



Novel planar and star-shaped molecules: Synthesis, electrochemical and photophysical properties

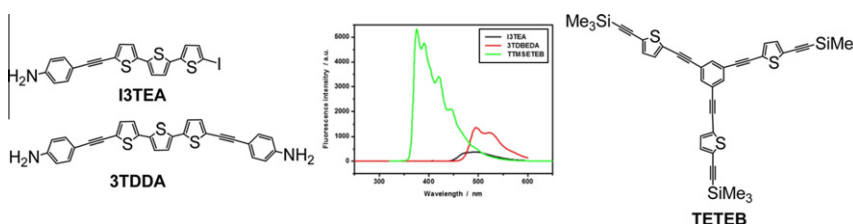
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HIGHLIGHTS

- ▶ Three novel materials **I3TEA**, **3TDDA** and **TETEB** were successfully synthesized.
- ▶ Their optical and electrochemical properties were investigated.
- ▶ The compounds were promising candidates for photovoltaic materials.

GRAPHICAL ABSTRACT



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ABSTRACT

Three novel planar and star-shaped molecules containing thiophene-functionalized group and acetylenic spacers, 4-((5'-iodo-[2,2':5',2''-terthiophen]-5-yl)ethynyl)aniline (**I3TEA**), 4,4'-([2,2':5',2''-terthiophene]-5,5''-diylbis(ethyne-2,1-diyl))dianiline (**3TDDA**), 1,3,5-tris((5-((trimethylsilyl)ethynyl)thiophen-2-yl)ethynyl)benzene (**TETEB**) were synthesized through Sonogashira coupling reaction. Their photophysical and electrochemical properties were explored by UV-vis, photoluminescence (PL) emission and DFT calculation. Three compounds possess unusual phenomena of PL, with the concentration of gradually decreased, the intensity of PL firstly increased and then decreased, this may be due to the aggregate-enhanced emission (AEE) effect and aggregation-caused quenching (ACQ) effect. Their spectroscopic data demonstrate that D- π -A- π -D structured organic dye **3TDDA** based on NH_2 as donor units and 3T as acceptor units with acetylenic spacers π -conjugated chain between them exhibits good luminescent properties. Dye **I3TEA** with donor(D)-acceptor(A) structure shows good charge transfer because of amino functional group and iodine atom. Octupolar organic π -conjugated star-shaped molecule **TETEB** possesses excellent luminescent properties because of its unique structure applied in the optoelectronic field. The redox curves and results of DFT calculations suggest that three compounds have low ionization potential and low E_{oxd} . All the good properties demonstrate three compounds could be promising candidates for photovoltaic materials.

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Introduction

Acetylenic-based conjugated polymers or oligomers have drawn much attention of a great many researchers due to their wide applications in photovoltaic devices [1–10]. Researchers are interested in an increase of the open circuit voltage, which is defined as the quasi-Fermi level splitting between the donor HOMO and the acceptor LUMO. However, this specific electronic parameter is involved in solar cells because of the electron-withdrawing

nature of the $\text{C}\equiv\text{C}$ group leading to an enhanced electron affinity, and consequently to a higher oxidation potential and a lower HOMO level [1–3,11–13]. Therefore, the materials of this kind used as donors may provide a new route to improve photovoltaic device performances. Recently, a large number of small molecules based photovoltaic devices have attracted much attention in bulk heterojunction solar cells attributed to their reproducible preparation, facile purification and easy functionalization [14–19]. The concept of heterojunction has already been exploited in dye-dye, polymer-dye, polymer-polymer and polymer-fullerene blend photovoltaic devices on a large scale [20–23]. In parallel, donor-acceptor π -conjugated polymers or oligomers are explored as active materials

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widely applied in the field of organic solar cells [24–27]. The design of the class of this material has two main purposes. One is to reduce the band gap of the molecule for broadening the range of absorption and the other is to study the relationship between different donor/acceptor chromophores and their corresponding properties of photophysics, electrochemistry, optics and electronics [14,28–32]. Ultimately, thiophene-based materials have attracted a great deal of attention for their potential applications in the fields of organic semiconductors due to their light weight, good chemical stability, high carrier mobility and the ease of structural tuning to adjust the optical, electronic and morphological properties for the time being [33–36]. It has been reported that oligothiophenes end-capped with strong electron donors as diphenylaminofluorenyl moieties have become highly efficient hole-transporting bis-dipolar emitters for organic light emitting diodes (OLEDs) [37].

At the same time, a large number of researchers also have drawn great interests in octupolar organic π -conjugated dendrimers containing C–C triple bonds facilitated electronic communication because of their novel structures, unique properties and unusually narrow band gaps in organic optoelectronic field [38,39]. More fascinating octupolar star-shaped molecules have continued to receive much attention due to their potential application as a kind of novel π -electronic material. Currently, the materials of this kind have been used as electron-transporting and light emitting layers in the fabrication of highly efficient electroluminescence (EL) devices. Great efforts have been made to design and synthesize more fascinating octupolar star-shaped molecules and to study their structure–property relationships in the recent years [40–43]. It is obvious that the polymers have been found to exhibit excellent photoluminescence (PL) and electroluminescence (EL) properties, so they have been widely used as light-emitting diodes, photovoltaic cells and even field effect transistors [44–46]. The selection of novel core structure is the key factor for the rational design of an optoelectronic molecule due to its crucial

properties dependence. Up to now, some of C_3 -symmetric functionalized groups have been used to build star-shaped molecules [47–58], but the total number is not much. By reason of what we said above, the incorporation of arylene ethynylene structural motifs into π -conjugated compounds is expected to render them more interesting and desirable properties and hence is of great interest to us.

In this paper, we synthesized two novel planar molecules 4-((5'-iodo-[2,2':5',2''-terthiophen]-5-yl)ethynyl)aniline (**I3TEA**), 4,4'-([2,2':5',2''-terthiophene]-5,5''-diylbis(ethyne-2,1-diyl))dianiline (**3TDDA**) and one octupolar organic π -conjugated star-shaped molecule 1,3,5-tris((5-((trimethylsilyl)ethynyl)thiophen-2-yl)ethynyl)benzene (**TETEB**) containing thiophene-functionalized group and acetylenic spacers. Their structures are shown in Fig. 1. All the objective compounds were successfully characterized with respect to UV–vis absorption spectroscopy, photoluminescence (PL) emission spectroscopy, density functional theory (DFT) calculation and cyclic voltammetry (CV). Three compounds display narrow band gaps and a slight aggregation induced emission (AIE) effect. D- π -A- π -D structured organic dye **3TDDA** based on NH_2 as donor units and 3T as acceptor units with acetylenic spacers π -conjugated chain between them possesses good luminescent properties. Dye **I3TEA** with donor(D)–acceptor(A) structure shows weak fluorescence intensity in comparison with dye **3TDDA** due to the presence of iodine. Polymer **TETEB** exhibits excellent luminescent properties probably applied in the optoelectronic field.

Experimental

Measurements and characterizations

1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 NMR Spectrometer with $DMSO-d_6$ and $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal reference. Infrared measurements with the KBr pellet technique were performed within the 4000 – 400 cm^{-1} region on a Bruker ALPHA FT-IR spectrometer. LC-MS were obtained from Agilent 6510 Accurate-Mass Q-TOF LC/MS system. Ultraviolet absorption (UV) spectra of these samples were recorded using a Hitachi U-4100 spectrometer. Photoluminescence (PL) measurements were recorded on a Hitachi F-4500 fluorescence spectrophotometer with a 150 W Xe lamp. Cyclic voltammetry (CV) measurement was performed on a CHI800 electrochemical instrument with a three-electrode cell in a solution of 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) in anhydrous chloroform at room temperature under nitrogen atmosphere with a scan rate of 100 mV/s. The working electrode was glass–carbon electrode, the counter electrode was a platinum wire, and the reference electrode was Ag/AgCl (Ag in 0.1 M $AgNO_3$ solution of MeCN) which was separated by a diaphragm. Ferrocene–ferrocenium (Fc/Fc^+) couple was chosen as internal standard. Thin-layer chromatography (TLC) was carried out with silica gel GF254 covered on plastic sheets and visualized by UV light, and flash column chromatographic separation was performed over silica gel.

Materials

2-Bromothiophene and 2,5-dibromothiophene were purchased from the China Medicine Shanghai Chemical Reagent Corp, China. All other chemicals were purchased from Aldrich and Acros and used as received without further purification. 4-Ethynylaniline [59], *N*-iodosuccinimide (**NIS**) [60], 2,2':5',2''-terthiophene (**3T**) [61], lithium diisopropylamide (**LDA**) [62] and trimethyl(thiophen-2-ylethynyl)silane [63] (**2**) were prepared according to the published procedures. Catalysts $Pd(PPh_3)_2Cl_2$ [64] and $Ni(dppp)Cl_2$ [65] were prepared from $PdCl_2$ and $NiCl_2 \cdot 6H_2O$ according to the

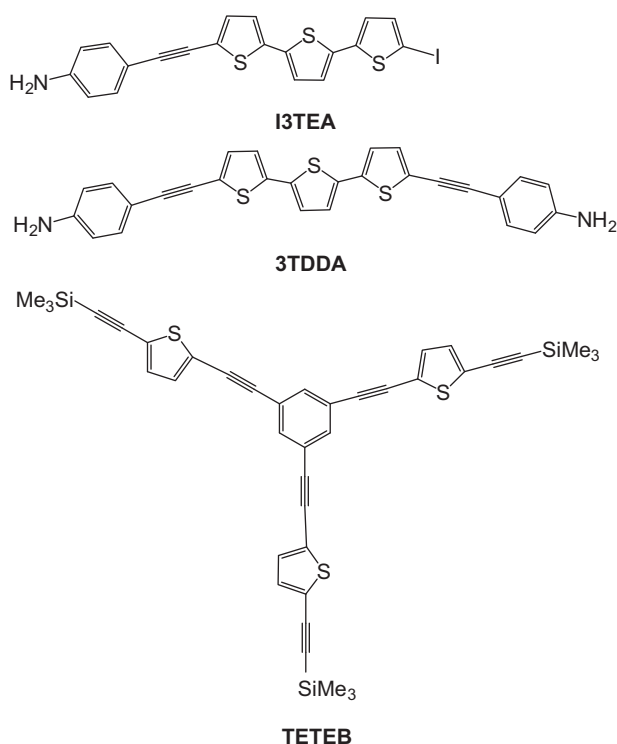


Fig. 1. The structures of compounds **I3TEA**, **3TDDA** and **TETEB**.

published literatures, respectively. Solvents were purified and dried according to the standard procedures.

Synthesis

Synthesis of ((5-iodothiophen-2-yl)ethynyl)trimethylsilane (**2**)

To a solution of diisopropylamine (3.4 g, 33.8 mmol) in diethyl ether (20 mL) at -78°C was added dropwise *n*-butyllithium (19.4 mL, 31.0 mmol, 1.60 M in hexane), and then stirred at -78°C for 15 min. The mixture was warmed to 0°C for 30 min and then re-cooled to -78°C . Trimethyl(thiophen-2-ylethynyl)silane (**1**) (2.8 g, 15.5 mmol) in diethyl ether (10 mL) at room temperature was then added dropwise to the LDA solution, and the solution was warmed from -78 to 0°C for 15 min. After re-cooling to -78°C , iodine (8.6 g, 33.8 mmol) in diethyl ether (60 mL) was added via cannula, and the solution was then warmed to room temperature and stirred overnight. The mixture was quenched with water, and the aqueous layer was extracted with diethyl ether. The combined organic layer was washed with brine and aqueous sodium thiosulfate, and then dried over magnesium sulfate. The solvent was removed under vacuum, and the crude product was purified by silica column chromatography eluting with petroleum ether to afford compound ((5-iodothiophen-2-yl)ethynyl)trimethylsilane [65] (**2**) (4.3 g, 90%) as a yellow liquid. The product was used instantly for the next step without further purification.

Synthesis of 1,3,5-triethynylbenzene (**4**)

The procedure was modified following the Sonogashira coupling protocol. 1,3,5-Tribromobenzene (31.5 g, 100 mmol) was dissolved in dry triethylamine (250 mL) under an atmosphere of nitrogen. Copper(I) iodide (191 mg, 1.0 mmol), dichlorobis(dibenzonitrile)palladium(II) (192 mg, 0.5 mmol) were added to the stirred solution. After addition of 2-methyl-3-butyn-2-ol (12.6 g, 150 mmol) in drops, the reaction mixture was refluxed for 12 h under nitrogen atmosphere. At the room temperature, the formed precipitate of triethylamine hydroiodide was filtered off and washed with diethyl ether (3×50 mL). The combined filtrates were dried over anhydrous Na_2SO_4 and evaporated to have the crude product. Re-crystallization of this crude product in 20 mL of ethanol at -20°C delivered white crystals of 2,2',2''-(benzene-1,3,5-triyltris(ethyne-2,1-diyl))tris(propan-2-ol) (**3**) (30.8 g, 95%). The hydrolysis of compound **3** was carried out by treatment with KOH (19.2 g) and toluene 150 mL under stirring at 110°C for 8 h. A standard work-up procedure involving evaporation of the organic solvent, extraction of the residue with diethyl ether, drying over Na_2SO_4 , and removal of the solvent under reduced pressure yielded 1,3,5-triethynylbenzene [66] (**4**) (13.0 g, 92%) as colorless needle crystals. m.p. $95.4\text{--}96.0^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3 , ppm) δ 3.10 (s, 3H), 7.57 (s, 3H).

Synthesis of 5,5''-diiodo-2,2':5',2''-terthiophene (**5**)

2,2':5',2''-Terthiophene (**3T**) (5.0 g, 20.2 mmol) and **NIS** (9.9 g, 44.5 mmol) were dissolved in a mixture of dry dichloromethane (50 mL) and glacial AcOH (50 mL). The mixture was shielded from light and stirred for 4 h at room temperature. Solvents were removed by evaporation. The residue was dissolved in 20 mL of mixture of dichloromethane and pentane (V:V = 3:1). Crystallization at -20°C gave rise to yellow crystals of 5,5''-diiodo-2,2':5',2''-terthiophene [67] (**5**) (8.5 g, 84%). The product was used instantly for the next step without further purification.

Synthesis of 4-((5''-iodo-[2,2':5',2''-terthiophen]-5-yl)ethynyl)aniline (**13TEA**)

Following the Sonogashira coupling procedure, 5,5''-diiodo-2,2':5',2''-terthiophene (**5**) (5.0 g, 10.0 mmol) was dissolved in dry

triethylamine (40 mL) and dry THF (50 mL) under an atmosphere of nitrogen. Copper(I) iodide (33.4 mg, 0.2 mmol), triphenylphosphine (46.7 mg, 0.2 mmol) and dichlorobis(triphenylphosphine)palladium(II) (66.9 mg, 0.07 mmol) were added to the stirred solution. 4-Ethynylaniline (1.2 g, 10.0 mmol) was dropped in and the mixture was heated to 50°C for 6 h. After cooling, the formed precipitate of triethylamine hydroiodide was filtered off and washed with diethyl ether. The combined filtrates were evaporated under reduced pressure, and the crude product was purified by silica column chromatography eluting with petroleum ether/ethyl acetate (V:V = 5:1) to afford compound **13TEA** (2.1 g, 42%) as an orange powder. m.p. $143\text{--}145^{\circ}\text{C}$; IR (KBr, cm^{-1}) ν 3411, 3332, 2923, 2188, 1600, 1514, 1461, 1377, 1282, 1176, 1067, 1015, 944, 829, 790, 533, 473; ^1H NMR (300 MHz, $\text{DMSO}-d_6$, ppm) δ 5.65 (s, 2H), 6.56 (d, $J = 8.7$ Hz, 2H), 7.08 (d, $J = 3.6$ Hz, 1H), 7.20 (d, $J = 8.7$ Hz, 2H), 7.23 (d, $J = 3.9$ Hz, 1H), 7.27–7.34 (m, 4H); ^{13}C NMR (75 MHz, DMSO , ppm) δ 79.0, 79.4, 107.8, 114.2, 122.9, 125.0, 125.1, 125.5, 126.1, 126.6, 132.8, 133.0, 135.1, 135.4, 136.7, 138.5, 141.9, 150.2.

Synthesis of 4,4'-([2,2':5',2''-terthiophene]-5,5''-diylbis(ethyne-2,1-diyl))dianiline (**3TDDA**)

Compound **3TDDA** was synthesized from 5,5''-diiodo-2,2':5',2''-terthiophene (**5**) (5.0 g, 10.0 mmol) and 4-ethynylaniline (2.3 g, 20.0 mmol) by the same procedure as compound **13TEA**. The crude product was purified by silica column chromatography eluting with petroleum ether/ethyl acetate (V:V = 3:1) to afford compound **3TDDA** (3.1 g, 64%) as an orange powder; IR (KBr, cm^{-1}) ν 3433, 3356, 2193, 1897, 1728, 1609, 1516, 1484, 1416, 1271, 1172, 1111, 1051, 960, 866, 830, 778, 621, 521, 475, 396; ^1H NMR (300 MHz, CDCl_3 , ppm) δ 3.68 (s, 1H), 3.85 (s, 2H), 4.10 (s, 1H), 6.47 (dd, $J_1 = J_2 = 2.1$ Hz, 2H), 6.64 (dd, $J_1 = J_2 = 3.9$ Hz, 2H), 6.83–6.92 (m, 1H), 6.97–7.05 (m, 2H), 7.06–7.17 (m, 2H), 7.32 (dd, $J_1 = 2.7$ Hz, $J_2 = 1.8$ Hz, 2H), 7.40 (dt, $J_1 = J_2 = 3.0$ Hz, $J_3 = J_4 = 2.1$ Hz, 2H), 7.80 (dd, $J_1 = J_2 = 4.8$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3 , ppm) δ 79.3, 82.1, 113.7, 114.7, 123.7, 124.5, 124.8, 125.1, 128.1, 130.8, 131.9, 132.8, 137.9.

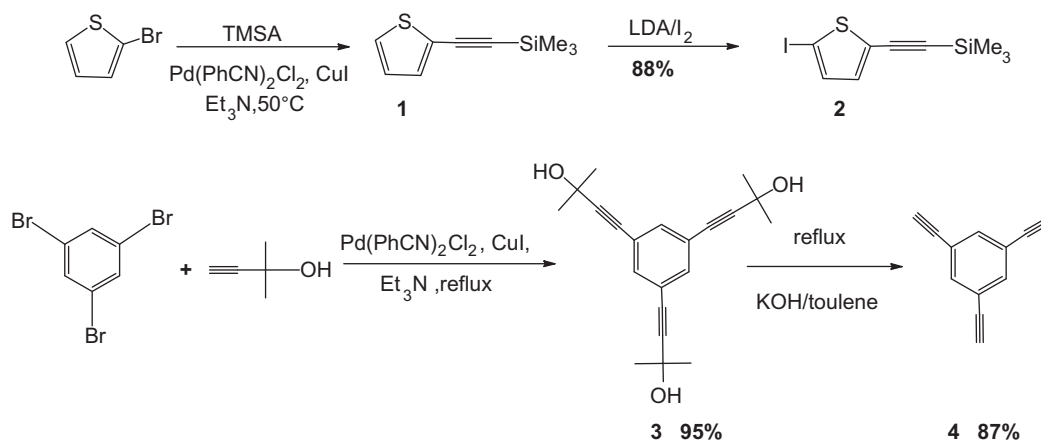
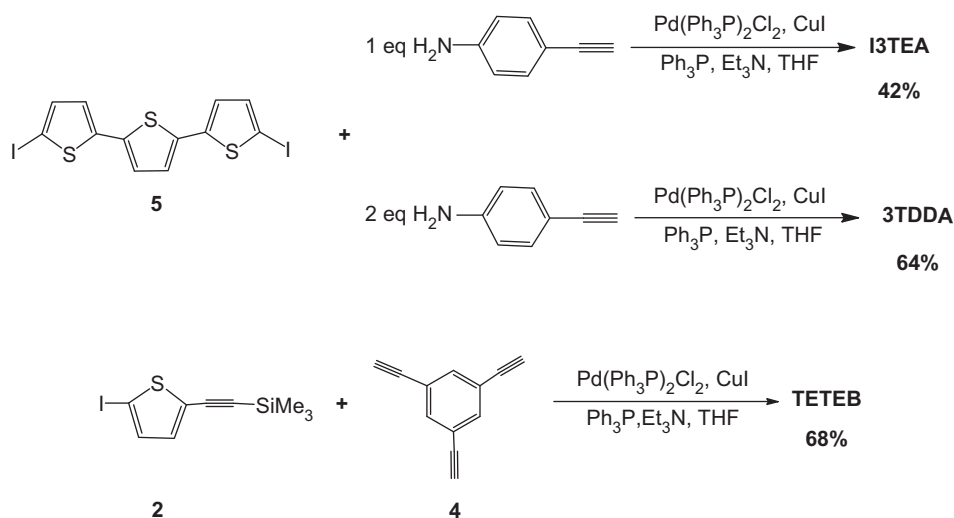
Synthesis of 1,3,5-tris((5-((trimethylsilyl)ethynyl)thiophen-2-yl)ethynyl)benzene (**TETEB**)

Compound **TETEB** was synthesized from ((5-iodothiophen-2-yl)ethynyl)trimethylsilane (**2**) (3.7 g, 12.0 mmol) and 1,3,5-triethynylbenzene (**4**) (0.6 g, 3.7 mmol) by the same procedure as compound **13TEA**. The crude product was purified by silica column chromatography eluting with petroleum ether/ethyl acetate (V:V = 25:1) to afford compound **TETEB** (1.72 g, 68%) as a pale yellow powder; m.p. $103\text{--}104^{\circ}\text{C}$; IR (KBr, cm^{-1}) ν 2963, 2928, 2858, 2147, 1582, 1463, 1410, 1380, 1251, 1201, 1165, 1095, 1031, 856, 804, 760, 698, 626, 554; ^1H NMR (300 MHz, CDCl_3 , ppm) δ 0.26 (s, 27H), 7.11 (s, 6H), 7.60 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3 , ppm) δ -0.03 , 78.5, 83.9, 92.1, 96.9, 123.8, 124.0, 125.4, 132.3, 132.7, 134.0; HRMS (ESI) calcd. for $\text{C}_{39}\text{H}_{36}\text{S}_3\text{Si}_3$ [M^+] 685.1320, found 685.1339.

Results and discussion

Synthesis and characterization

Schemes 1 and 2 illustrate the synthetic routes for the investigated compounds **13TEA**, **3TDDA** and **TETEB**. All of the compounds were prepared by the Sonogashira coupling reaction. The synthetic reactions were controlled by TLC. These materials are readily soluble in common solvents such as THF, diethyl ether, dichloromethane and chloroform, allowing them to be easily purified by column chromatography. The objective products were characterized by IR,

Scheme 1. Synthesis of monomers **2** and **4**.Scheme 2. Synthetic routes to **13TEA**, **3TDDA** and **TETEB**.

NMR and MS. The results are consistent with the expected chemical structures.

Photophysical properties

Absorption spectra

The UV–vis absorption spectra of the three novel compounds **13TEA**, **3TDDA** and **TETEB** were recorded in CHCl_3 ($C = 1.0 \times 10^{-5} \text{ M}$) shown in Fig. 2. In the solution, each compound shows two distinct absorption bands, one broad absorption band is around at 300–500 nm, 330–500 nm, 250–450 nm for **13TEA**, **3TDDA** and **TETEB**, respectively. The long wavelength band is a dipole-allowed, $\pi-\pi^*$ electron transition absorption band of the conjugated π -electron system of the core of the mesogens. This band corresponds to the transition from the ground state to the lowest excited singlet state of the molecule. The narrow absorption band between 230 and 300 nm corresponds to a transition to a higher-lying singlet state [68,69]. The absorption of the star-shaped molecule **TETEB** reveals two absorbance peaks at 339 and 362 nm, indicating a weak shoulder similar to $\pi-\pi^*$ transitions. The absorption maximum of $\pi-\pi^*$ transitions for compound **3TDDA** was gradually red-shifted in comparison of **13TEA** from 401 to 420 nm with elongation of the π -conjugation length. This can be rationalized by the increased intermolecular $\pi-\pi$ interaction with the expanding

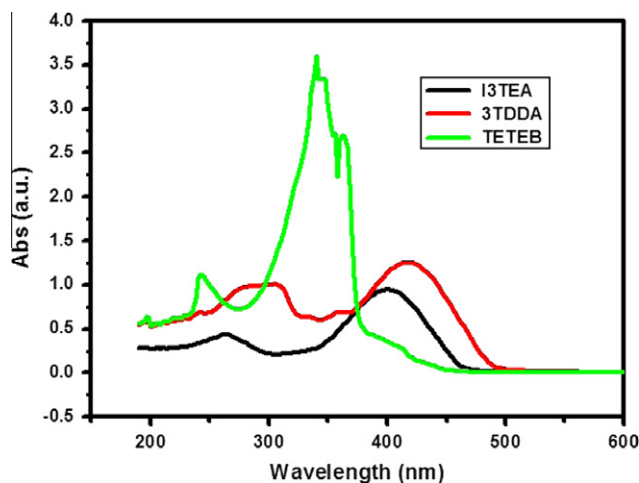


Fig. 2. UV–vis absorption spectra of the dyes **13TEA**, **3TDDA** and **TETEB** in chloroform solution ($1.0 \times 10^{-5} \text{ M}$).

of the π -conjugation. The onset absorption wavelengths were 466 nm for **13TEA**, 493 nm for **3TDDA**, 448 nm for **TETEB**, respectively. However, the onset absorption wavelengths were increased

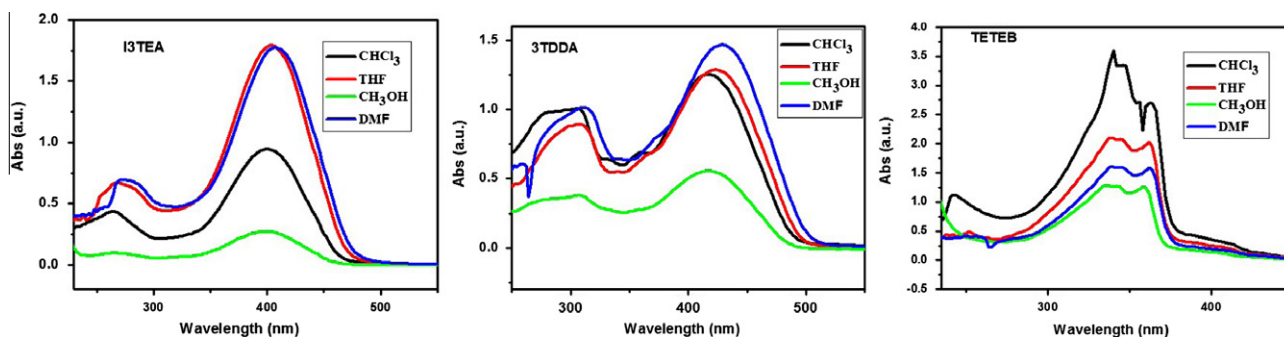


Fig. 3. UV-vis absorption spectra of compounds **13TEA**, **3TDDA** and **TETEB** in different solvents (1.0×10^{-5} M).

Table 1

The optical characteristics of three compounds in four different solvents.

Compound	Solvents/the absorption maximum wavelengths λ_{max} (nm)			
	CHCl ₃	THF	CH ₃ OH	DMF
13TEA	401	402	403	407
3TDDA	420	421	422	430
TETEB	339	340	341	343

by the increased conjugation effect [70–72]. Therefore, the HOMO–LUMO gaps obtained from the end-absorption are 2.66 eV for **13TEA**, 2.52 eV for **3TDDA**, and 2.77 eV for **TETEB**, respectively.

Effect of solvent on the absorption spectra

Typical absorption spectra of compounds **13TEA**, **3TDDA** and **TETEB** in different four solvents such as CHCl₃, THF, CH₃OH and DMF ($C = 1.0 \times 10^{-5}$ M) were shown in Fig. 3 and the corresponding absorption wavelength maxima of the three compounds were presented in Table 1. As shown in Table 1, absorption wavelength maxima for **13TEA** in different solvents varied from 401 to 407 nm, 420 to 430 nm for **3TDDA**, and 339 to 341 nm for **TETEB**, respectively. With the increase of polarity of solvents, the absorption peak of three compounds was slightly red-shifted. This shift suggested that the absorption maximum of π – π^* transition energy decreased, which allowed the π – π^* electron transition. The absorption spectra of compounds **13TEA**, **3TDDA** and **TETEB** in different solvents exhibit different absorption intensities, however, the three compounds in CH₃OH show the weakest absorption intensities. This phenomenon may be due to the formation of the intramolecular hydrogen bond.

Fluorescence spectra

The chloroform solutions containing **13TEA** and **3TDDA** exhibited a bright green-yellow fluorescence even under daylight, while compound **TETEB** showed an orange-yellow fluorescence. Photoluminescence (PL) emission spectra of compounds **13TEA**, **3TDDA** and **TETEB** were measured in chloroform with a concentration of 1.0×10^{-6} M (Fig. 4). The corresponding PL emission maximal wavelengths are located at 482, 496 and 375 nm, respectively. It can be found that their intensity of fluorescence differs from each other. The fluorescence intensity of compound **13TEA** is extremely weak compared with the other two compounds. This may be due to the heavy atom effect. Heavy atom substitution (such as iodine in the aromatic ring) could result in higher intersystem crossing efficiency as well as higher triplet yields [73–75]. For compound **13TEA**, the donor–acceptor structure character resulting from the electron-donating amino functional group and electron-withdrawing iodine atom is in favor of dipole–dipole interactions between molecules. Therefore, **13TEA** exhibited fluorescence quenching.

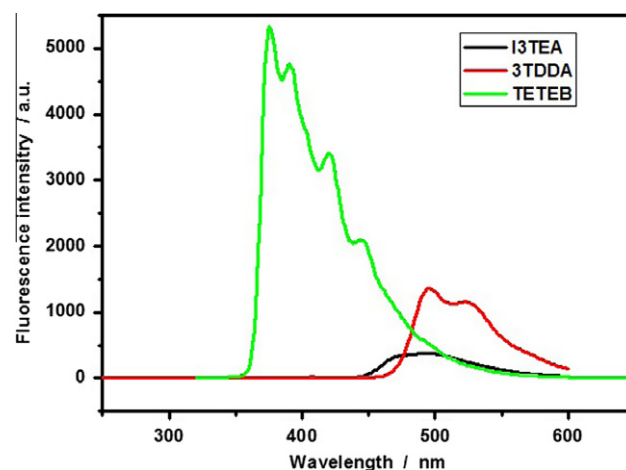


Fig. 4. Photoluminescence emission (PL) spectra of the three compounds in CHCl₃ (1.0×10^{-6} M).

However, the other two compounds were highly fluorescent at room temperature. It should be noted that the spectrum of **TETEB** reveals four pronounced peaks centered at 375, 390, 418 and 446 nm, respectively. While, for **3TDDA**, one pronounced peak centered at 496 nm and one weak shoulder centered at 525 nm. This indicates the existence of molecular conformation deviation between the ground state and the excited state. It is well worth noting that **TETEB** shows a broader band and the fluorescence intensity is much stronger than the corresponding intensity of the others. Meanwhile, the result also indicates that their structure–property relationships of the novel octupolar organic π -conjugated star-shaped molecule on the conjugated backbone by acetylenic spacers and thiophene-functionalized group could effectively influence the fluorescence intensities (up to 5364 a.u.) in the emission spectra. Therefore, octupolar organic π -conjugated star-shaped molecule **TETEB** exhibits excellent luminescent property probably used as luminescent materials.

Effect of the concentration on the emission spectra

In order to further study the effect of the concentration on the fluorescence emission intensity, we observed the fluorescence emission spectra of compounds **13TEA**, **3TDDA** and **TETEB** in chloroform solution with different concentrations shown in Fig. 5. The emission spectra of **13TEA** show two emission bands, one broad emission band in the range of 430–600 nm, another narrow emission band in the range of 390–420 nm. The two peaks of the two bands are located at 407 and 494 nm and the emission maximal peak centered at 494 nm in the range of the concentration from 5.0×10^{-4} to 1.0×10^{-6} M. This indicates no existence of molecu-

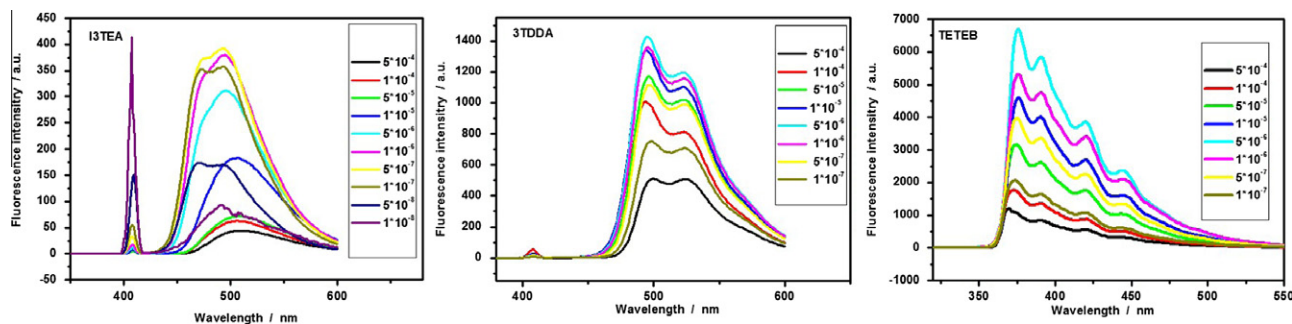


Fig. 5. PL spectra of three compounds in chloroform solution with different concentrations.

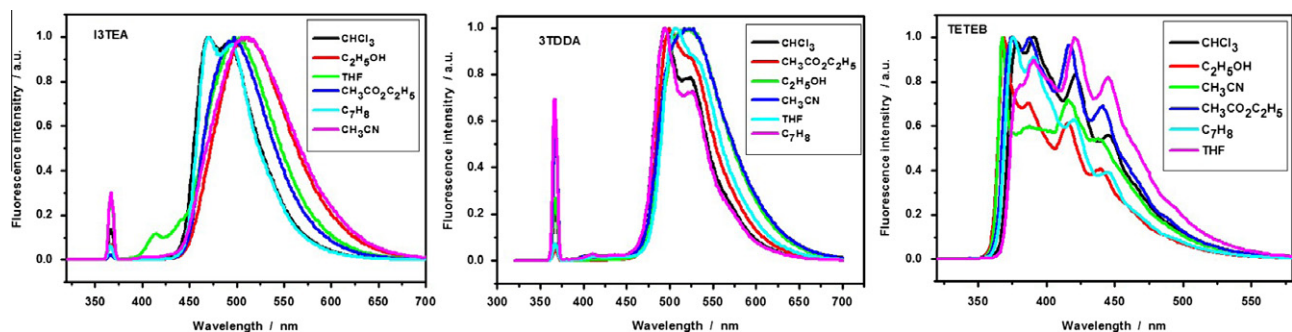


Fig. 6. Normalized emission spectra of these compounds in different solvents with the concentration of 1.0×10^{-6} M.

lar conformation deviation between the ground state and the excited state. The emission spectra exhibit three emission peaks with the concentration from 5.0×10^{-7} to 1.0×10^{-8} M. In the range of 430–600 nm a new weak shoulder peak was found during this broad emission band. The three peaks are located at 407, 470 and 494 nm and the emission maximal peak centered at 470 nm. This may be attributed to the existence of molecular conformation deviation between the ground state and the excited state in this concentration range. The fluorescence intensities of **I3TEA** in chloroform decreased significantly (from 392 to 80 a.u.) in this concentration range during the broad emission band, but the fluorescence intensities increased significantly (from 34 to 416 a.u.) during the narrow emission band. This indicates that **I3TEA** does not aggregate in diluted solution. For **3TDDA**, the emission spectra exhibit two emission bands and three peaks, one broad emission band in the range of 450–600 nm, another narrow emission band in the range of 400–415 nm. The three peaks of the two bands are located at 408, 496 and 522 nm and the emission maximal peak centered at 496 nm. The fluorescence intensities of **3TDDA** in chloroform increased significantly (from 510 to 1440 a.u.) with the concentration from 5.0×10^{-4} to 5.0×10^{-6} M. However, the fluorescence intensities decreased significantly (from 1355 to 757 a.u.) with the concentration from 1.0×10^{-6} to 1.0×10^{-7} M during the broad emission band, but the fluorescence intensities have no significant change during the narrow emission band. The difference of the fluorescence behavior between **I3TEA** and **3TDDA** may be attributed to the heavy atom effect of iodine in **I3TEA** and different aggregates in different concentrations. For **TETEB**, the emission spectra exhibit four emission peaks, the four peaks are located at 375, 390, 418 and 446 nm, respectively, and the emission maximal peak centered at 375 nm. The fluorescence intensities of **TETEB** in chloroform increased significantly (from 1235 to 6714 a.u.) with the concentration from 5.0×10^{-4} to 5.0×10^{-6} M. However, the fluorescence intensities decreased significantly (from 5364 to 2042 a.u.) with the concentration from 1.0×10^{-6} to

Table 2

The optical characteristics of the dyes in six various solvents.

Compound	Solvents/the emission maximum wavelengths $\lambda_{\max}$ (nm)					
	C ₇ H ₈	CHCl ₃	CH ₃ COOC ₂ H ₅	THF	C ₂ H ₅ OH	CH ₃ CN
I3TEA	470	470	496	500	510	510
3TDDA	494	495	499	507	523	526
TETEB	376	376	375	421	369	368

1.0×10^{-7} M. Based on the results, it can be concluded that the three compounds have the concentration aggregate-enhanced emission (AEE) effect [76] and aggregation-caused quenching (ACQ) effect [77].

Effect of solvent on the emission spectra

Normalized fluorescence spectra of the three compounds in various solvents such as C₇H₈, CHCl₃, CH₃COOC₂H₅, THF, C₂H₅OH and CH₃CN ($C = 1.0 \times 10^{-6}$ M) are recorded in Fig. 6 and the corresponding emission maximum wavelengths are summarized in Table 2. As depicted in Fig. 6, the emission maxima for **I3TEA** and **3TDDA** had a red-shift, but the emission maxima for compound **TETEB** had a blue-shift with the increasing the polarity of solvents from toluene to acetonitrile. The results might be resulted from the difference in the dipole moment of compounds **I3TEA** and **3TDDA** in the excited state and the ground state. The relaxed excited state would be energetically stabilized relative to the ground state with increasing the polarity of solvents and a significant red-shift of the fluorescence band was observed. The stronger the interaction of solute and solvent is, the lower the energy of the excited state is, and the larger the red-shift of the emission band is. However, the **TETEB** is on the contrary. Furthermore, the fluorescence intensities of **TETEB** have a significant change in the different solvents. Fluorescence spectra of the three compounds in various solvents with different polarities had similar fluorescence emission

spectra, which suggested that the fluorescence emission could occur from the first excited state S_1 to the ground state S_0 .

Theoretical calculations

In order to gain insight into geometrical configuration and photophysical properties and charge transfer modes, the ground-state optimized geometries and electronic structures of compounds **I3TEA**, **3TDDA** and **TETEB** were calculated with Gaussian 03 software by making full use of density functional theory (DFT) based on the Becke's three parameter gradient-corrected functional (B3LYP) with a polarized 6-31G(d) basis [78]. The geometries of ground-state optimized structures and the electron-density distribution of HOMO, HOMO–1 and LUMO, LUMO+1 of optimized structures are showed in Figs. 7a and 7b, respectively. Fig. 7a shows the compounds **I3TEA** and **3TDDA** have good planar structures and **TETEB** is an octupolar organic π -conjugated star-shaped molecule. The HOMO, HOMO–1 and LUMO, LUMO+1 energies and energy band gaps calculated by DFT were listed in Table 3. The DFT

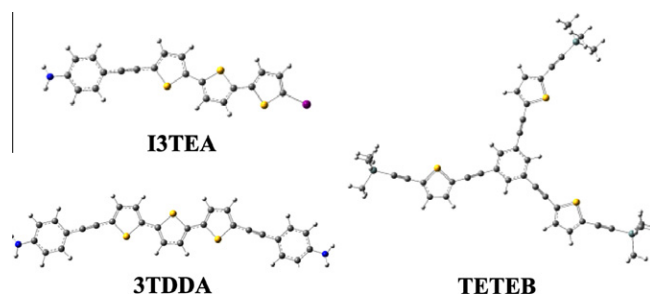


Fig. 7a. Optimized geometries of **I3TEA**, **3TDDA** and **TETEB**. Atom coloring: white, hydrogen; gray, carbon; yellow, sulfur; purple, iodine; blue, nitrogen; green, silicon. Isosurface cut-off value: 0.02. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

calculated results show that the introduction of additional thiophene units stabilizes the LUMO energy levels through increased length of conjugation. The amino substitution on the phenyl ring,

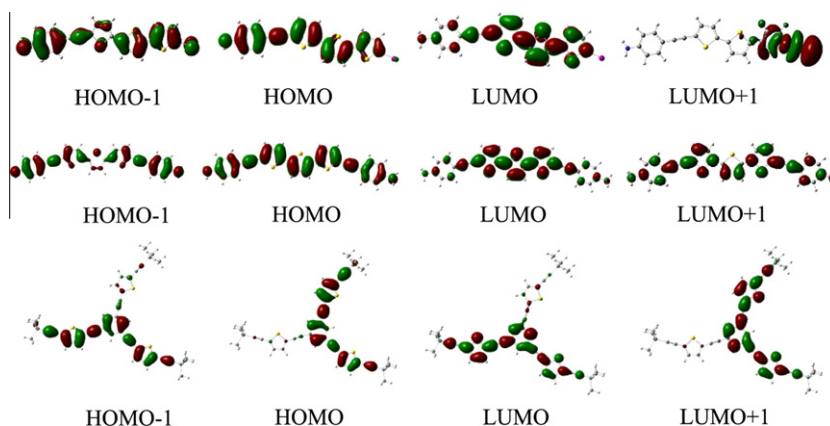


Fig. 7b. The frontier molecular orbitals of **I3TEA** (top), **3TDDA** (middle) and **TETEB** (bottom) calculated with TD-DFT on B3LYP/6-31G*.

Table 3

Summaries of physical, electrochemical and DFT calculated measurements of the compounds.

Compound	Optical and electrochemical characteristics					DFT calculation				
	E_{ox} (V)	HOMO ^a (eV)	λ_{onset} ^b (nm)	E_g^{optb} (eV)	LUMO ^c (eV)	HOMO (eV)	LUMO (eV)	E_g (eV)	HOMO–1 (eV)	LUMO+1 (eV)
I3TEA	0.66	–5.46	466	2.66	–2.80	–4.85	–1.92	2.93	–5.64	–1.19
3TDDA	1.20	–5.69	493	2.52	–3.17	–4.59	–1.92	2.67	–5.13	–1.12
TETEB	0.91	–5.41	448	2.77	–2.64	–5.53	–2.02	3.51	–5.54	–2.02

^a HOMO = $4.8 + E_{ox}$.

^b Obtained from UV spectra $E_g^{opt} = 1240/\lambda_{onset}$.

^c LUMO = HOMO – E_g^{opt} .

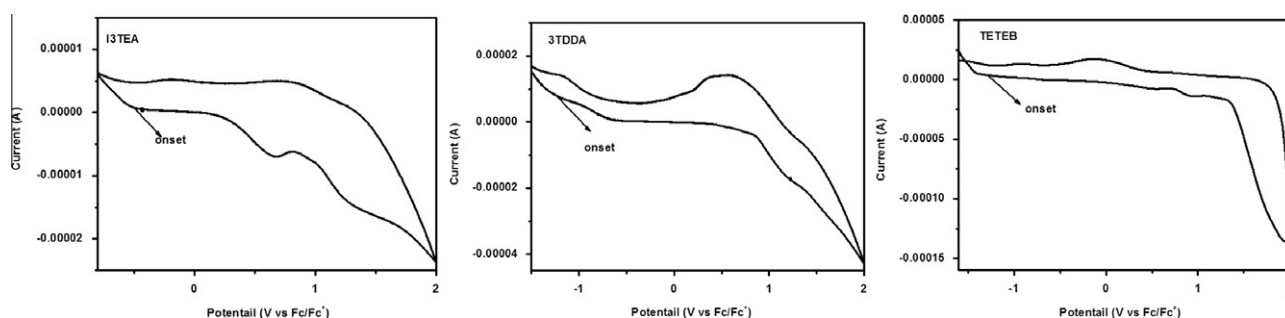


Fig. 8. CV curves measured in CHCl_3 ($C = 1.0 \times 10^{-3} \text{ M}$) of **I3TEA**, **3TDDA** and **TETEB**.

however, destabilized the LUMOs of compounds **I3TEA** and **3TDDA**. As expected, elongation of the π -conjugation length decreased the π - π^* band gap energy in the order of $E_g(\text{I3TEA}) > E_g(\text{3TDDA})$.

Electrochemical properties

The electrochemical properties of compounds **I3TEA**, **3TDDA** and **TETEB** were measured by cyclic voltammetry in chloroform with a concentration of 1.0×10^{-3} M as shown in Fig. 8. All of the compounds showed irreversible redox properties. The oxidation potentials (E_{ox}) calculated directly from onset potential of cyclic voltammograms oxidative $E_{1/2}$ values were 0.66 V for **I3TEA**, 1.20 V for **3TDDA**, and 0.91 V for **TETEB**, with the corresponding HOMO energy levels as -5.46 , -5.69 and -5.41 eV, respectively. The LUMO energy levels were calculated from HOMO and optical band gap values. Hence, the corresponding LUMO energy levels were -2.80 , -3.17 , and -2.64 eV, respectively. The related experimental data are summarized in Table 3. The electrochemical and optical data were in good agreement with the DFT calculation. The good optical and electrochemical properties of these compounds are extremely important characteristics in the conceptions of materials in photovoltaic application.

Conclusions

In this work, we have successfully synthesized two novel planar and one octupolar organic π -conjugated star-shaped molecules containing thiophene-functionalized group and acetylenic spacers, **I3TEA**, **3TDDA** and **TETEB**. Their photophysical and electrochemical properties were further investigated. Their excellent luminescent properties indicated that the three compounds could be used as promising luminescent materials in the optoelectronic field. Their electrochemical properties and the results of DFT calculation demonstrated that the compounds possessed rich electronic character, which suggested that they can use as organic electronic materials.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2013.01.047>.

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