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Synthesis, Characterization and Properties of Novel Star-Shaped π-Conjugated Oligomers with Triphenylamine Core

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Four new star-shaped π -conjugated oligomers (**TPA-CZ3**, **TPA-TPA3**, **TPA-PTZ3** and **TPA-BT3**) with triphenylamine as a core and different electron-donating ability groups, carbazole, triphenylamine, phenothiazine and bithiophene, as peripheral units have been designed and synthesized via the Heck reaction. These oligomers show good solubility in common organic solvents. Their photophysical, electrochemical, electronic structure and charge transfer properties between these star-shaped π -conjugated oligomers and *N*,*N*-bis(1-ethylpropyl)-3,4:9,10-perylene bis(tetracarboxyl diimide) (EP-PDI) have been investigated by UV-vis absorption spectra, photoluminescence (PL) spectra, cyclic voltammetry (CV) measurement, theoretical calculations and fluorescence quenching. The results show that the absorptions and fluorescences of **TPA-CZ3**, **TPA-TPA3** and **TPA-PTZ3** are red shifted with the electron-donating ability of the peripheral unit increasing from carbazole to triphenylamine and phenothiazine. In addition, although the bithiophene group has a weaker electron-donating ability than carbazole, triphenylamine and phenothiazine, the absorption and fluorescence of **TPA-BT3** have a red shift than those of **TPA-CZ3**, **TPA-TPA3** and **TPA-PTZ3**. The triphenylamine core and the peripheral units can constitute a large conjugated structure. The fluorescence quenching properties indicate that efficient charge transfer can happen between the star-shaped oligomers and EP-PDI.

Keywords triphenylamine, star-shaped oligomer, synthesis design, electron-donor ability, conjugation length

Introduction

Organic molecules with a large conjugated plane are a type of classic functional materials. The chromophores can be connected each other by single, double or triple bonds to form a large conjugated structure. Especially, the chromophores connected by *trans* double bonds are in the same plane and can lead to a large conjugated system. Organic molecules with a larger conjugated system usually have a narrow band gap and can absorb the sunlight in the long wavelength, which increases the probability of these materials to be utilized in solar cell.^[1]

Star-shaped triphenylamine (TPA) based π -conjugated systematic compounds are one of the most extensively studied classes of organic compounds. The TPA unit possesses a three-dimensional propeller structure that makes the TPA containing molecules exhibit an amorphous structure and good solubility. Moreover, the TPA cored compounds have high hole mobility and are widely used as hole-transporting materials in organic light-emitting diodes (OLEDs),^[2] sensitizers in dyesensitized solar cells (DSSCs)^[3] and photovoltaic cells.^[4] It has been found that the electronic energy levels and optical properties of these type molecules can be controlled by modifying the peripheral units.

Some star-shaped D- π -A structured molecules containing TPA as the core and donor unit have been designed and synthesized for the applications as solutionprocessable organic photovoltaic donor materials. In these molecules, the peripheral units are composed of acceptor units^[5] or a combination of acceptor units and π bridges^[6,7] or a combination of acceptor units and donor units.^[8] However, a systematic investigation on the

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synthesis and properties of star-shaped molecules containing TPA as a core and different electron-donating ability groups as peripheral units are still scarce.^[9,10] On the other hand, the absorption of the star-shaped molecules in which the TPA core and the peripheral units are connected by double bonds has a red shift than that of the star-shaped molecules in which the TPA core and the peripheral units are connected by single or triple bonds.^[7,11]

Carbazole, triphenylamine, phenothiazine and bithiophene are four excellent hole-transporting chromophores. Their derivatives are often used as the hole-transporting materials for organic light-emitting diodes $(OLEDs)^{[12,13]}$ and organic solar cells $(OSCs)^{[7,14]}$ due to the good hole-transporting property, high charge mobility and high thermal stability.^[10,15] Nevertheless, the electron-donating ability of these four hole-transporting chromophores are different, *i.e.* bithiophene < carbazole < triphenylamine < phenothiazine. We think that combination of the triphenylamine core with hole-transporting chromophores of different electron-donating ability to form a series of star-shaped molecules should bring about some new electrical and photophysical properties and applications.

In this present work, we designed and synthesized four new star-shaped π -conjugated oligomers with triphenylamine as a core and carbazole, triphenylamine, phenothiazine and bithiophene, as peripheral units, which are connected by trans double bonds. These oligomers show good solubility in common organic solvents. The optical, electrochemical, electronic structure and fluorescence quenching properties were investigated. The results indicate that the absorption and fluorescence of the molecules are influenced by the electron-donating ability and conjugation length of the peripheral units. The triphenylamine core and the peripheral units can constitute a large conjugated structure. The fluorescence quenching properties indicate that efficient charge transfer can happen between the starshaped oligomers and N,N'-bis(1-ethylpropyl)-3,4:9,10perylene bis(tetracarboxyl diimide) (EP-PDI).

Experimental

Materials

2-Bromothiophene, Ni(dpp)Cl₂ and methyltriphenylphosphonium bromide were purchased from Acros. Triphenylamine, carbazole and phenothiazine were obtained from Beijing Chemical Reagent Company. DMSO and POCl₃ were purchased from Beijing Chemical Plant. Palladium acetate, potassium phosphate, potassium iodide and potassium iodate were obtained from Shanghai Chemical Reagent Company. All the other chemicals and solvents were purchased from Tianjin Chemical Reagent Company. DMF was dried over anhydrous MgSO₄ for 24 h, and then obtained by vacuum distillation. CH₂Cl₂, CHCl₃ and acetonitrile were refluxed for 24 h with anhydrous CaCl₂, and then distilled under the protection of nitrogen. THF and toluene were refluxed for 24 h with sodium, and when appearing blue after added dibenzophenone, distilled under the protection of nitrogen.

Instrument

¹H NMR spectra were measured using a Bruker AVANCE-500 NMR spectrometer spectrometer and a Varian Mercury-300 NMR. The elemental analysis was carried out with an American PERKIN ELMER 2400LS II CHNS-Ovelemental analyzer. The infrared spectroscopy spectra were recorded via the KBr pellet method by using a Bruker IFS266V FTIR spectrophotometer. The mass spectra were recorded on a Kratos MALDI-TOF mass system, and the spectrum was recorded in the linear mode with anthracene-1,8,9-triol as the matrices. UV-visible absorption spectra were measured using a Shimadzu UV-3100 spectrophotometer. The photoluminescence spectra of spin-cast films and solutions were measured with an RF-5301PC fluorophotometer. Electrochemical measurements were performed with a Bioanalytical Systems BAS 100 B/W electrochemical workstation.

N-Ethylcarbazole (1) In a 100-mL round bottom flask under nitrogen, sodium hydroxide (0.18 g) was added to 60 mL of DMSO. After the solution was vigorously stirred for 30 min, carbazole (5.01 g, 30 mmol) was added. After 1 h, ethyl bromide (3.24 g, 30 mmol) was dropped into the reaction mixture slowly. The mixture was heated to reflux temperature with stirring for 12 h. The reaction mixture was condensed to remove DMSO, and then was poured into a large amount of water (150 mL) and extracted using CH_2Cl_2 (70 mL×3). The organic phase was dried over anhydrous magnesium sulfate, and then the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography using petroleum ether as the eluent to give 4.68 g of white solid with a yield of 80%.

N-Ethylcarbazole-3-carboxaldehyde (2) In a 100-mL round bottom flask, a solution of phosphorus oxychloride (3.2 mL) in DMF (10 mL) was dropped slowly into the solution of *N*-ethylcarbazole (7.8 g, 40 mmol) in DMF (60 mL). The mixture was heated for 4 h at 80 °C. After cooling to room temperature, the mixture was poured into water (150 mL), and the solution was filtered to give crude product as yellow solids. The crude product was purified by column chromatography using a cosolvent (dichloromethane/petroleum ether, 1 : 3, *V/V*) as the eluent to give 4.7 g of shallow yellow solid with a yield of 53%.

N-Ethyl-3-vinylcarbazole (3)^[16] In a 100-mL round bottom flask, methyltriphenylphosphonium bromide (4.29 g, 12 mmol) and *N*-ethylcarbazole-3-aldehyde (2.23 g, 10 mmol) were dissolved in 20 mL of freshly distilled THF, and then the flask was put in an ice-water bath and a solution of potassium *tert*-butoxide (1.68 g, 15 mmol) in THF was dropped slowly into this mixture. After the solution mixture reacted for 5 h, THF solvent was removed using a rotary evaporator. The crude product was purified by column chromatography using petroleum ether as the eluent to give 1.53 g of white solid with a yield of 69%. m.p. 66-67 °C. ¹H NMR (500 MHz CDCl₃) δ : 1.45 (m, 3H), 4.35 (m, 2H), 5.19 (d, J=11.5 Hz, 1H), 5.77 (d, J=17.5 Hz, 1H), 6.90 (m, 1H), 7.24 (m, 1H), 7.35 (d, J=8.5 Hz, 1H), 7.40 (d, J=8.5 Hz, 1H), 7.46 (t, J=8.5 Hz, 1H), 7.57 (d, J=8.5 Hz, 1H), 8.09-8.10 (m, 2H).

p-Diphenylaminobenzaldehyde (4) In a 100-mL round bottom flask, a solution of phosphorus oxychloride (3.2 mL) in DMF (10 mL) was dropped slowly into the solution of triphenylamine (9.28 g, 40 mmol) in DMF (60 mL). The mixture was reacted for 2 h at 45 °C, cooled to room temperature, poured into some water, and then the solution was filtered to give crude product as yellow solid. The crude product was purified by column chromatography using a cosolvent (dichloromethane/petroleum ether, 1 : 2, *V/V*) as the eluent to give 7.5 g of shallow yellow solid with a yield of 69%. m.p. 148–150 °C. ¹H NMR (500 MHz, CDCl₃) δ : 7.01 (d, *J*=8.5 Hz, 2H, Ar), 7.17 (m, 6H, Ar), 7.34 (m, 4H, Ar), 7.67 (d, *J*=9.5 Hz, 2H, Ar), 9.85 (s, 1H, CHO).

Vinyltriphenylamine (5) In a 100-mL round bottom flask, methyltriphenylphosphonium bromide (8.57 g, 24 mmol) and *p*-diphenylaminobenzadehyde (5.46 g, 20 mmol) were dissolved in 20 mL of freshly distilled THF, and then the flask was put in an ice-water bath and a solution of potassium tert-butoxide (3.36 g, 30 mmol) in THF was dropped slowly into this mixture. After the solution mixture was reacted for 10 h, it was poured into ice water to end the reaction. The aqueous solution was extracted with dichloromethane (20 mL \times 3), and the organic phase was dried over anhydrous magnesium sulfate and the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography using a cosolvent (dichloromethane/ petroleum ether, 1 : 1, V/V) as the eluent to give 3.74 g of white solid with a yield of 69%. ¹H NMR (500 MHz CDCl₃) δ : 5.06 (d, J=10.8 Hz, 1H), 5.53 (d, J=17.5 Hz, 1H), 6.54 (dd, J=10.8, 17.5 Hz, 1H), 6.92-7.03 (m, 10H), 7.15-7.22 (m, 4H).

N-(2-Ethyl)-phenothiazine (6)^[17] Compound 6 was synthesized in the similar method to synthesize compound 1, and carbazole was substituted with phenothiazine. The product was white solid with a yield of 85%.

9-(2-Ethyl)-phenothiazine-3-carbaldehyde (7) Compound 7 was synthesized in the similar method to synthesize compound 2, and *N*-ethylcarbazole was substituted with *N*-(2-ethyl)-phenothiazine. The product was shallow yellow solid with a yield of 56%.

3-Ethyl-9-(2-ethyl)-phenothiazine (8) Compound **8** was synthesized in the similar method to synthesize compound **3**, and *N*-ethylcarbazole-3-aldehyde was substituted with 3-aldehyde-9-(2-ethyl)-phenothiazine. The product was shallow yellow solid with a yield of 63%.

Bithiophene (9) In a 100 mL three-neck flask Grignard reagent [prepared from magnesium turnings (0.16 g, 7 mmol) and 2-bromothiophene (1.17 g, 7 mmol) in THF (40 mL) under reflux] was added dropwise to a solution of 2-bromothiophene (0.78 g, 4.0 mmol), Ni(dppp)Cl₂ (11 mg, 0.5 mol%) in THF (10 mL) under stirring at room temperature. After the mixture was refluxed for 8 h, the reaction was quenched with HCl (2 mol/L), and extracted with CH_2Cl_2 (20 mL×3). The organic phase was dried, and the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography using petroleum ether as the eluent to give 0.47 g of colorless crystal with a yield of 71%. m.p. 32-33 °C. ¹H NMR (CDCl₃, 500 MHz, TMS) δ: 7.02 (dd, J=4.8, 3.6 Hz, 2H), 7.20 (m, 4H). Anal. calcd for C₈H₆S₂: C 57.79, H 3.64; found C 57.49, H 3.54.

5-(2-Thienyl)thiophene-2-carboxaldehyde (10)In a 250 mL ampoule, bithiophene (2.087 g, 12.5 mol) was dissolved in 20 mL of THF. The solution was cooled to -80 °C and to which solution (1.6 mmol/mL, 8.63 mL, 13.8 mmol) of N-butyllithium in N-hexane was dropped. After the mixture solution was stirred for 20 min at -80 °C, 0.97 mL (12.5 mmol) of DMF was added and the ampoule was heated to room temperature. After 1 h, the reaction solution was poured into ice-water (50 mL), extracted with CH_2Cl_2 (35 mL×3). The organic phase was dried over anhydrous magnesium sulfate and the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography using a cosolvent (petroleum ether/ dichloromethane, 10: 1, V/V) as the eluent to give 2.09 g of colorless solid with a yield of 86%. ¹H NMR $(CDCl_3, 500 \text{ MHz}, TMS) \delta$: 7.08 (t, J=9.0 Hz, 1H), 7.25 (d, J=4.0 Hz, 1H), 7.36 (s, 1H), 7.37 (s, 1H), 7.67 (d, J = 4.0 Hz, 1H), 9.86 (s, 1H). Anal. calcd for C₉H₆OS₂: C 55.64, H 3.11; found C 55.59, H 3.14.

2-(2-Thienyl)-5-vinylthiophene (11) Compound **11** was synthesized in the similar method to synthesize compound **3**, and *N*-ethylcarbazole-3-aldehyde was substituted with 5-(2-thienyl)thiophene-2-carboxaldehyde. The product was colorless liquid with a yield of 57%. ¹H NMR (CDCl₃, 500MHz, TMS) δ : 5.13 (d, *J*= 11.0 Hz, 1H), 5.53 (d, *J*=17.0 Hz, 1H), 6.75-6.78 (dd, *J*=11.0, 17.5 Hz, 1H), 6.84 (d, *J*=3.5 Hz, 1H), 6.96 (t, *J*=8.5 Hz, 1H), 7.00 (d, *J*=3.5 Hz, 1H), 7.14 (d, *J*= 3.5 Hz, 1H), 7.18 (d, *J*=5.0 Hz 1H). Anal. calcd for C₁₀H₈S₂: C 62.46, H 4.19; found C 62.50, H 4.14.

Tris-(4-iodophenyl)amine (12) 30 mL of glacial acetic acid was added to a mixture of triphenylamine (2.45 g, 10 mmol) and potassium iodide (3.4 g, 100 mmol). The reaction mixture was refluxed under argon until a clear, yellow solution was obtained. KIO₃ (2.4 g, 11 mmol) was added in small portions, and the mixture was refluxed to colorless. Thereafter 20 mL of NaSO₃ solution (5 *w*%) was added to precipitate the white crude product. The residue was filtered off and chromatographed on silica gel column (ethyl acetate/petro-

leumether=1:15, V/V) to produce 4.95 g ivory-white solid of tris-(4-iodophenyl)amine with a yield of 79%. ¹H NMR (CDCl₃, 500 MHz, TMS) δ : 6.80 (d, J=8.5 Hz, 6H), 7.53 (d, J=9.0 Hz, 6H). Anal. calcd for C₁₈H₁₂I₃N: C 34.70, H 1.94, N 2.25; found C 34.69, H 1.94, N 2.23.

General procedure for synthesis of the star-shaped oligomers

Tris-(4-iodophenyl)amine (4 mmol), vinyl derivatives (16 mmol), K_3PO_4 (18 mmol) and palladium acetate (0.24 mmol) were added to a round-bottom flask, and then 2 mL DMAC was added. The mixture was reacted for 24 h at 110 °C under the protection of N₂, then cooled to room temperature. Thereafter some water was added to precipitate the solid. The residue was filtered off and chromatographed on silica gel column (petroleumether/dichloromethane = 1 : 3, *V/V*) to produce the compound.

TPA-CZ3 Shallow yellow solid with a yield of 44%, m.p. 118 °C. ¹H NMR (CDCl₃, 500 MHz, TMS) δ : 1.45 (m, 9H), 4.37 (m, 6H), 7.17 (m, 9H), 7.26 (m, 6H), 7.40 (t, *J*=16.0 Hz, 6H), 7.48 (t, *J*=16.5 Hz, 9H), 7.68 (d, *J*=8.5 Hz, 3H), 8.13 (d, *J*=7.5 Hz, 3H), 8.23 (d, 3H). MALDI/TOF MS calcd for C₆₆H₅₄N₄ 902.4, found 903.3. Anal. calcd for C₆₆H₅₄N₄: C 87.77, H 6.03, N 6.20; found C 87.68, H 6.12, N 6.21.

TPA-TPA3 Yellow solid with a yield of 47%, m.p. 173 °C. ¹H NMR (CDCl₃, 500 MHz, TMS) δ : 6.97 (s, 6H), 7.04 (m, 12H), 7.08–7.12 (m, 18H), 7.26 (m, 12H), 7.38 (m, 12H). MALDI/TOF MS calcd for C₇₈H₆₀N₄ 1052.5, found 1053.3. Anal. calcd for C₇₈H₆₀N₄: C 88.94, H 5.74, N 5.32; found C 88.99, H 5.78, N 5.23.

TPA-PTZ3 Yellow solid with a yield of 38%, m.p. 123 °C. ¹H NMR (CDCl₃, 500 MHz, TMS) δ : 1.43 (m, 9H), 3.93 (m, 6H), 6.968–6.929 (m, 15H), 7.091 (m, 6H), 7.15 (m, 6H), 7.28 (m, 6H), 7.37 (d, *J*=8.5 Hz, 6H). MALDI/TOF MS calcd for C₆₆H₅₄N₄S₃ 998.4, found 999.2. Anal. calcd for C₆₆H₅₄N₄S₃: C 79.32, H 5.45, N 5.61; found C 79.39, H 5.44, N 5.55.

TPA-BT3 Orange solid with a yield of 39%, m.p. 110 °C. ¹H NMR (CDCl₃, 500 MHz, TMS) δ : 6.86 (d, J=16.0 Hz, 3H), 6.94 (d, J=3.5 Hz, 3H), 7.02-7.04 (m, 3H), 7.07-7.11 (m, 12H), 7.18 (d, J=3.0 Hz, 3H), 7.22 (d, J=5.0 Hz, 3H), 7.37 (m, 6H). MALDI/TOF MS calcd for C₄₈H₃₃NS₆ 815.1, found 815.6. Anal. calcd for C₄₈H₃₃NS₆: C 70.64, H 4.08, N 1.72; found C 70.65, H 4.99, N 1.73.

Results and Discussion

Synthesis and characterization

The general synthetic routes toward the intermediates and oligomers are shown in Scheme 1 and Scheme 2. The intermediates carbazole aldehyde (2), triphenylamine aldehyde (4) and phenothiazine aldehyde (7) were synthesized by Vilsmeier reaction, and phosphorus oxychloride and DMF acted as the acylating agent. Bithiophene aldehyde (10) was synthesized by using *n*-butyllithium and DMF as the acylating agent, and the key to success lies in the control of the anhydrous and anaerobic conditions. The vinylation synthesis reaction adopted Wittig reaction. In these processes, it was important to seriously control the reaction temperature and dropping rate of the reactants.

The star-shaped oligomers, **TPA-CZ3**, **TPA-TPA3**, **TPA-PTZ3** and **TPA-BT3**, were synthesized by palladium-catalyzed Heck reaction and the *trans* double bond of the molecules were characterized by infrared spectroscopy. The typical absorption peak for *trans* double bond is located at $980-965 \text{ cm}^{-1}$, and the four molecules have obvious absorption at around 960 cm⁻¹, which indicates the double bonds in the molecules adopt a *trans* structure. Furthermore, the structures of the oligomers were also confirmed by NMR and mass spectrometry. The four star-shaped oligomers are soluble in common organic solvents, such as CH₂Cl₂, THF and DMF.

Optical properties

Figure 1 shows the normalized UV-vis absorption and photoluminescence (PL) spectra of the four starshaped oligomers in dilute CH_2Cl_2 solution (10⁻⁶ mol/L). The relevant spectroscopic data of these oligomers in CH₂Cl₂ solution are summarized in Table 1. For the UV-Vis absorption spectra, all the four oligomers display multiple absorption bands. The ca. 300 nm relatively weak absorption band can be assigned to the π - π * transition of the oligomers, while the ca. 400 nm strong absorption band arises from the intramolecular charge transfer (ICT) transition between the triphenvlamine core and the peripheral groups. For TPA-CZ3, TPA-**TPA3** and **TPA-PTZ3**, their absorption and PL spectra are red shifted with the electron-donating ability of the peripheral units increasing from carbazole to triphenylamine and phenothiazine. Specially, for the oligomer **TPA-BT3**, although the bithiophene group has a weaker electron-donating ability than the other three groups, the absorption and PL spectra of TPA-BT3 have a red shift than those of the other three star-shaped oligomers, TPA-CZ3, TPA-TPA3 and TPA-PTZ3. We think the reason for this phenomenon is that TPA-BT3 has a longer conjugation length than TPA-CZ3, TPA-TPA3 and TPA-PTZ3 because the conjugated unit for the latter three star-shaped oligomers is stilbene, but for TPA-BT3 the conjugated unit is styrene-thiophene. On the other hand, the absorption of TPA-BT3 has a red shift compared with that of the star-shaped molecule in which the TPA core and the peripheral units are connected by single bonds.^[13]

Figure 2 shows the normalized UV-vis absorption and PL spectra of the four star-shaped oligomers in thin solid films. The relevant spectroscopic data are summarized in Table 1. The absorption and fluorescence behavior of the molecules in the solid films is similar to

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Scheme 1 Synthetic route to the intermediates



Scheme 2 Synthetic route to the star-shaped oligomers



those in solution, except for several nanometers of red shift due to the aggregation effect. The phenomenon that the UV-vis absorption and PL spectra in solid films have a red shift compared with those in solution indicates that these star-shaped oligomers tend to arrange in a direction parallel to the substrate, and this arrangement can enhance the solar absorption in the longer wavelength and the charge carrier transport in the direction perpendicular to the substrate.^[18] These properties make these star-shaped oligomers have the potential application in solar cells.

Electrochemical properties

The electrochemical characteristics of **TPA-CZ3**, **TPA-TPA3**, **TPA-PTZ3** and **TPA-BT3** were investigated by cyclic voltammetry (CV) in anhydrous ace-



Figure 1 Normalized absorption (a) and photoluminescence (PL) (excited at 365 nm) (b) spectra of the star-shaped oligomers in dilute dichloromethane solution $(1 \times 10^{-6} \text{ mol/L})$.



Figure 2 Normalized absorption (a) and PL (excited at 365 nm) (b) spectra of the star-shaped oligomers in thin solid film.

Compound	$\lambda_{\max}^{abs,sol}/nm, \varepsilon_{\max}/(mol^{-1} \cdot L \cdot cm^{-1})$	$\lambda_{\max}^{em,sol}/nm$	$\lambda_{\rm max}{}^{\rm abs, film}/{\rm nm}$	$\lambda_{\max}^{em, film}/nm$
TPA-CZ3	399, 94680	463	402	485
TPA-TPA3	409, 98330	469	413	496
TPA-PTZ3	417, 93940	499	426	516
TPA-BT3	434, 131600	513	442	519

 Table 1
 Optical properties of the four star-shaped oligomers

tonitrile, using a platinum button as working electrode, a platinum wire as counter electrode, an Ag/AgNO₃ as reference electrode, and tetrabutylammonium perchlorate (0.1 mol/L) as supporting electrolyte. Ferrocene was used as the internal standard and showed a peak at +0.13 V versus Ag/Ag⁺. During the anodic scan, all the four star-shaped oligomers exhibit quasireversible oxidation waves (see Figure 3). From the onset oxidation potential (E_{ox}^{onset}) and the onset reduction potential (E_{red}^{onset}) of the molecules, the HOMO and LUMO energy levels as well as the electrochemical energy band gap ($E_{g,El}$) can be calculated according to the following equations:

$$E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.67) \text{ eV}$$

 $E_{\text{LUMO}} = -(E_{\text{red}}^{\text{onset}} + 4.67) \text{ eV}$

$$E_{g}$$
=ELUMO-EHOMO

The electrochemical parameters are summarized in Table 2. The electron-donating ability of the four peripheral units is as follows: bithiophene<carbazole< triphenylamine<phenothiazine, so the onset oxidation potentials of **TPA-CZ3**, **TPA-TPA3** and **TPA-BT3** arise from the triphenylamine group and are nearly identical. However, as for **TPA-PTZ3**, the onset oxidation potential is attributed to the phenothiazine group. Because the electron-donating ability of phenothiazine group is strong than that of triphenylamine group, the onset oxidation potential of **TPA-PTZ3** is smaller than those of the other three star-shaped oligomers.



Figure 3 Cyclic voltammetry curves of the star-shaped oligomers film on platinum electrode in 0.1 mol/L acetonitrile solution of tetrabutylammonium perchlorate at a scan rate of 100 mV/s.

2.57

gomers						
Compound	$E_{\rm ox}^{\rm onset}$ /	$E_{\rm red}^{\rm onset}$ /	HOMO/	LOMO/	$E_{\rm g,EL}$	Eg,Opt b/
Compound	V	V	eV	eV	eV	eV
TPA-CZ3	0.38	_	-5.05	-2.35 ^a	_	2.70
ТРА-ТРАЗ	0.30	_	-4.97	-2.31^{a}	_	2.66

-4.86

-2.29

Table 2 Electrochemical properties of the four star-shaped oli-

TPA-BT3 0.33 –2.15 –5.00 –2.58 2.48 2.42 ^{*a*} LUMO energy levels obtained by HOMO+ $E_{g,Opt}$. ^{*b*} $E_{g,Opt}$ values were calculated from the absorption band edge of the molecule films, $E_{g,Opt} = 1240 \lambda_{edge}$.

Theoretical calculation

0.19

TPA-PTZ3

The ground-state geometry and electron-state-density distribution of the HOMO and LUMO energy levels of **TPA-BT3**, **TPA-CZ3**, **TPA-PTZ3** and **TPA-TPA3** have been fully optimized using density functional theory (DFT) based on the B3LYP method with a 6-31G* basis in Gaussian 03 program package. The HOMO and LUMO pictograms and corresponding energy levels for the four star-shaped oligomers are presented in Figure 4. The calculation results demonstrate that the three phenyls of the triphenylamine core and adjacent aromatic rings of the peripheral units constitute a large conjugated planar structure, respectively. The HOMO energy levels of the four star-shaped oligomers distribute



Figure 4 HOMO and LUMO pictograms and corresponding energy levels of TPA-CZ3, TPA-TPA3, TPA-PTZ3 and TPA-BT3 obtained at B3LYP/6-31G* level.

mainly on the centered triphenylamine core with some extending to the adjacent aromatic rings of the peripheral units. As for the LUMO energy levels, they are two quasidegenerate virtual orbitals for each oligomer. Moreover, they distribute mainly on the part of the peripheral units close to the triphenylamine core with some extending to the triphenylamine core. Distinguishingly, **TPA-BT3** shows better delocalization of electron density, which should arise from the longer conjugation length than the other oligomers. In general, the theoretical HOMO energy levels of these oligomers are consistent with those obtained from electrochemical measurement, and the theoretical band gaps agree with their optical band gaps. The LUMO energy levels exhibit some bias. The differences between the theoretical and electrochemical and optical values are a wellknown consequence of performing calculations that lack medium-related factors.

Fluorescence quenching properties

Based on the optical and electrochemical properties of the four star-shaped oligomers, an energy level diagram of the star-shaped oligomers and EP-PDI is presented in Figure 5. It can be seen that all the four molecules have an energy level matching relationship of electron donor-acceptor with EP-PDI, which indicates that the excimer can dissociate efficiently at the interface of the donor and acceptor. PL quenching in donoracceptor composites is a useful indication for the efficient charge transfer between the two components.^[19] Figure 6 shows the PL spectra of four star-shaped oligomers : EP-PDI composite solutions with different concentrations of EP-PDI. The concentration of the star-shaped oligomers are 5×10^{-2} mol/L, and the mole blend ratio between the star-shaped oligomers and EP-PDI ranges from 10:1 to 10:50. It can be seen that the PL of the star-shaped oligomers are gradually quenched with the concentration of EP-PDI increasing, and when the mole blend ratio is 10:50, most of the PL of the star-shaped oligomers are quenched. The observation obviously indicates that efficient charge transfer can happen between the star-shaped oligomers and EP-PDI.



Figure 5 Energy diagram of the star-shaped oligomers and EP-PDI.

Conclusions

Four novel star-shaped π -conjugated oligomers consisting of triphenylamine as a core and different electron-donating ability groups, carbazole, triphenylamine, phenothiazine and bithiophene, as peripheral units have



Figure 6 PL spectra of the four star-shaped oligomers : EP-PDI composite solutions with different concentrations of EP-PDI (the concentration of oligomers is constant: 5×10^{-2} mol/L, and the blend ratio is molar ratio).

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been synthesized via the Heck reaction. These oligomers exhibit good solubility in common organic solvents. Their photophysical, electrochemical and PL quenching properties were investigated. The results show that the absorption and fluorescence of these starshaped π -conjugated oligomers can be tuned through changing the electron-donating ability and conjugation length of the peripheral units. The triphenylamine core and the peripheral units can constitute a large conjugated structure. The fluorescence quenching properties confirm that efficient charge transfer can happen between the star-shaped oligomers and EP-PDI.

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