped symmetric PAHs owning luminescent properties, BPTB and BTTB exhibited good blue luminescent properties. These new compounds also exhibited good thermal stabilities with decomposition temperatures in the range of 340 ~ 423 ^{o}C. All of the compounds had good electronic transmission capacities, especially the BPTNB and BTTNB with nitro substituent. These compounds shown potential for use in the OLED field, in addition, also have good potential for use in the field of biological probe, dyes and so on.

Acknowledgments

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