

SYNTHESIS, PROPERTIES AND ELECTROPOLYMERIZATION OF STAR-SHAPED OLIGOTHIOPHENES WITH HEXAKIS(FLUOREN-2-YL)BENZENE AS CORE*

Yang Zou, Yuan Liu, Jin-gui Qin and Chu-luo Yang**

Department of Chemistry, Hubei Key Lab on Organic and Polymeric Opto-Electronic Materials, Wuhan University, Wuhan 430072, China

Abstract Star-shaped oligothiophenes with hexakis(fluoren-2-yl)benzene (HFB) as cores were designed and synthesized. Grafting thiophene units to HFB results in a bond flattening of the core, and makes the molecules a flipping-twist shape. Their thermal, photophysical and electrochemical properties were studied. Highly cross-linked conjugated polymers can be produced by electropolymerization of **T1–T3**.

Keywords: Star-shaped molecules; Hexakis(fluoren-2-yl)benzene; Oligothiophene; Electropolymerization.

INTRODUCTION

Oligothiophene and its derivatives are among the most frequently used π -conjugated materials for organic electronic devices due to their optical and packing properties^[1–7]. Besides typical linear oligothiophenes, thiophene derivatives with higher dimensionalities such as star-shaped, macrocycles, dendrimers were synthesized^[8–11]. Star-shaped molecules can be considered to be intermediates of conjugated small molecules and polymers, and can feature the best of both sets of attributes, *e.g.*, precise molecular weight, high thermal stability, good solubility and excellent film-forming properties^[12]. Recently star-shaped oligothiophenes with various cores such as benzene, truxene, triphenylamine, trithienobenzene were synthesized and applied in liquid crystal materials, field effect transistors, solar cells and *etc*^[13–17]. Because of its rigid backbone and strong S-S intermolecular interaction, linear oligothiophene without alkyl chains shows poor solubility. Therefore, long alkyl chains were often introduced to thiophene to improve its solubility. Müllen and Bäuerle's works suggest that oligothiophenes with bulky twisted or star-shaped structure also show good solubility even it is free from long alkyl chains^[18, 19].

Thiophene derivatives with unblocked α -position can be electropolymerised to form oligomer/polymer. Star-shaped oligothiophenes can even form dendrimers or crosslinked structure upon electropolymerization: *e.g.*, Guyard and co-workers synthesized a series of oligothiophene with 3D structure by electropolymerization of 1,3,5-tri(thiophen-2-yl)benzene^[20]; Müllen's group synthesized polyphenylene dendrimers built around a tetraphenylmethane core and decorated with terthiophene units and found them with unique conductivity^[19]; Advincula's group synthesized oligothiophenes with naphthalene diimides and the conjugated polymer network

* This work was financially supported by the National Science Fund for Distinguished Young Scholars of China (No. 51125013).

** Corresponding author: Chu-luo Yang (杨楚罗), E-mail: clyang@whu.edu.cn

Invited paper dedicated to Professor Fosong Wang on the occasion of his 80th birthday

Received January 17, 2013; Revised February 3, 2013; Accepted February 5, 2013

doi: 10.1007/s10118-013-1286-8

films formed by its electropolymerization reaction are highly active in both the p- and n-doping processes^[21].

Recently, we synthesized some star-shaped molecules with hexakis(fluoren-2-yl)benzene (HFB) core and found them to be good light emitting materials and hole-transporting materials^[22, 23]. The HFB core is a highly twisted structure confirmed by its crystal structure. What's more, long alkyl chains can be facilely grafted on C-9 of fluorene units to improve solubility. In this paper, we designed and synthesized HFB cored oligofluorenes. The HFB core showed good solubility, furthermore, the six-armed structure allowed these molecules to form stable condensed film upon electropolymerization. Their thermal, photophysical properties were also studied, and the relationship between the structures and properties was discussed.

EXPERIMENTAL

Materials and Instruments

Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification. Solvents for synthesis were purified by routine procedure and distilled under dry argon prior to use. 5-Trimethylstannyl-2,2'-dithienyl, 2-tri(*n*-butyl)stannylterthiophene and 1,2-bis(7-bromo-9,9-dihexyl-9*H*-fluoren-2-yl)ethyne were prepared according to the literature^[22, 24].

¹H-NMR and ¹³C-NMR spectra were measured on a MECUYR-VX300 spectrometer. Elemental analyses of carbon, hydrogen and nitrogen were performed on a Vario EL III microanalyzer. EI mass spectra were measured on a ZAB 3F-HF mass spectrophotometer. MALDI-TOF mass spectra were performed on a Bruker BIFLEX III TOF mass spectrometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 K min⁻¹ from 20 °C to 300 °C under argon atmosphere. The glass transition temperature (*T*_g) was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 K min⁻¹ from 25 °C to 600 °C. UV-Vis absorption spectra were recorded on a Shimadzu UV-2550 recording spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (oxidation scan) at room temperature with a CHI voltammetric analyzer. *n*-Bu₄PF₆ (0.1 mol/L) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode and an Ag wire pseudoreference electrode with ferrocenium-ferrocene (Fc⁺/Fc) as the internal standard. Cyclic voltammograms were obtained at a scan rate of 100 mV s⁻¹. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. Single-crystal X-ray diffraction data were obtained from a Bruker AXS Smart CCD diffractometer using a graphite-monochromated MoK α (λ = 0.071073 nm) radiation at 77 K. The data were collected using the $\omega/2\theta$ scan mode and corrected for Lorentz and polarization effects as well as the absorption during data reduction using Shelxtl 97 software.

General Procedure for 1,2-Bis(9,9-dihexyl-7-(oligothiophen-2-yl)-9*H*-fluoren-2-yl)ethyne **A1**, **A2** and **A3**

To a mixture of 1,2-bis(9,9-bis(6-bromohexyl)-9*H*-fluoren-2-yl)ethyne (3.00 g, 3.50 mmol), Pd(PPh₃)₄ (0.315 g, 0.45 mmol) and tributyl(oligothiophen-2-yl)stannane (10.7 mmol) was added degassed *N,N*-dimethylformamide (DMF) (75 mL). The mixture was stirred at 60 °C under argon for 48 h. After cooling to room temperature, the resulting mixture was quenched with 2 mL of 4 mol/L HCl in 1,4-dioxane. Then the resulting mixture was poured into ice-water and extracted with chloroform. The combined organic layer was washed with dilute HCl and then water, dried over Na₂SO₄ and then the residue solvent was removed under reduced pressure. The residue was then purified with a silicon gel column using chloroform/hexane (*V/V*) 1:10 for **A1**, 1:5 for **A2** and 1:3 for **A3** as the eluent to obtain the final product.

A1: white powder, yield: 61%. ¹H-NMR (300 MHz, CDCl₃, δ): 7.70–7.55 (m, 36H), 7.40–7.39 (m, 6H), 7.31–7.29 (m, 6H), 7.13–7.11 (m, 6H), 2.02 (t, 24H, *J* = 8.1 Hz), 1.15–1.06 (m, 72H), 0.79–0.74 (m, 36H), 0.65 (m, 24H). ¹³C-NMR (75 MHz, CDCl₃, δ): 148.37, 148.26, 141.44, 140.32, 140.22, 129.47, 127.55, 121.50,

119.87, 118.03, 90.07, 54.78, 40.68, 31.77, 30.12, 23.66, 23.05, 14.16. EI MS: Calcd for $C_{60}H_{70}S_2$: 854.5. Found: 854.3. Anal. Calcd for $C_{60}H_{70}S_2$ (%): C 84.25; H 8.25. Found: C 84.01; H 7.93.

A2: light yellow powder, yield 53%. ^1H -NMR (300 MHz, $CDCl_3$, δ): 7.70–7.55 (m, 40H), 7.32–7.31 (m, 6H), 7.20–7.18 (m, 6H), 7.06–7.04 (m, 6H), 2.02 (t, 24H, $J = 8.1$ Hz), 1.36–1.07 (m, 72H), 0.79–0.75 (m, 36H), 0.66 (m, 24H). ^{13}C -NMR (75 MHz, $CDCl_3$, δ): 148.88, 148.46, 141.73, 140.12, 140.07, 129.87, 127.47, 121.38, 119.32, 118.13, 90.33, 55.68, 40.657, 31.68, 30.03, 23.46, 23.02, 14.18. EI MS: Calcd for $C_{68}H_{74}S_4$: 1018.5. Found: 1018.1. Anal. Calcd for $C_{68}H_{74}S_4$ (%): C 80.10; H 7.32. Found: C 79.73; H 6.99.

A3: yellow powder, yield 26%. ^1H -NMR (300 MHz, $CDCl_3$, δ): 7.71–7.57 (m, 48H), 7.39–7.30 (m, 18H), 2.00 (m, 24H), 1.15–1.06 (m, 72H), 0.79–0.74 (m, 36H), 0.66 (m, 24H). ^{13}C -NMR (75 MHz, $CDCl_3$, δ): 148.82, 148.46, 141.37, 140.24, 140.11, 129.36, 127.58, 121.52, 119.57, 118.01, 90.33, 55.08, 40.72, 31.85, 30.22, 23.47, 23.07, 14.18. MALDI-TOF MS: Calcd for $C_{76}H_{78}S_6$: 1182.4. Found: 1182.1. Anal. Calcd for $C_{76}H_{78}S_6$ (%): C 77.11; H 6.64. Found: C 76.78; H 6.98.

General Procedure for 1,2,3,4,5,6-Hexakis(9,9-dihexyl-7-(oligothiophen-2-yl)-9H-fluoren-2-yl)benzene **T1**, **T2** and **T3**

To a mixture of 1,2-bis(9,9-dihexyl-7-(oligothiophen-2-yl)-9H-fluoren-2-yl)ethyne (3 mmol) and dicobaltoctacarbonyl (52 mg, 0.15 mmol) was added 60 mL of degassed 1,4-dioxane. The solution was refluxed under argon for 24 h. The resulting mixture was poured into water, the solid was collected by filtration. The crude product was purified by column chromatography using chloroform/hexane (V/V) 1:10 for **T1**, 1:5 for **T2** and 1:3 for **T3** as the eluent to obtain the final product.

T1: white powder, yield 90%. ^1H -NMR (300 MHz, $CDCl_3$, δ): 7.38–7.36 (m, 18H), 7.29–7.21 (m, 18H), 7.11 (s, 6H), 7.05–7.00 (m, 6H), 6.83 (d, 6H, $J = 7.8$ Hz), 1.79–1.76 (m, 24H), 1.06 (m, 24H), 0.91 (m, 48H), 0.74 (m, 36H), 0.27 (m, 24H). ^{13}C -NMR (75 MHz, $CDCl_3$, δ): 146.82, 145.02, 140.94, 136.56, 136.08, 135.29, 133.37, 128.28, 124.85, 123.37, 121.84, 120.10, 119.68, 118.08, 115.45, 113.43, 50.22, 36.05, 27.00, 25.40, 18.94, 18.91, 9.57. MALDI-TOF MS: Calcd for $C_{180}H_{210}S_6$: 2564.5. Found: 2564.5. Anal. Calcd for $C_{180}H_{210}S_6$ (%): C 84.25; H 8.25. Found: C 83.88; H 7.92.

T2: white powder, yield 85%. ^1H -NMR (300 MHz, $CDCl_3$, δ): 7.37–7.35 (m, 18H), 7.29–7.20 (m, 18H), 7.10 (s, 6H), 7.04–7.00 (m, 18H), 6.82 (d, 6H, $J = 7.8$ Hz), 1.79–1.76 (m, 24H), 1.06 (m, 24H), 0.91 (m, 48H), 0.74 (m, 36H), 0.27 (m, 24H). ^{13}C -NMR (75 MHz, $CDCl_3$, δ): 145.64, 144.52, 140.55, 136.48, 136.28, 135.11, 133.22, 128.39, 124.32, 123.21, 121.54, 120.17, 119.44, 118.00, 117.45, 114.86, 113.53, 50.12, 36.00, 26.57, 25.24, 18.68, 18.88, 9.56. MALDI-TOF MS: Calcd for $C_{204}H_{222}S_{12}$: 3057.4. Found: 3058.1. Anal. Calcd for $C_{204}H_{222}S_{12}$ (%): C 80.10; H 7.32. Found: C 79.79; H 6.94.

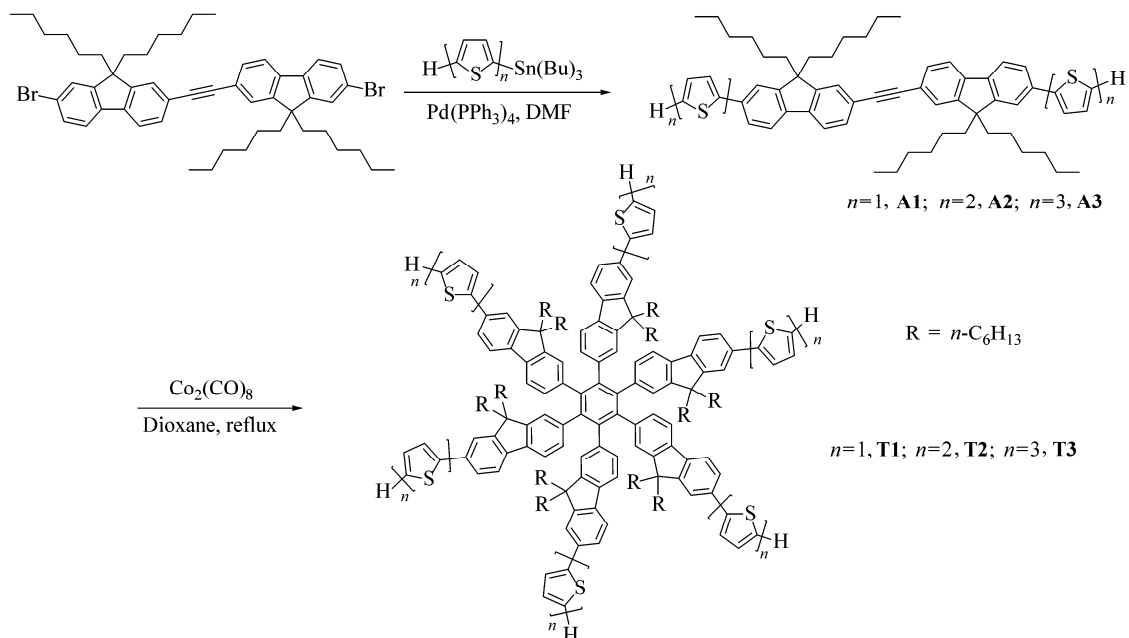
T3: white powder, yield 80%. ^1H -NMR (300 MHz, $CDCl_3$, δ): 7.35–7.33 (m, 18H), 7.28–7.20 (m, 18H), 7.10 (s, 6H), 7.03–6.89 (m, 30H), 6.82 (d, 6H, $J = 7.8$ Hz), 1.79–1.76 (m, 24H), 1.06 (m, 24H), 0.91 (m, 48H), 0.74 (m, 36H), 0.27 (m, 24H). ^{13}C -NMR (75 MHz, $CDCl_3$, δ): 144.73, 143.56, 140.54, 135.78, 135.48, 134.81, 133.02, 127.69, 123.62, 122.55, 120.84, 120.67, 118.57, 117.40, 116.32, 115.42, 114.86, 113.53, 50.12, 36.01, 26.56, 25.23, 18.57, 18.78, 9.57. MALDI-TOF MS: Calcd for $C_{228}H_{234}S_{18}$: 3549.3. Found: 3549.4. Anal. Calcd for $C_{228}H_{234}S_{18}$ (%): C 77.11; H 6.64. Found: C 76.85; H 6.48.

RESULTS AND DISCUSSION

Synthesis

The synthetic routes and molecular structures of the three star-shaped compounds are depicted in Scheme 1. These star-shaped oligothiophenes were synthesized by convergent core-creating approach as we previously applied for star-shaped oligofluorenes. The alkyne derivatives **A1–A3** were obtained by using Stille coupling reaction of 1,2-bis(9,9-bis(6-bromohexyl)-9H-fluoren-2-yl)ethyne with the corresponding tributyl(oligothiophen-2-yl)stannane. Then, **T1–T3** were obtained using dicobaltoctacarbonyl catalyzed cyclotrimerisation of **A1–A3** in the yields of 80%–90%. All of the compounds exhibit good solubility in the common solvents, such as dichloromethane, tetrahydrofuran, toluene and chlorobenzene. All compounds were fully characterized by

$^1\text{H-NMR}$, $^{13}\text{C-NMR}$, mass spectrometry and elemental analysis and the data were all in good agreement with the designed structures.



Scheme 1 The synthetic routes of **T1–T3**

X-ray Crystallography

Colorless crystals of **T1** suitable for X-ray crystallography were grown by evaporating its toluene solution. Its molecular structure is shown in Fig. 1. The crystal belongs to $C2/c$ monoclinic space group. The six fluorene arms are twisted with respect to the benzene ring in order to alleviate the steric hindrance. However, unlike we previously reported^[23], the shape of the hexakis(fluoren-2-yl)benzene core were influenced by peripheral thiophene units, the dihedral angles between fluorene and central benzene are all around 66° , resulting in a flipping-twist shape of the molecule.

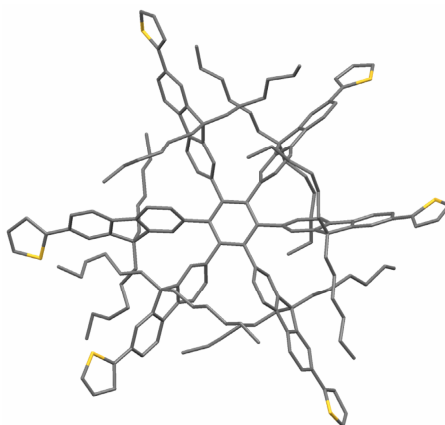


Fig. 1 Single crystal structures of **T1** (Hydrogen atoms were omitted for clarity.)

Crystal data of **T1**: $\text{C}_{180}\text{H}_{210}\text{S}_6$, $C2/c$ monoclinic, unit cell dimensions $a = 2.7432(4)$ nm, $b = 3.8346(5)$ nm, $c = 1.8262(3)$ nm, $\alpha = 90^\circ$, $\beta = 119.305(2)^\circ$, $\gamma = 90^\circ$, $V = 16.751(4)$ nm³, $z = 4$, $M_r = 2565.84$, $D_c = 1.017$ g/cm³, $F(000) = 5544.0$, $\mu = 0.129$ mm⁻¹

Thermal Properties

The thermal properties of **T1–T3** were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As shown in Fig. 2, all compounds exhibit high decomposition temperature (T_d) above 430 °C. DSC curves indicated these star-shaped oligothiophenes are crystal compounds. The melting points (T_m) are 307, 277 and 241 °C for **T1–T3** respectively, and the glass transition temperatures (T_g) are 132, 123 and 110 °C for **T1–T3** respectively. The T_m and T_g gradually reduce as oligothiophene units stretch. In Fig. 2(b), **T3** shows two peaks, while **T1** and **T2** show only one sharp peak corresponding to their melting temperature. In Fig. 2(c), the **T1** and **T2** show a significant endothermic peak, indicating the formation of higher ordered mesophases; While for **T3**, no endothermic peak was observed. This agreed well with star-shaped oligothiophenes reported in literature^[25].

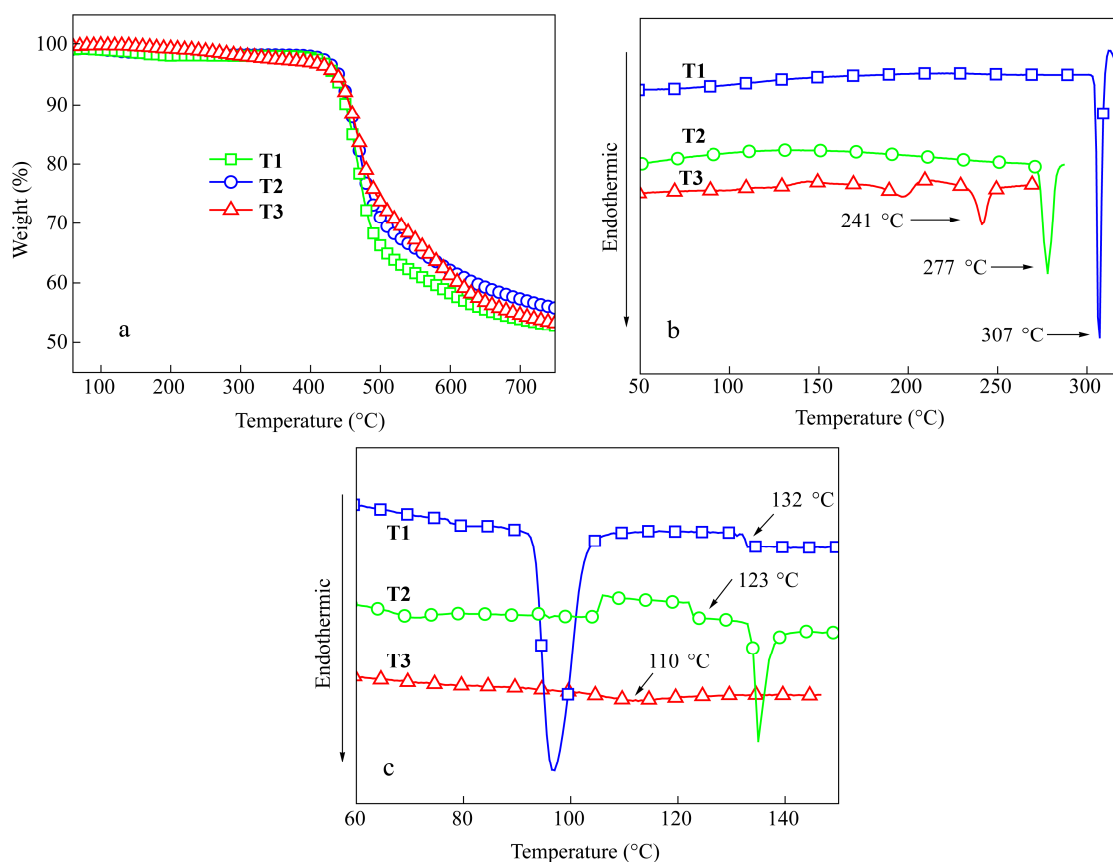


Fig. 2 (a) TGA thermograms of **T1–T3**, (b) first heating and (c) second heating of DSC traces of **T1–T3**

Photophysical Properties

The absorption spectra of **T1–T3** in chloroform solution show intense π - π^* absorption bands, which progressively red-shift from 304 nm to 403 nm with increasing thiophene units (Fig. 3a). The absorption spectrum of each compound in solid state film reveals remarkable red-shift and broadening compared to that in solution (Fig. 3b). PL spectra are also bathochromic from **T1** to **T3**, with the maximum emissions from 370 to 413 nm in solution (Fig. 3c) and from 382 nm to 486 nm in the solid state (Fig. 3d). The significant red-shift and broadened spectra in film compared to those in solution indicate these oligothiophenes possess strong intermolecular interaction in condensed state which can be often observed in thiophene derivatives.

Electrochemical Properties

Cyclic voltammetry (CV) experiments were conducted to probe the electrochemical properties of the star-shaped

oligothiophenes (Fig. 4). With the extension of the oligothiophene units at each arm, each onset potential (E_{onset}) displays a negative shift. The E_{onset} values are 0.33, 0.17 and 0.01 V for **T1–T3** respectively, and the HOMO levels are calculated to be -5.13 , -4.97 and -4.81 eV, indicating they are all good electron donating materials. Notably, **T1–T3** show no overlapped oxidation waves assigned to the through-space interaction between each arm which is often observed in hexaarylbenzene derivatives^[22, 26, 27]. That is because the holes are delocalized on peripheral oligothiophene moieties^[28]. Thermal, photophysical and electrochemical data of **T1–T3** are summarized in Table 1.

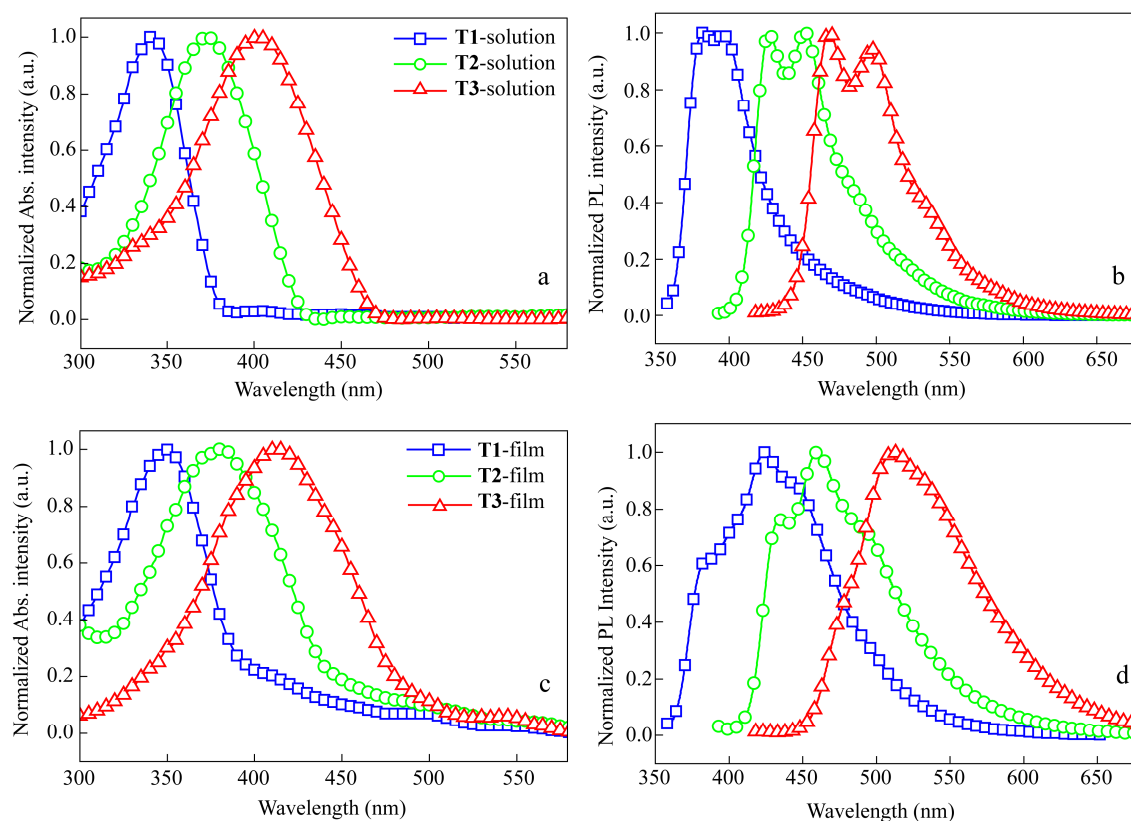


Fig. 3 Absorption and emission spectra of **T1–T3** in chloroform (a), (b) and thin film (c), (d)

Like other thiophene derivatives with unblocked α -position, **T1–T3** can be electropolymerised upon repeating scan. A transparent insoluble film can be observed at electrode upon repeating scan, which can be led by cross-linked architecture of the polymer. The electropolymerization peaks are 0.1, 0, -0.1 V for **T1–T3** respectively, which follows the trend of the HOMO energies of corresponding oligothiophenes. The film formed by electropolymerization of these star-shaped oligothiophenes might be potential optoelectronic materials, further investigation and application are in progress.

Table 1. Thermal, photophysical and electrochemical data of **T1–T3**

Compound	T_g ($^{\circ}\text{C}$) ^a	T_d ($^{\circ}\text{C}$) ^b	λ_{abs} (nm) ^c	λ_{em} (nm) ^c	E_g^{opt} (eV) ^d	E_{ox} (V) ^e	HOMO (eV)	LUMO (eV)
T1	132	437	340	382	3.27	0.33	-5.13	-1.86
T2	123	437	374	428	2.90	0.17	-4.97	-2.07
T3	110	437	403	468	2.65	0.01	-4.81	-2.16

^a Measured on the second heating scans at 10 K min^{-1} from $25\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$; ^b 5% weight loss, measured with scan rate of 10 K min^{-1} from $20\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ under argon; ^c Measured for $1 \times 10^{-6}\text{ mol/L}$ chloroform solutions;

^d Estimated from the edge of low-energy absorption edge; ^e Recorded at scan rate = 100 mV s^{-1} ; $E_{1/2}(\text{ferrocene}) = 0.232\text{ V}$ versus AgNO_3/Ag reference electrode

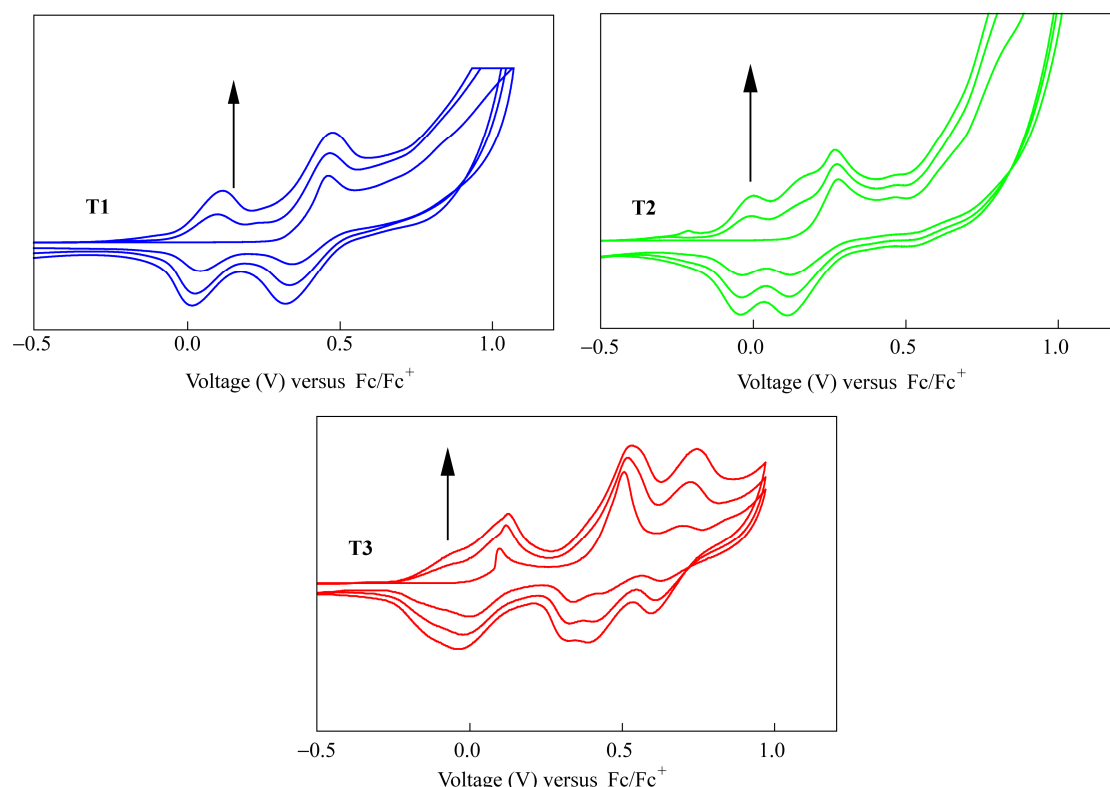


Fig. 4 Cyclic voltammograms of **T1–T3** in CH_2Cl_2 for oxidation (versus Fc/Fc^+)

CONCLUSIONS

In this paper, star-shaped oligothiophenes with HFB as the core were designed and synthesized. Grafting thiophene units to HFB results in a bond flattening of the core, making molecule a flipping-twist shape. Their thermal, photophysical and electrochemical properties were fully characterized. **T1–T3** show aggregate emission in condensed state. A highly cross-linked conjugated polymer can be obtained by electropolymerization of **T1–T3**.

REFERENCES

- 1 Meng, H., Bao, Z., Lovinger, A.J., Wang, B.C. and Majsce, A.M., *J. Am. Chem. Soc.*, 2001, 123: 9214
- 2 Brabec, C.J., Gowrisanker, S., Halls, J.J. M., Laird, D., Jia, S. and Williams, S.P., *Adv. Mater.*, 2010, 22: 3839
- 3 Hou, J., Chen, H.Y., Zhang, S., Li, G. and Yang, Y., *J. Am. Chem. Soc.*, 2008, 130: 16144
- 4 Mishra, A., Ma, C.Q. and Bäuerle, P., *Chem. Rev.*, 2009, 109: 1141
- 5 Wong, W.W.H., Ma, C.Q., Pisula, W., Mavrinskiy, A., Feng, X., Seyler, H., Jones, D.J., Müllen, K., Bäuerle, P. and Holmes, A.B., *Chem. Eur. J.*, 2011, 17: 5549
- 6 Chen, S., Liu, Y., Qiu, W., Sun, X., Ma, Y. and Zhu, D., *Chem. Mater.*, 2005, 17: 2208
- 7 Wong, W.W.H., Ma, C.Q., Pisula, W., Yan, C., Feng, X., Jones, D.J., Müllen, K., Janssen, R.A.J., Bäuerle, P. and Holmes, A.B., *Chem. Mater.*, 2009, 22: 457
- 8 Xia, C., Fan, X., Locklin, J., Advincula, R.C., Gies, A. and Nonidez, W., *J. Am. Chem. Soc.*, 2004, 126: 8735
- 9 Pei, J., Wang, J.L., Cao, X.Y., Zhou, X.H. and Zhang, W.B., *J. Am. Chem. Soc.*, 2003, 125: 9944
- 10 Harpham, M.R., Süzer, O.Z.N., Ma, C.Q., Bäuerle, P. and Goodson, T., *J. Am. Chem. Soc.*, 2009, 131: 973

- 11 Sun, X.B., Liu, Y.Q., Chen, S.Y., Qiu, W.F., Yu, G., Ma, Y.Q., Qi, T., Zhang, H.J., Xu, X.J. and Zhu, D.B., *Adv. Funct. Mater.*, 2006, 16: 917
- 12 Kanibolotsky, A.L., Perepichka, I.F. and Skabara, P.J., *Chem. Rev.*, 2010, 39: 2695
- 13 Geng, Y., Fechtenkotter, A. and Müllen, K., *J. Mater. Chem.*, 2001, 11: 1634
- 14 Sun, Y.M., Xiao, K., Liu, Y.Q., Wang, J.L., Pei, J., Yu, G. and Zhu, D.B., *Adv. Funct. Mater.*, 2005, 15: 818
- 15 Nicolas, Y., Blanchard, P., Levillain, E., Allain, M., Mercier, N. and Roncali, J., *Org. Lett.*, 2003, 6: 273
- 16 Ponomarenko, S.A., Kirchmeyer, S., Elschner, A., Huisman, B.H., Karbach, A. and Drechsler, D., *Adv. Funct. Mater.*, 2003, 13: 591
- 17 Cravino, A., Roquet, S., Alévêque, O., Leriche, P., Frère, P. and Roncali, J., *Chem. Mater.*, 2006, 18: 2584
- 18 John, H., Bauer, R., Espindola, P., Sonar, P., Heinze, J. and Müllen, K., *Angew. Chem. Int. Ed.*, 2005, 44: 2447
- 19 Ma, C.Q., Mena-Osteritz, E., Debaerdemaeker, T., Wienk, M.M., Janssen, R.A.J. and Bäuerle, P., *Angew. Chem. Int. Ed.*, 2007, 119: 1709
- 20 Cherioux, F. and Guyard, L., *Adv. Funct. Mater.*, 2001, 11: 305
- 21 Ponnampati, R., Felipe, M.J. and Advincula, R., *Macromolecules*, 2011, 44: 7530
- 22 Zou, Y., Ye, T., Ma, D., Qin, J. and Yang, C., *J. Mater. Chem.*, 2012, 22: 23485
- 23 Zou, Y., Zou, J., Ye, T., Li, H., Yang, C., Wu, H., Ma, D., Qin, J. and Cao, Y., *Adv. Funct. Mater.*, 2012, doi: 10.1002/adfm.201202286
- 24 Bilge, A., Zen, A., Forster, M., Li, H., Galbrecht, F., Nehls, B.S., Farrell, T., Neher, D. and Scherf, U., *J. Mater. Chem.*, 2006, 16: 3177
- 25 Geng, Y., Fechtenkotter, A. and Mullen, K., *J. Mater. Chem.*, 2011, 11: 1634
- 26 Rathore, R., Burns, C.L. and Abdelwahed, S.A., *Org. Lett.*, 2004, 6: 1689
- 27 Chebny, V.J., Shukla, R. and Rathore, R., *J. Phys. Chem. A*, 2006, 110: 13003
- 28 Lambert, C., *Angew. Chem. Int. Ed.*, 2005, 44: 7337