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Synthesis, crystal structure, and polymerization of butterfly-shaped thieno[3,2-b]thiophene oligomers⁺

Ying Liu, Qida Liu, Xingye Zhang, Ling Ai, Yang Wang, Ruixiang Peng and Ziyi Ge*

A series of new butterfly-shaped thieno[3,2-*b*]thiophene oligomers with phenyl and thiophene units were synthesized through Suzuki coupling and Stille coupling reactions. The optical and thermal properties of these materials can be tuned by varying both substituents and the conjugation length. The crystal structures have been determined and showed a *syn-* or *anticlinal* conformation in the crystal of molecule **4**. The electronic properties of the monomers and their electropolymerization ability are discussed and rationalized as a function of their molecular structure. Moreover, stable cross-linked conjugated polymers were formed by electropolymerization.

Introduction

Thiophenes are one of the most important classes of heterocyclic compounds, not only as key structural units of compounds with interesting biological activities but also in the field of material chemistry. Interest in thiophenes has been extended to fused thiophenes, such as thieno[3,2-b]thiophenes. Indeed, these and closely related materials with the incorporation of rigid thieno-[3,2-b]thiophene units in conjugated oligomers or polymers have been developed to improve their electronic properties and to optimize the performance of the corresponding devices, for example, organic field-effect transistors (OFETs),1-6 organic light-emitting diodes (OLEDs),^{7,8} photovoltaics.⁹ In fact, the performance of a functional material is strongly dependent on its molecular organization and structure. The arrangement, namely the packing motif, plays a very important role in the performance of an organic electronic device. Therefore, design of functional molecular solid-state structures, or arrangements, through tuning of the intermolecular interactions is important. In this paper, we present a facile route to precisely obtain a novel type of "butterfly-shaped" molecular material, wherein one thieno [3,2-b] thiophene acts as the planar backbone, and phenyl or thiophene acts as the branches. Novel butterfly thieno[3,2-b]thiophene derivatives functionalized with phenyl or thienyl aromatic groups at the α - and β -positions were synthesized by Suzuki and Stille coupling reactions according

Fax: +86-574-86685043; Tel: +86-574-86690273

to Scheme 1 and their crystal structures, optical, and electrochemical properties were investigated.

Experimental

General procedures

Chemicals were purchased from Acros, Aldrich and used as received. 2,3,5,6-Tetrabromothieno[3,2-*b*]thiophene was prepared as outlined in the literature.¹¹ Solvents and other normal reagents were obtained from the Sinopharm Chemical Reagent Co., Ltd. (SCRC). Solvents for reactions and photophysical measurements (chloroform, THF, *etc.*) were all distilled after dehydration according to conventional methods.

Instrumentation

The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DMX 400 NMR spectrometer. Chemical-shift data for each signal were reported in ppm units with tetramethylsilane (TMS) as internal reference, where δ (TMS) = 0. MS spectra were recorded on a Micromass GCT-MS spectrometer. Elemental analyses were performed on a Carlo Erba model 1160 elemental analyzer.

Syntheses

Preparation of 3

To a solution of 2 (1.38 g, 3 mmol) and phenylboronic acid (2.44 g, 20 mmol) dissolved in THF (300 mL) was added an aqueous 2 M potassium carbonate solution (50 mL). The mixture was bubbled with nitrogen for 30 min. Tetrakis-(triphenylphosphine)palladium (0) (345 mg, 0.3 mmol) was then added. The mixture was heated to 80 $^{\circ}$ C for 48 hours under a nitrogen atmosphere. The reaction was

Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China. E-mail: geziyi@nimte.ac.cn;

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Scheme 1 Synthetic route of molecules 3–6.

cooled to room temperature and poured into water (500 mL) to give a precipitate. After the obtained materials were purified by multiple Soxhlet extraction using methanol and acetone, they were purified by gradient sublimation. Further purification was carried out by sublimation along a temperature gradient of 250–180–100 °C at 10^{-2} Pa in a N₂ atmosphere to obtain a colorless crystal block of **3**. The resulting colorless crystal block was suitable for X-ray analysis. 0.74 g, 56% yields. MALDI-TOF: 443.7; ¹H NMR (400 MHz, CDCl₃): δ = 7.47 (m, 4H), 7.37 (m, 4H), 7.34 (m, 8H), 7.27 (m, 4H) ppm; ¹³C NMR (CDCl₃): δ = 139.05, 139.01, 135.09, 134.61, 130.68, 129.35, 129.07, 128.80, 128.53, 127.65; anal. calcd for C₃₀H₂₀S₂: C, 81.04; H, 4.53; S, 14.42%; found: C, 80.87; H, 4.56; S, 14.52%.

Preparation of 4 and 5

Compounds 4 and 5 were prepared according to the procedure used for 3 and by the Suzuki coupling reaction between 2 (1.38 g, 3.0 mmol) and α -thiopheneboronic acid (1.92 g, 15 mmol). The obtained materials were purified by multiple Soxhlet extraction using methanol, acetone and chloroform. The chloroform solvent was removed to give a yellow solid. Further purification was carried out by sublimation along a temperature gradient of 250–180–100 °C at 10⁻² Pa in a N₂ atmosphere to obtain a yellow crystal block of 4. The resulting yellow crystal block was suitable for X-ray analysis. 0.7 g, (50%). MALDI-TOF: 468.0; ¹H NMR (400 MHz, acetone- d_6): δ = 7.64 (dd, *J* = 6.8 Hz, 2H), 7.60 (dd, *J* = 6.8 Hz, 2H), 7.32 (dd, *J* = 4.8 Hz, 2H), 7.29 (dd, *J* = 4.8 Hz, 2H), 7.20 (dd, *J* = 6.8 Hz, 2H), 7.14

(dd, J = 6.8 Hz, 2H) ppm; ¹³C NMR (CDCl₃): $\delta = 138.32$, 135.27, 135.12, 133.08, 128.15, 127.51, 127.36, 127.29, 126.41, 124.77; anal. calcd for C₂₂H₁₂S₆: C, 56.37; H, 2.58; S, 41.05%; found: C, 56.03; H, 2.62; S, 41.39%.

The black residue was purified by sublimation as colorless solids to give 5. Further purification was carried out by sublimation along a temperature gradient of 250–180–100 °C at 10^{-2} Pa in a N₂ atmosphere to obtain a yellow crystal prism of 5. The resulting yellow crystal prism was suitable for X-ray analysis. 0.22 g (15%). MS: 461; ¹H NMR (400 MHz, CDCl₃): δ = 7.48 (d, *J* = 3.6 Hz, 2H), 7.42 (d, *J* = 4.0 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 2H) ppm; anal. calcd for C₁₄H₆Br₂S₄: C, 36.38; H, 1.31; Br, 34.57; S, 27.75%; found: C, 36.07; H, 1.35; Br, 35.06; S, 27.58%.

Preparation of 6

2 (1.38 g, 3 mmol) and tributyl(5-hexylthiophen-2-yl)stannane (9.16 g, 20 mmol) were dissolved in toluene (300 mL). The mixture was bubbled with nitrogen for 30 min. Bis(triphenylphosphine)-palladium(n)chloride (226 mg, 0.3 mmol) was then added. The mixture was heated to 120 °C for 48 hours under a nitrogen atmosphere. The reaction was cooled to room temperature and the toluene was removed. The obtained solids were purified by multiple Soxhlet extraction using methanol and ethanol. The solvent of ethanol was removed to give yellow solid. Recrystallization from ethanol gave yellow solids. 1.8 g (75%), mp: 75 °C. MALDI-TOF: 804.2; ¹H NMR (400 MHz, acetone- d_6): $\delta = 7.14$ (d, J = 3.6 Hz, 2H), 7.10 (d, J = 3.6 Hz, 2H), 6.89 (d, J = 3.6 Hz, 2H), 6.84 (d, J = 3.2 Hz, 2H), 2.82–2.89 (m, 8H), 1.64–1.74 (m, 8H), 1.39–1.44 (m, 24H),

1.33–1.36 (m, 12H) ppm; anal. calcd for $C_{46}H_{60}S_6$: C, 68.60; H, 7.51; S, 23.89; found: C, 68.42; H, 7.59; S, 24.15%.

X-ray crystallography

Crystallographic data for 3: chemical formula: C₃₀H₂₀S₂; formula weight (M): 444.58; temperature: 293(2) K; monoclinic; $P2_1/c$; a = 6.1134(12), b = 12.529(3), c = 14.622(3) Å, $\alpha = 90.00^\circ$, $\beta = 92.51(3)^{\circ}$, $\gamma = 90.00^{\circ}$; V = 1118.9(4) Å³; Z = 2; $\rho_{calcd} = 1.320$ g cm^{-3} ; number of reflections collected: 11 099; final *R* = 0.0444, wR = 0.1151. Crystallographic data for 4: chemical formula: $C_{22}H_{12}S_6$; formula weight (M): 468.68; temperature: 113(2); monoclinic; $P2_1/n$; a = 6.1799(12), b = 7.6986(15), c =21.307(4) Å, $\alpha = 90.00^{\circ}$, $\beta = 97.69(3)^{\circ}$, $\gamma = 90.00^{\circ}$; V =1004.6(3) Å³; Z = 2; $\rho_{calcd} = 1.549 \text{ g cm}^{-3}$; number of reflections collected: 6086; final R = 0.1182, wR = 0.3378. Crystallographic data for 5: chemical formula: $C_{14}H_6Br_2S_4$; formula weight (*M*): 462.25; temperature: 113(2); monoclinic; $P2_1/c$; a = 3.9007(11), b = 11.814(3), c = 15.453(3) Å, $\alpha = 90.00^{\circ}, \beta = 94.644(14)^{\circ}, \gamma =$ 90.00°; V = 709.8(3) Å³; Z = 2; ρ_{calcd} = 2.163 g cm⁻³; number of reflections collected: 1223; final R = 0.0971, wR = 0.2700. From the crystallographic data of compound 5, it is found that there is a large and unexplained residual electron density of 2.65 in this structure, located at (0.0656, 0.7156, 0.0961) and at a distance of 1.29 Å from the Br atoms.

Results and discussion

Thieno[3,2-b]thiophene $(1)^{10}$ was chosen as the parent compound and was easily converted to 2,3,5,6-tetrabromothieno[3,2-b]thiophene (2) in high yield with bromine (Br_2) -CHCl₃.¹¹ The target compound 3 was then assembled via palladium-catalyzed Suzuki coupling reactions of 2 with phenylboronic acid under reflux for 24 h in the aqueous K₂CO₃ and tetrahydrofuran (THF) in 56% yield. This is a new method to synthesize compound 3, which avoids the photochemical reaction conditions and bothersome purification steps that previous methods suffered from.12,13 The target compounds 4 and 5 were obtained via Suzuki coupling reactions of 2 with α -thiopheneboronic acid in different ratios. Compound 6 was synthesized via an excess of tributyl(5-hexylthiophen-2-yl)stannane¹⁴ with compound 2 to ensure completion of the Stillecoupling reaction in 75% yield. The solubility of compound 6 is the best in this series of target compounds, while compounds 4 and 5 are slightly soluble in common organic solvents (such as CHCl₃ and THF). The target compounds were characterized by NMR spectroscopy, mass spectrometry (MS), and elemental analysis.

The thermal properties of the new thieno[3,2-*b*]thiophene oligomers have been evaluated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under an argon atmosphere. TGA measurements were carried out on a TA SDT 2960 instrument under a dry nitrogen flow, heating from room temperature to 550 °C, at a heating rate of 10 °C min⁻¹. DSC analyses were performed on a TA DSC 2010 instrument under a dry N₂ flow at a heating rate of 10 °C min⁻¹. All compounds showed significant thermal stability (T_d), with 2% weight loss, values higher than 275 °C. The T_d

values of compounds **3** and **4** were 319 °C and 346 °C respectively. Compound **5** demonstrated the lowest stability ($T_d = 275$ °C) due to the presence of two bromo-moieties. In contrast, compound **6** bearing four 2-hexylthiophene units between the thieno[3,2-*b*]thiophene, exhibited the decomposition temperature as high as 406 °C. The heating and cooling DSC scans of the compound **3** show no glass transitions from room temperature up to 275 °C, due to dense molecular packing.^{15,16} DSC analysis revealed that compounds **4** and **5** exhibit reversible thermal transitions at 250 °C and 235 °C, respectively. Compound **6** containing four hexyl chains exhibited a lower melting point at 75 °C than compounds **4** and **5**.

Because of their virtual insolubility in organic solvents, compounds **3**, **4** and **5** were purified by gradient sublimation along a temperature gradient of 250–180–100 °C at 10^{-2} Pa in a N₂ atmosphere. X-ray crystal structure measurements were carried out in the reflection mode using a Rigaku MM-007 X-ray diffraction system (Mo-K α radiation, $\lambda = 0.71073$ Å). The resulting colorless crystal block of **3**, the yellow crystal block of **4** and the yellow crystal prism of **5** were suitable for X-ray analysis.

As shown in Fig. 1, all molecules display an inner flat, symmetric molecular geometry, while the peripheral phenyl or thienyl units adopt twisted forms, connecting with the thieno[3,2-b]thiophene like a flying butterfly. The three molecular structures lie about an inversion center at the mid-point of the central C-C bond of the thieno[3,2-b]thiophene. The dihedral angles of 35.8° and 59.4° are observed between the thieno[3,2-b]thiophene and phenyl rings in molecule 3, and 22.0° and 77.8° between the thieno [3,2-b] thiophene and thienyl rings in molecule 4, and 7.6° between the thieno [3,2-b] thiophene and thienyl rings in molecule 5. The molecular sheets for compound 3 piled up in the a-axis direction, and formed a columnar stacking with an interplanar separation of 3.85 Å (Fig. 1a). Between the stacks, the interaction is reinforced by close intermolecular C–H··· π contacts, which are significantly different from intermolecular S···S contacts found in most other fused thiophenes.^{17–19} From Fig. 1b, a peculiar structural feature of the compound 4 was prepared with disordered S atoms. Interestingly, the four thiophene rings at the α - and β positions of the central unit can freely form a syn- or anticlinal conformation. The population ratio is about 68:32 for the ring connected to C2 and 89:11 for the ring connected to C3 from the crystal data. A similar situation has been observed for the tetrathienylthiophene system.²⁰ One of the conformations in the molecule 4 was S atoms in four thienyl arms facing each other (Fig. 1e) and the other in the opposite direction (Fig. 1d).

As shown in Fig. 2, ¹H NMR spectra reveal the two sets of protons with a splitting characteristic for the thiophene unit because the protons of the two thiophenes at α - (2,5 position of thieno[3,2-*b*]thiophene core) and β -positions (3,6 position of thieno[3,2-*b*]thiophene core) are not equivalent (labelled a-c and a'-c'), because the protons of the thienyl arms at the α -positions are more involved in conjugation with the central core than those at the β -position. This is confirmed by the difference in the corresponding dihedral angles between the plane of the core and that of the arms.



Fig. 1 Crystal structures of **3** (a), **4** (b, d, e), and **5** (c) with 40% probability ellipsoids. [Hydrogen atoms were omitted for clarity in (a) and (b). Symmetry operators indicated by "A" in the atom labels: (-x, 1 - y, 1 - z) for compound **3**; (1 - x, 2 - y, -z) for compound **4**; (1 - x, 1 - y, -z) for compound **5**.]



The optical absorption spectra of compounds **3–6** in THF solutions are shown in Fig. 3. Compounds **3**, **4**, **5**, and **6** exhibit maximum absorption at 339, 361, 367, and 374 nm, respectively, but a shoulder peak appears in the spectra at 275 nm for compound **4** and at 290 nm for compound **6**. Compounds **4** and **6** all have oligothiophene branches (thiophene or 2-hexylthiophene). The connection between each thiophene unit includes α - and β -position linkages with the thieno[3,2-*b*]thiophene core. The α -linkage thiophene segment provides the best π -electron conjugation, and β -linkages between the branches may lead to the shoulder peaks, which is in agreement with previously reported related research on substituted thiophene substituted compound **6** exhibit a small redshift similar to that of



Fig. 3 Normalized absorption spectra of compounds $\ensuremath{\textbf{3-6}}$ in tetrahydrofuran solution.

thiophene substituted compound **4**. In contrast to their absorption spectra, only one emission peak was observed in the emission spectra of these compounds. The emission peaks shift from 420 to 593 nm upon gradually changing the conjugated branches. These results demonstrate that the compounds can be electronically fine-tuned by manipulating the branch segments. The optical bandgap of the compounds can be deduced from the longest-wavelength absorption edge. The band gaps of **4**, **5**, and **6** with thiophene units (2.92, 2.98, and 2.82 eV, respectively) are narrow compared to that of phenyl units **3** (3.23 eV).

The electronic properties of these compounds were investigated by cyclic voltammetry (CV). CV measurements were carried out on a computer-controlled CHI660C instrument at RT using vacuumdeposited thin film (thickness of the oligomer: 10 nm) onto indium tin oxide (ITO)-coated glass as a working electrode in order to estimate the oxidative stability of thin films of the oligomers. A platinum rod was used as a counter electrode, Ag/AgCl as a reference electrode, dichloromethane (dried by distillation over CaH₂) as a solvent and 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte, the scan rate being 100 mV s⁻¹. The CV plots displaying oxidation processes and reduction potentials below zero voltage could not be observed, which are shown in Fig. 4. We could see that the highest occupied molecular orbital (HOMO) levels of the four compounds show a slight increase as the number of thiophene rings increases. The HOMO level is raised in energy by -5.61, -5.37, -5.55 and -5.28 eV, whereas the LUMO level is estimated to be -2.38, -2.45, -2.57 and -2.46 eV in 3, 4, 5, and 6, respectively.

For all four monomers, multiple potential scans on the ITO electrode were carried out. No polymerization was observed for phenyl end-caped compound 3 and the α -position-blocked compound 6. This result is not surprising because it is wellknown that polymerization takes place easily at the α -position of thiophenes.^{21–24} As shown in Fig. 4, compounds 4 and 5 are more susceptible to being deposited as polymer films on the electrodes by potential cycling. The electrochemical studies of the films of poly(4) (the polymers of 4) and poly(5) (the polymers of 5) both showed switching from yellow, brown to purple in color. The gradual increase in the current response and the new broad peak observed at lower potentials are typical characteristics of conducting-polymer formation on the electrode surfaces.²⁵⁻³¹ The onset oxidation potentials of poly(4) and poly(5) are higher than those of the monomers 4 and 5. Moreover, the electrochemical processes of the films are very stable, with no obvious changes in the cyclic voltammetry during subsequent repeat scanning.

For optical studies, monomer 5 was electropolymerized on an indium tin oxide (ITO) transparent electrode under different



Fig. 4 Cyclic voltammograms of compounds 3-6 in CH₂Cl₂ (a). Electropolymerization of 4 (b) and 5 (c), repeat potential scanning 10 cycles.



Fig. 5 UV-vis absorption spectra of poly(5) films deposited on ITO.

polymerization conditions. Fig. 5 shows the absorption spectra of the poly(5) films deposited by cyclic voltammetry over 2, 5, and 10 cycles. In this way, the photophysical properties of the polymers could be investigated under different polymerization conditions. The red-shift of the absorption and band broadening indicate that the polymers have an extended conjugation system compared to the monomers. The absorption maxima of the polymers are all quite close to that of polyalkylthiophenes (434 nm).³² The results suggest the formation of the dendritic hyperbranched polythiophenes. Because of the ease of synthesis of the monomer, larger quantities of polymers are likely to be achieved by chemical polymerization with iron(m) chloride and this is currently under investigation.

Conclusions

A series of new conjugated oligomers based on the thieno[3,2-*b*]thiophene core with phenyl and thiophene units were successfully synthesized by a facile synthetic route and could be described as having a butterfly-like shape. The synthetic route would also be applicable to the preparation of various functional materials by modifying thieno[3,2-*b*]thiophene. It was demonstrated that the optical and thermal properties of these materials can be fine-tuned by varying both substituents and the conjugation length. Moreover, the molecular structures have an inversion center at the mid-point of the central C–C bond of the thieno[3,2-*b*]thiophene. The crystals of 4 freely formed a *syn-* or *anticlinal* conformation. The thiophene functionalized monomers are susceptible to being deposited by electropolymerization, which results in the formation of electroactive polymers.

References

- 1 Y. Liu, C.-a. Di, C. Du, Y. Q. Liu, K. Lu, W. Qiu and G. Yu, *Chem.-Eur. J.*, 2010, **16**, 2231.
- 2 H.-S. Kim, Y.-H. Kim, T.-H. Kim, Y.-Y. No, S. Pyo, M. H. Yi, D. Y. Kim and S.-K. Kwon, *Chem. Mater.*, 2007, **19**, 3561.
- 3 P. Liu, Y. Wu, H. L. Pan, Y. N. Li, S. Gardner, B. S. Ong and S. P. Zhu, *Chem. Mater.*, 2009, 21, 2727.
- 4 Y.-Y. Noh, R. Azumi, M. Goto, B.-J. Jung, E. Lim, H.-K. Shim,
 Y. Yoshida, K. Yase and D.-Y. Kim, *Chem. Mater.*, 2005,
 17, 3861.

- 5 E. Lim, B.-J. Jung, J. Lee, H.-K. Shim, J.-I. Lee, Y. S. Yang and L.-M. Do, *Macromolecules*, 2005, 38, 4531.
- 6 I. Mcculloch, M. Heeney, C. Bailey, K. Genevicius,
 I. Macdonald, M. Shkunov, D. Sparrowe, S. Tierney,
 R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline,
 M. D. Mcgehee and M. F. Toney, *Nat. Mater.*, 2006, 5, 328.
- 7 J. H. Seo, E. B. Namdas, A. Gutacker, A. J. Heeger and G. C. Bazan, *Adv. Funct. Mater.*, 2011, 21, 3667.
- 8 W. Tang, L. Ke, L. Tan, T. Lin, T. Kietzke and Z.-K. Chen, *Macromolecules*, 2007, **40**, 6164.
- 9 H. Bronstein, Z. Chen, R. S. Ashraf, W. Zhang, J. Du, J. R. Durrant, P. S. Tuladhar, K. Song, S. E. Watkins, Y. Geerts, M. M. Wienk, R. A. J. Janssen, T. Anthopoulos, H. Sirringhaus, M. Heeneynad and I. McCulloch, *J. Am. Chem. Soc.*, 2011, **133**, 3272.
- 10 S.-H. Jung, H. K. Kim, S.-H. Kim, Y. H. Kim, S. C. Jeoung and D. Kim, *Macromolecules*, 2000, 33, 9277.
- 11 L. S. Fuller, B. Iddon and K. A. Smith, *J. Chem. Soc., Perkin Trans.* 1, 1997, 3465.
- N. Matsumura, H. Tanaka, Y. Yagyu, K. Mizuno, H. Inoue, K. Takada, M. Yasui and F. Iwasaki, *J. Org. Chem.*, 1998, 63, 163.
- 13 S. Singh, M. M. Bhadbhade, K. Venkatesan and V. Ramamurthy, *J. Org. Chem.*, 1982, 47, 3550.
- 14 J. L. Brusso, O. D. Hirst, A. Dadvand, S. Ganesan, F. Cicoira, C. M. Robertson, R. T. Oakley, F. Rosei and D. F. Perepichka, *Chem. Mater.*, 2008, 20, 2484.
- 15 T. Qi, Y. Q. Liu, W. Qiu, H. Zhang, X. Gao, Y. Liu, K. Lu, C. Du, G. Yu and D. Zhu, *J. Mater. Chem.*, 2008, 18, 1131.
- 16 S. Yao and K. D. Belfield, J. Org. Chem., 2005, 70, 5126.
- X.-C. Li, H. Sirringhaus, F. Garnier, A. B. Holmes, S. C. Moratti, N. Feeder, W. Clegg, S. J. Teat and R. H. Friend, *J. Am. Chem. Soc.*, 1998, **120**, 2206.

- 18 Y. Mazaki and K. Kobayashi, J. Chem. Soc., Perkin Trans. 2, 1992, 761.
- 19 Y. Liu, Y. Wang, W. Wu, Y. Liu, H. Xi, L. Wang, W. Qiu, K. Lu, C. Du and G. Yu, *Adv. Funct. Mater.*, 2009, **19**, 772.
- 20 T. Benincori, V. Bonometti, F. De Angelis, L. Falciola, M. Muccini, P. R. Mussini, T. Pilati, G. Rampinini, S. Rizzo, S. Toffanin and F. Sannicol, *Chem.-Eur. J.*, 2010, 16, 9086.
- 21 P. Leriche, F. Piron, E. Ripaud, P. Frère, M. Allain and J. Roncali, *Tetrahedron Lett.*, 2009, **50**, 5673.
- 22 T. Taerum, O. Lukoyanova, R. G. Wylie and D. F. Perepichka, *Org. Lett.*, 2009, **11**, 3230.
- 23 B. C. Thompson, K. A. Abboud, J. R. Reynolds, K. Nakatani and P. Audebert, *New J. Chem.*, 2005, **29**, 1128.
- 24 X. Sun, Y. Q. Liu, S. Chen, W. Qiu, G. Yu, Y. Ma, T. Qi,
 H. Zhang, X. Xu and D. Zhu, *Adv. Funct. Mater.*, 2006, 16, 917.
- 25 G. E. Collis and A. K. Burrell, J. Org. Chem., 2003, 68, 8974.
- 26 P. Audebert, J. M. Catel, G. Le Coustumer, V. Ducheneta and P. Hapiot, *J. Phys. Chem. B*, 1998, **102**, 8661.
- 27 E. A. Dragu, S. Nica, M. Raicopol, A. Baran, D.-F. Anghel,
 B. Cojocaru, L. Tarko and A. C. Razus, *Tetrahedron Lett.*, 2012, 53, 2611.
- 28 J. L. Reddinger and J. R. Reynolds, Chem. Mater., 1998, 10, 1236.
- 29 S. Y. Jang, G. A. Sotzing and M. Marquez, *Macromolecules*, 2002, **35**, 7293.
- 30 C. O. Too, G. G. Wallace, A. K. Burrell, G. E. Collis, D. L. Officer, E. W. Boge, S. G. Brodie and E. J. Evans, *Synth. Met.*, 2001, **123**, 53.
- 31 S. Scheib and P. Bauerle, J. Mater. Chem., 1999, 9, 2139.
- 32 J. Pei, J. L. Wang, X. Y. Cao, X. H. Zhou and W. B. Zhang, J. Am. Chem. Soc., 2003, 125, 9944.