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Synthesis of linear monodisperse vinylene-linked phenothiazine oligomers

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Abstract—A series of linear monodisperse vinylene-linked phenothiazine oligomers have been synthesized by alternate Heck reaction and Wittig reaction in good yields. It was found that their absorption and fluorescence emission bands red-shifted with increasing phenothiazine units due to extending of the conjugated degree. The fluorescent quantum yield increased from OPTZ1 to OPTZ6, and the Φ_F of OPTZ6 was close to phenothiazine-based polymers.

Conjugated oligomers have received much attention in recent years,[1] because they possess fascinating potential applications in organic light emitting diodes,[2] field-effected transistors,[3] and photovoltaic cells.[4] Monodisperse conjugated oligomers have well-defined chemical structures,[5] so they become ideal models for understanding the structure–property relationships of the corresponding polymers.[6] Many oligomers with desired function have been synthesized, such as oligothiophenes,[7] oligocarbazoles,[8] oligofluorenes,[9] oligophenylenes,[10] oligoanilines,[11] and so on. It was well known that linear conjugated oligomers not only represent the simplest models of molecular wires, but also give low bandgaps (Eg), which may lead to true 'organic metals' or fabrication of LEDs operating in the IR.[12]

Phenothiazine is a well-known pharmaceutical compound bearing electron-rich sulfur and nitrogen heteroatoms. In one hand, it has low oxidation potentials, and stable radical cation can be easily generated.[13] In another hand, the phenothiazine ring is nonplanar with a butterfly conformation in the ground state, which is quite different from carbazole and fluorene.[14] Such special conformation can impede the molecular aggregation and the formation of intermolecular excimer, which may lead to promising electronic and optical properties.[15] For instance, phenothiazine has been used as electron donor in ECL (electrogenerated chemluminescence), and EL (electroluminescence) materials.[16–18] Müller's group reported the synthesis and the electronic properties of alkynylated phenothiazines and phenothiazinyl triads.[13b,c] Till now, linear monodisperse vinylene-linked oligophenothiazines have not been reported. Herein, we present the synthesis of a series of new linear π-conjugated phenothiazine oligomers (OPTZs **1**–**6**).

Stilbenoid OPTZs were prepared by alternate Heck reaction and Wittig reaction,[19] and the synthetic routes were illustrated in Scheme 1. In order to improve the solubility, we introduced octyl group into the 10-position of phenothiazine ring by N-alkylation reaction. Compound **1** (OPTZ1) was prepared in a yield of 92% through Wittig reaction between methyltriphenylphosphoniumiodine and 3-formyl-phenothiazine **7**, which was obtained from 10-octylphenothiazine via Vilsmeier reaction with a yield of 77%. Compound **13** (3-formyl-7-bromo-10-octylphenothiazine) was an important intermediate for us to extend the ethenyl phenothioazine units, and it can be gained by bromination of compound **7**.[14a] Then, compound **2** (OPTZ2) was synthesized from methyltriphenylphosphoniumiodine and FOPTZ2 **8**, which was prepared by Heck reaction of OPTZ1 and **13**, via Wittig reaction with a yield of 92%. Accordingly, using alternate Heck reaction and Wittig reaction, we gained OPTZs (compounds **3**–**6**) in good yields of

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Keywords: Phenothiazine; Oligomers; Heck reaction; Wittig reaction.

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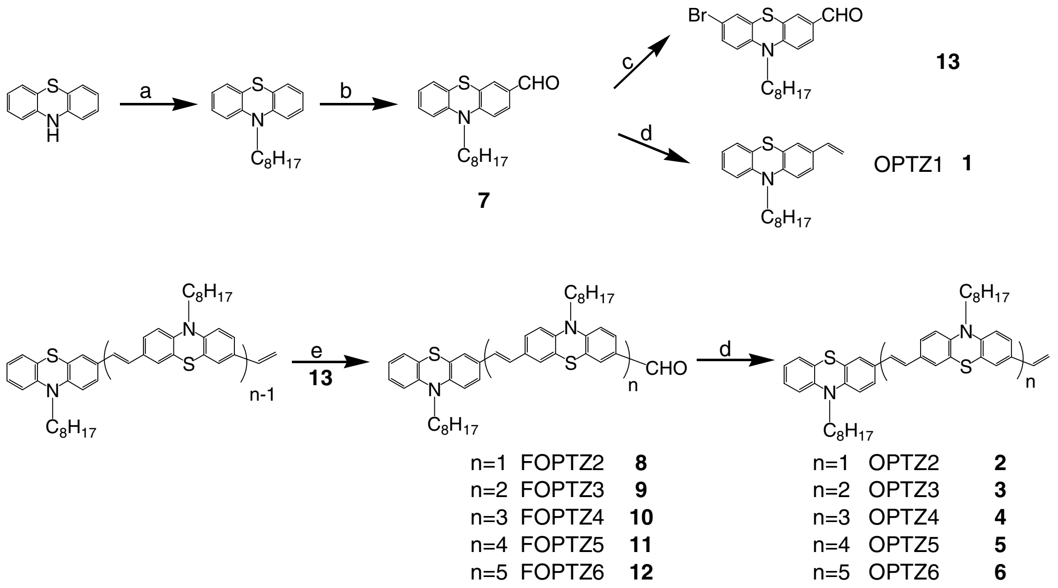

Scheme 1. Reagents and conditions: (a) NaH, DMF, *n*-$C_8H_{17}Br$, 0 °C, rt; (b) $POCl_3$, DMF, $ClCH_2CH_2Cl$, 90 °C; (c) Br_2, AcOH; (d) Ph_3PCH_3I, *t*-BuOK, THF, rt, 2 h; (e) $Pd(OAc)_2$, K_2CO_3, DMF, Bu_4NBr, 110 °C, 10 h.

91–92%. All the intermediates and the final products were purified by column chromatography and recrystallization, and they have good solubility in common solvents, including tetrahydrofuran, toluene, ethyl acetate, and dichloromethane. The molecular structures were characterized with FT-IR, ^{1}H NMR, elemental analysis, and MALDI/TOF mass spectroscopy.[20] The oligomers from OPTZ2 to OPTZ6 exhibit an IR absorption band around 960 cm^{-1} arising from the wagging vibration of the trans-double bond (C=C).[21,22] ^{1}H NMR spectra also confirmed that the vinylene groups were in trans-conformation because no peak appeared at 6.56 ppm assigned to the proton in cis-double bond (C=C).[9b,22] MALDI/TOF-MS spectra showed peaks matching the calculated molecular weight, and some fragmentation peaks were found due to the cleavage of *N*-octyl bond.[9d]

The UV–vis absorption spectra of OPTZs in dilute solutions (4×10^{-6} mol/L) were shown in Figure 1. It was clear that the absorption bands of OPTZ1 appeared at 270 nm and 320 nm. For OPTZ2-OPTZ6, the absorption bands red-shifted compared with those of OPTZ1, for example, the absorption bands of OPTZ2 were located at 276 and 396 nm, and 307 and 422 nm for OPTZ6, respectively (See Table S1). It suggested that the increase of phenothiazine–vinylene units resulted in the decrease of Eg due to extending of the conjugated length of oligomers. Furthermore, the mole extinction coefficient at 302 nm increased linearly from OPTZ1 to OPTZ6 (as shown in Fig. S1), while no deviation from the slope was observed. Combining with the fact that each oligomer obeyed Beer's law very well, we could deduce that no intermolecular π-interaction happened for these oligomers in dilute solutions. Figure 2 shows the normalized absorption spectra of OPTZs in the films, similar red-shift behaviors of the absorption bands were observed from OPTZ1 to OPTZ6. In addition, the absorption bands of OPTZs in the film red-shifted more than ca. 15 nm compared with those in the corresponding solutions, suggesting the formation of π-aggregations in the solid states. Figure 3 shows the

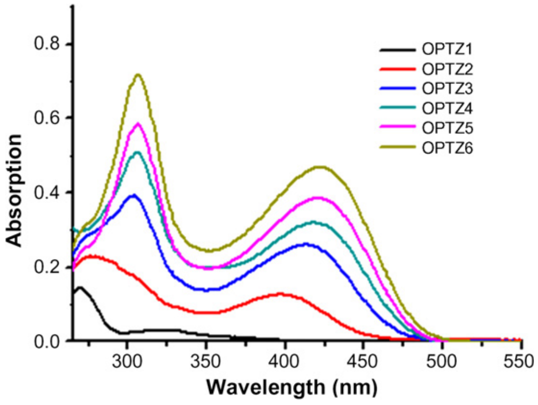

Figure 1. UV–vis absorption spectra of OPTZs in THF (4×10^{-6} mol/L).

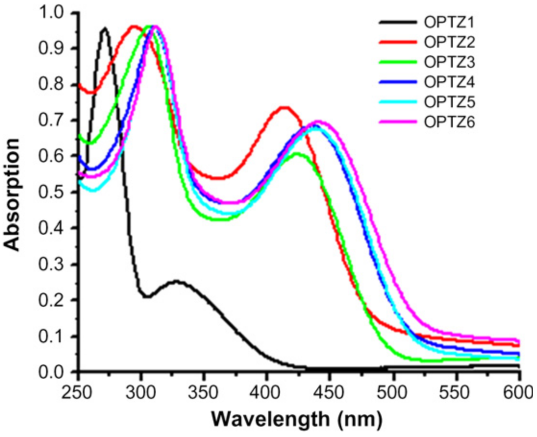

Figure 2. Normalized UV–vis absorption spectra of OPTZs in the films.

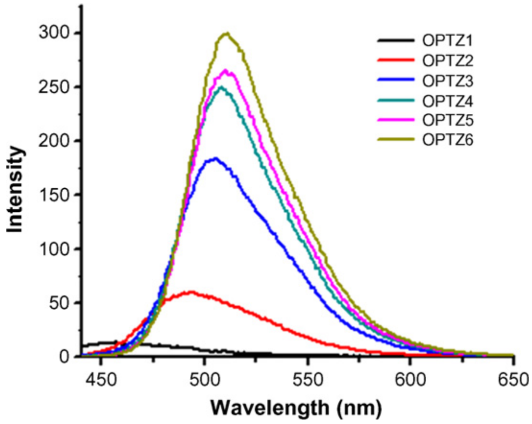

Figure 3. Fluorescence emission spectra of OPTZs in THF (4×10^{-6} mol/L).

fluorescence emission spectra of OPTZs in THF (4×10^{-6} mol/L). It was found that the emission bands of OPTZ2-OPTZ6 red-shifted from that of OPTZ1 because of enlarging of the conjugated degree. The fluorescence intensity enhanced more significantly from OPTZ1 to OPTZ4, and less from OPTZ4 to OPTZ6. Therefore, we deemed that molecular coplanation could be increased by introduction of vinylene unit,[14c] but its increased degree might be saturated when the conjugated chain was enlarged to a certain extent. The fluorescence emission bands of the oligomers in the films also red-shifted compared with those in the dilute solutions as shown in Figure 4. The fluorescent quantum yield was measured in THF with quinine sulfate as the standard (see Table 1), and it increased from OPTZ1 to OPTZ6. The Φ_F of OPTZ6 was very close to phenothiazine-based polymers.[14b,c]

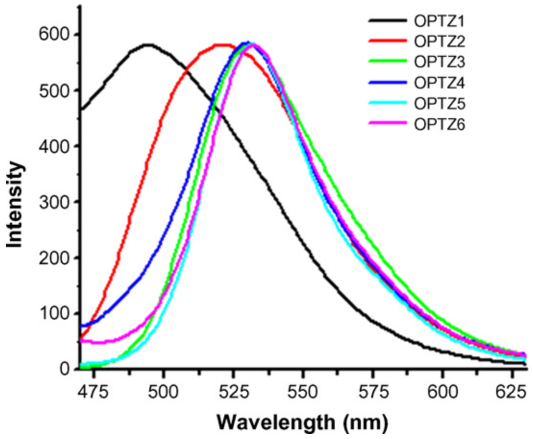

Figure 4. Normalized fluorescence emission spectra of OPTZs in the films.

Table 1. Fluorescence quantum yields (Φ_F) of OPTZs in THF

Oligomers	OPTZ1	OPTZ2	OPTZ3	OPTZ4	OPTZ5	OPTZ6
Φ_F[a]	0.20	0.28	0.35	0.37	0.36	0.41

[a] The fluorescence quantum yields were determined against quinine sulfate in 0.1 N H_2SO_4 ($\Phi_F = 0.546$) as the standard, $\lambda_{ex} = 365$ nm.

In conclusion, we presented a facile synthesis of novel linear vinylene-linked phenothiazine oligomers by alternate Heck reaction and Wittig reaction in good yields. Their absorption bands as well as fluorescence emission ones exhibited red-shift with increasing phenothiazine–vinylene units because of the enlargement of the conjugated degree. The strong photoluminescence of oligomers reveals that they possess potential application in optical devices.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.09.002.

References and notes

1. (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537–554; (b) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350–1377; (c) Schwab, P. F. H.; Smith, J. R.; Michl, J. *Chem. Rev.* **2005**, *105*, 1197–1280; (d) Roncali, J. *Acc. Chem. Res.* **2000**, *33*, 147–156.
2. Van Hutten, P. F.; Wideman, J.; Meetsma, A.; Hadziioannou, G. *J. Am. Chem. Soc.* **1999**, *121*, 5910–5918.
3. (a) Katz, H. E. *J. Mater. Chem.* **1997**, *7*, 369–376; (b) Schon, J. H.; Dodabalapur, A.; Kloc, C.; Batlogg, B. *Science* **2000**, *290*, 963–965; (c) Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716–8721.
4. (a) de la Cruz, J. L. D.; Hahn, U.; Nierengarten, J. F. *Tetrahedron Lett.* **2006**, *47*, 3715–3718; (b) Eckert, J. F.; Nicoud, J. F.; Nierengarten, J. F.; Liu, S. G.; Echegoyen, L.; Barigelletti, F.; Armaroli, N.; Ouali, L.; Krasnikov, V.; Hadzioannou, G. *J. Am. Chem. Soc.* **2000**, *122*, 7467–7479.
5. Frere, P.; Raimundo, J. M.; Blanchard, P.; Delaunay, J.; Richomme, P.; Sauvajol, J. L.; Orduna, J.; Garin, J.; Roncali, J. *J. Org. Chem.* **2003**, *68*, 7254–7265.
6. *Electronic Materials: The oligomer approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1997.
7. (a) Elandaloussi, E. H.; Frère, P.; Richomme, P.; Orduna, J.; Garin, J.; Roncali, J. *J. Am. Chem. Soc.* **1997**, *119*, 10774–10784; (b) Jestin, I.; Frère, P.; Blanchard, P.; Roncali, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 942–945; (c) Jestin, I.; Frère, P.; Mercier, N.; Levillain, E.; Stievenard, D.; Roncali, J. *J. Am. Chem. Soc.* **1998**, *120*, 8150–8158.
8. (a) Xu, T. H.; Lu, R.; Jin, M.; Qiu, X. P.; Xue, P. C.; Bao, C. Y.; Zhao, Y. Y. *Tetrahedron Lett.* **2005**, *46*, 6883–6886; (b) Xu, T. H.; Lu, R.; Liu, X. L.; Zheng, X. Q.; Qiu, X. P.; Zhao, Y. Y. *Org. Lett.* **2007**, *9*, 797–800; (c) Xu, T. H.; Lu, R.; Qiu, X. P.; Liu, X. L.; Xue, P. C.; Tan, C. H.; Bao, C. Y.; Zhao, Y. Y. *Eur. J. Org. Chem.* **2006**, 4014–4020; (d) Zhao, Z. J.; Zhao, Y. X.; Lu, P.; Tian, W. J. *J. Phys. Chem. C* **2007**, *111*, 6883–6888.

9. (a) Li, B. S.; Li, J.; Fu, Y. Q.; Bo, Z. S. *J. Am. Chem. Soc.* **2004**, *126*, 3430–3431; (b) Liu, Q.; Liu, W. M.; Yao, B.; Tian, H. K.; Xie, Z. Y.; Geng, Y. H.; Wang, F. S. *Macromolecules* **2007**, *40*, 1851–1857; (c) Lee, S. H.; Nakamura, T.; Tsutsui, T. *Org. Lett.* **2001**, *3*, 2005–2007; (d) Kanibolotsky, A. L.; Berridge, R.; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. *J. Am. Chem. Soc.* **2004**, *126*, 13695–13702.
10. (a) Wang, S. J.; Oldham, W. J.; Hudack, R. A.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695–5709; (b) Gomez-Escalonilla, M. J.; Langa, F.; Rueff, J. M.; Oswald, L.; Nierengarten, J. F. *Tetrahedron Lett.* **2002**, *43*, 7507–7511.
11. Louie, J.; Hartwig, J. F. *Macromolecules* **1998**, *31*, 6737–6739.
12. (a) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89–112; (b) Roncali, J. *Chem. Rev.* **1997**, *97*, 173–206; (c) Baigent, D. R.; Hamer, P. J.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1995**, *71*, 2175.
13. (a) Okamoto, T.; Kuratsu, M.; Kozaki, M.; Hirotsu, K.; Ichimura, A.; Matsushita, T.; Okada, K. *Org. Lett.* **2004**, *6*, 3493–3496; (b) Krämer, C. S.; Zeitler, K.; Müller, T. J. J. *Tetrahedron lett.* **2001**, *42*, 8619–8624; (c) Krämer, C. S.; Müller, T. J. J. *Eur. J. Org. Chem.* **2003**, *18*, 3534–3548.
14. (a) Krämer, C. S.; Zeitler, K.; Müller, T. J. J. *Org. Lett.* **2000**, *2*, 3723–3726; (b) Kong, X. X.; Kulkarni, A. P.; Jenekhe, S. A. *Macromolecules* **2003**, *36*, 8992–8999; (c) Wu, T. Y.; Chen, Y. *J. Polym. Sci., Part A: Chem.* **2002**, *40*, 4452–4462; (d) Hwang, D. H.; Park, M. J.; Lee, C. H. *Synth. Met.* **2005**, *152*, 205–208.
15. (a) Sailer, M.; Rominger, F.; Müller, T. J. J. *J. Organomet. Chem.* **2006**, *691*, 299–308; (b) Zhang, X. H.; Choi, S. H.; Choi, D. H.; Ahn, K. H. *Tetrahedron Lett.* **2005**, *46*, 5273–5276; (c) Cho, N. S.; Park, J. H.; Lee, S. K.; Lee, J.; Shim, H. K.; Park, M. J.; Hwang, D. H.; Jung, B. J. *Macromolecules* **2006**, *39*, 177–183; (d) Sun, X. B.; Liu, Y. Q.; Xu, X. J.; Yang, C. H.; Yu, G.; Chen, S. Y.; Zhao, Z. H.; Qiu, W. F.; Li, Y. F.; Zhu, D. B. *J. Phys. Chem. B* **2005**, *109*, 10786–10792.
16. (a) Bucci, N.; Müller, T. J. J. *Tetrahedron Lett.* **2006**, *47*, 8323–8327; (b) Bucci, N.; Müller, T. J. J. *Tetrahedron Lett.* **2006**, *47*, 8329–8332.
17. (a) Lai, R. Y.; Fabrizio, E. F.; Lu, L. D.; Jenekhe, S. A.; Bard, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 9112–9118; (b) Lai, R. Y.; Kong, X. X.; Jenekhe, S. A.; Bard, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 12631–12639; (c) Kulkarni, A. P.; Wu, P. T.; Kwon, T. W.; Jenekhe, S. A. *J. Phys. Chem. B* **2005**, *109*, 19584–19594.
18. (a) Kim, G. W.; Cho, M. J.; Yu, Y. J.; Kim, Z. H.; Jin, J. I.; Kim, D. Y.; Choi, D. H. *Chem. Mater.* **2007**, *19*, 42–50; (b) Hwang, D. H.; Kim, S. K.; Park, M. J.; Lee, J. H.; Koo, B. W.; Kang, I. N.; Kim, S. H.; Zyung, T. *Chem. Mater.* **2004**, *16*, 1298–1303; (c) Fungo, F.; Jenekhe, S. A.; Bard, A. J. *Chem. Mater.* **2003**, *15*, 1264–1272.
19. (a) Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581; (b) Heck, H. F.; Nolley, J. P. *J. Org. Chem.* **1972**, *37*, 2320–2322; (c) Horner, L.; Hoffmann, H. G.; Klahre, G. *Chem. Ber.* **1959**, *92*, 2499.
20. Compound **1**: ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) $\delta = 7.25$–7.07 (4H, m), 6.95–6.73 (3H, m), 6.60–6.55 (1H, m), 5.61–5.58 (1H, d), 5.13–5.11 (1H, d), 3.87–3.77 (2H, m), 1.86–1.68 (2H, m), 1.46–1.36 (2H, m), 1.38–1.18 (8H, m), 0.93–0.81 (3H, t). IR (THF, cm^{-1}): 2931, 2854, 1465, 1334, 1249, 902, 818, 733. Elemental Anal. Calcd for $C_{22}H_{27}N_1S_1$: C, 78.29; H, 8.06; N, 4.15; S, 9.50. Found: C, 78.32; H, 8.05; N, 4.17. MS, *m*/*z*: calcd: 337.5, found: 337.3. Compound **2**: mp: 72.0–74.0 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm), $\delta = 7.25$–7.04 (8H, m), 6.91–6.88 (1H, m), 6.85–6.76 (6H, m), 6.61–6.55 (1H, m), 5.62–5.58 (1H, d), 5.14–5.11 (1H, d), 3.94–3.68 (4H, m), 1.82–1.74 (4H, m), 1.45–1.38 (4H, m), 1.33–1.21 (16H, m), 0.86 (6H, t). IR (KBr, cm^{-1}): 2916, 2850, 1601, 1469, 1367, 1240, 964, 910, 744. Elemental Anal. Calcd for $C_{44}H_{52}N_2S_2$: C, 78.52; H, 7.79; N, 4.16; S, 9.53. Found: C, 78.55; H, 7.86; N, 4.11. MS, *m*/*z*: calcd: 673.03, found: 673.9. Compound **3**: mp: 31.0–33.0 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) $\delta = 7.27$–7.03 (12H, m), 6.97–6.70 (11H, m), 6.61–6.55 (1H, m), 5.62–5.58 (1H, d), 5.14–5.12 (1H, d), 3.97–3.64 (6H, m),1.84–1.74 (6H, m), 1.45–1.38 (6H, m), 1.34–1.25 (24H,m), 0.90–0.84 (9H, t). IR (KBr, cm^{-1}): 2920, 2850, 1061, 1468, 1360, 1246, 955, 812, 744. Elemental Anal. Calcd for $C_{66}H_{77}N_3S_3$: C, 78.60; H, 7.70; N, 4.17; S, 9.54. Found: C, 78.81; H, 7.52; N, 4.19. MS, *m*/*z*: calcd: 1008.5, found: 1009.2. Compound **4**: mp: 128.0–130.0 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm), $\delta = 7.27$–7.11 (17H, m), 6.92–6.72 (14H, m), 6.61–6.55 (1H, m), 5.62–5.58 (1H, d), 5.14–5.12 (1H, d), 3.96–3.69 (8H, m), 1.84–1.76 (8H, m), 1.45–1.39 (8H, m), 1.34–1.21 (32H, m), 0.87 (12H, t). IR (KBr, cm^{-1}): 2924, 2852, 1601, 1475, 1362, 1255, 958, 814, 746. Elemental Anal. Calcd for $C_{88}H_{102}N_4S_4$: C, 78.64; H, 7.65; N, 4.17; S, 9.54. Found: C, 78.75; H, 7.59; N, 4.09. MS, *m*/*z*: calcd: 1344.0, found: 1344.2. Compound **5**: mp: 123.0–125.0 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) 7.28–7.04 (21H, m), 6.92–6.75 (18H, m), 6.61–6.55 (1H, m), 5.62–5.59 (1H, d), 5.14–5.12 (1H, d), 3.97–3.68 (10H, m), 1.84–1.76 (10H, m), 1.46–1.39 (10H, m), 1.34–1.22 (40H, m), 0.91–0.84 (15H, t). IR (KBr, cm^{-1}): 2922, 2852, 1601, 1475, 1362, 1254, 959, 812, 746. Elemental Anal. Calcd for $C_{110}H_{127}N_5S_5$: C, 78.66; H, 7.62; N, 4.17; S, 9.55. Found: C, 78.61; H, 7.76; N, 4.23. MS, *m*/*z*: calcd: 1679.5, found: 1679.3. Compound **6**: mp: 134.0–136.0 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm) $\delta = 7.27$–7.04 (27H, m), 6.93–6.71 (20H, m), 6.61–6.56 (1H, m),5.62–5.59 (1H, d), 5.14–5.12 (1H, d), 3.96–3.68 (12H, m), 1.84–1.76 (12H, m), 1.46–1.39 (12H, m),1.35–1.21 (48H, m), 0.91–0.83 (18H, t). IR (KBr, cm^{-1}): 2922, 2850, 1601, 1473, 1362, 1255, 957, 812, 746. Elemental Anal. Calcd for $C_{132}H_{152}N_6S_6$: C, 78.68; H, 7.60; N, 4.17; S, 9.55. Found: C, 78.77; H, 7.72; N, 4.13. MS, *m*/*z*: calcd: 2015.0, found: 2014.3.
21. (a) Wang, Q.; Yu, L. P. *J. Am. Chem. Soc.* **2000**, *122*, 11806–11811; (b) Mikroyannidis, J. A. *Chem. Mater.* **2003**, *15*, 1865–1871.
22. He, F.; Xia, H.; Tang, S.; Duan, Y.; Zeng, M.; Liu, L. L.; Li, M.; Zhang, H. Q.; Yang, B.; Ma, Y. G.; Liu, S. Y.; Shen, J. C. *J. Mater. Chem.* **2004**, *14*, 2735–2740.