Dyes and Pigments 81 (2009) 152–155

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

The synthesis and photochromic properties of two bis(phosphine) ligands based on dithienylethene backbone and their oxides, sulfurets and selenides

Jun Yin, Yan Lin, Xiufang Cao, Guang-Ao Yu, Haiyang Tu, Sheng Hua Liu*

Key Laboratory of Pesticide and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, PR China

ARTICLE INFO

Article history:
Received 27 July 2008
Received in revised form
7 October 2008
Accepted 7 October 2008
Available online 21 October 2008

Keywords:
Photochromics
Dithienylethene
Phosphine ligands
Oxides
Sulfurets
Selenides

ABSTRACT

A phosphor atom was introduced into photochromic dithienylethene and the corresponding dithienylethene bis(phosphine)ligands were obtained by the lithiation of 1,2-bis-(5-chloro-2-methylthien-3-yl) cyclopentene in the presence of *n*-butyllithium which were then reacted with Ph_2PCl or Cy_2PCl, respectively. The bis(phosphine)ligands were oxidised with H_2O_2, sulfurated by S_8 and selenated by Se and their structures were characterized.

1. Introduction

Photochromic compounds have attracted much attention due to their ability for optical memory media [1–10] and photo-optical switches [11–20]. Among various types of photochromic compounds, diarylethene is the most promising compounds for the application due to their thermally irreversible and fatigue resistant photochromic performance [21–34].

As a current research goal for photochromic dithienylethene is to develop novel structures and unique properties, an effective method is to modify the structure by functionalizing the group R in Fig. 1. Several papers have described the properties and application of diarylethene derivatives in which nitrogen ligands were used. [21–31] Branda and co-workers [35] synthesized a 1,2-dithienylethene compound bearing a bis(phosphine) group and indicated that this type of compound represented a new class of photo-responsive ligands and that steric and electronic differences existed between two photogenerated isomers. In this work, several dithienylethene bis(phosphine)ligands and derivatives were synthesized and their photochromic properties were investigated.

2. Results and discussion

2.1. Synthesis of dithienylethene bis(phosphine)ligands **2**, 3 and derivatives **4**–**9**

The dithienylethene bis(phosphine)ligands **2**, **3** and derivatives **4**–**9** were synthesized according to Fig. 2. 1,2-Bis-(5-chloro-2-methylthien-3-yl)cyclopentene [36] was reacted with *n*-butyllithium at room temperature and the ensuing compound was treated with Ph_2PCl (ed note: care required) and Cy_2PCl (ed note: care required) under an argon atmosphere to give **2** and **3**, in 85% and 82% yield, respectively. Then compounds **2** and **3** were oxidated by H_2O_2, sulfurated by S_8 and selenated by Se to give more stable derivatives **4**–**9** in 58–92% yields.

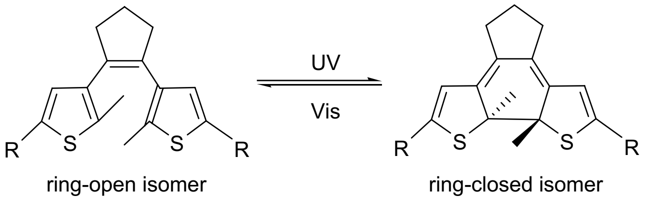

Fig. 1. Reversible photocyclization reactions of dithienylethene.

---

* Corresponding author. Tel./fax: +86 27 67867725.
E-mail address: chshliu@mail.ccnu.edu.cn (S.H. Liu).

0143-7208/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2008.10.006

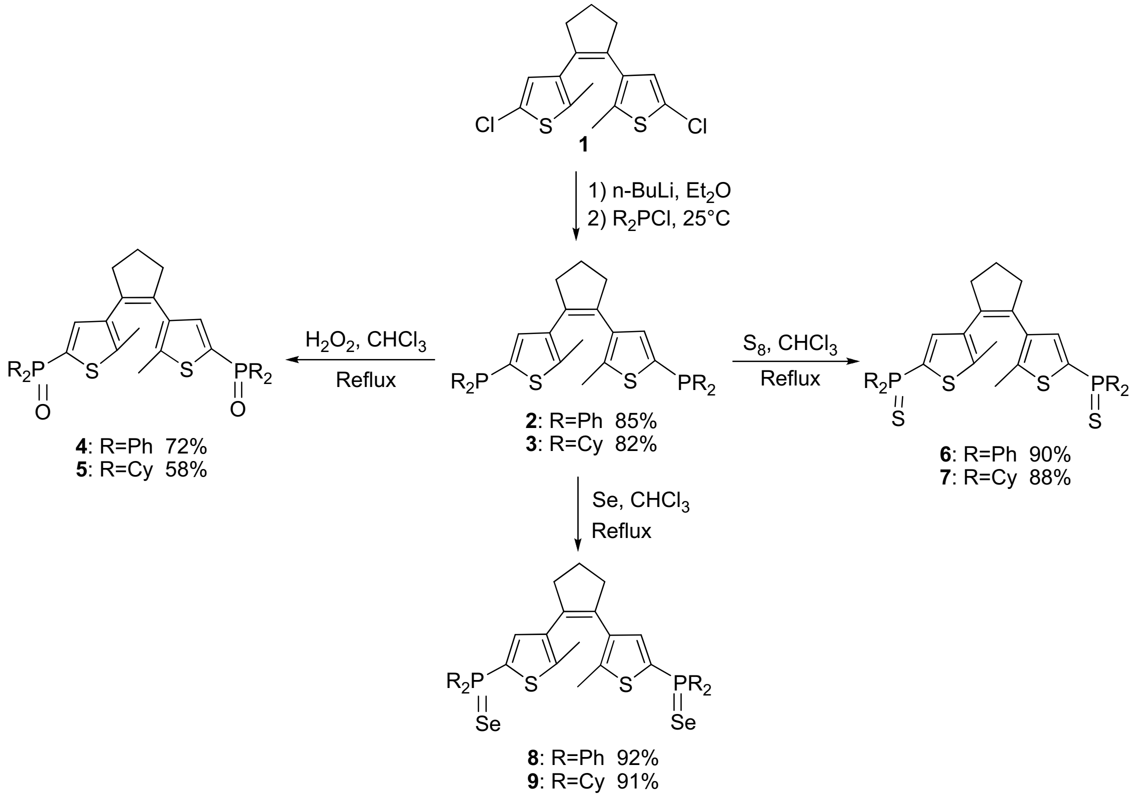

Fig. 2. Synthesis of dithienylethene bis(phosphine)ligands and derivatives **2**–**9**.

These compounds were characterized by NMR and elemental analyses. The ^{31}P NMR spectra of compounds **2** and **3** showed a singlet at −20.03 and −9.10 ppm. The derivatives **4**, **6** and **8** of diphenylphosphine ligands displayed a singlet at 19.75, 31.56 and 20.97 ppm shift, respectively. While the derivatives **5**, **7** and **9** of dicyclohexylphosphine ligand showed at 44.82, 53.68 and 45.76 ppm shift, respectively. The ^{31}P NMR spectra of compounds **2** and **8** are similar to those of corresponding compounds reported by Branda [35]. Furthermore, the ^{1}H NMR spectra of compounds **2**–**9** showed clearly that these compounds had C_2 symmetry. All the thienyl-H resonances of compounds **2**–**9** were doublet due to the effect of the phosphor atom, which was good in agreement with Branda's report [35].

2.2. Photochromic reaction

All synthesized dithienylethene compounds **2**~**9** undergo reversible photochromic reactions in dichloromethane by alternating irradiation with UV light and visible light with different wavelength cutoff filters. Fig. 3 shows the absorption spectra of bis(phosphine) ligand **3** induced by photoirradiation in dichloromethane. Upon irradiation with UV light, the increase of a new absorption bands were observed at 497 nm along with the decrease of the absorption band at 240 nm, which corresponds to the ring-closed form. Furthermore, the colorless dichloromethane solution turns into red immediately. In addition, a well defined isosbestic

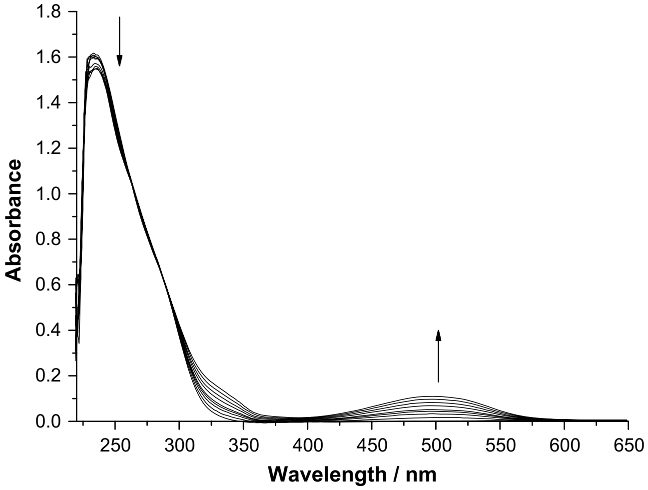

Fig. 3. UV/vis absorption spectra of compound **3** (2.0×10^{-5} mol/L) in CH_2Cl_2 upon irradiation with UV light at 0, 2, 4, 6, 8 s...

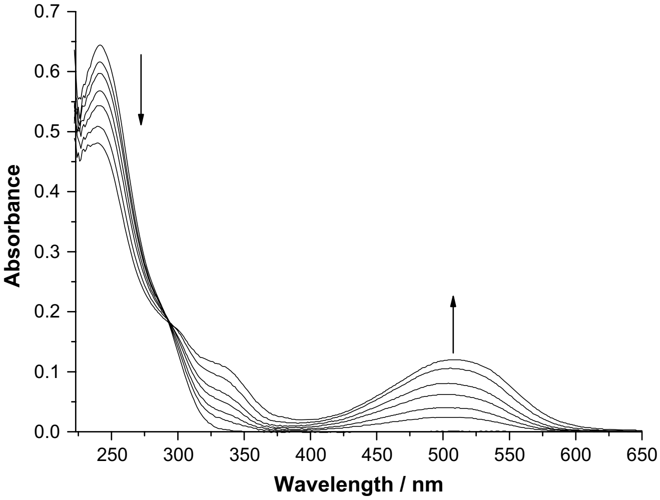

Fig. 4. UV/vis absorption spectra of compound **7** (2.0×10^{-5} mol/L) in CH_2Cl_2 upon irradiation with UV light at 0, 2, 4, 6, 8 s...

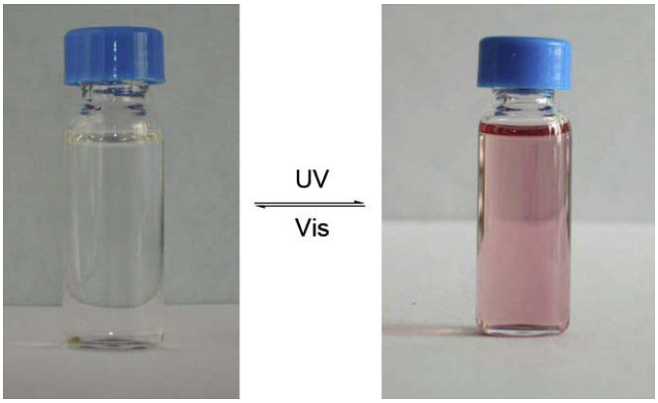

Fig. 5. Photograph of the color change of a CH_2Cl_2 solution of compound **7**.

point was observed at 284 nm, which indicated that compound **3** was clearly converted to a photocyclized product. Upon irradiation with light of a wavelength longer than 500 nm, the red solution reverted to colorless.

Just as for **3**, sulfuret **7** underwent photochromism upon irradiation with UV light in dichloromethane (Fig. 4). Before irradiation, compound **7** showed the absorption maximum at 241 nm. Upon irradiation with UV light, the dithienylethene transformed into ring-closed form at 505 nm and turns into red solution as shown in Fig. 5. Upon irradiation with light of wavelength longer than 510 nm, the red solution reverted to colorless. The data of absorption maximum for other compounds are summarized in Table 1.

HPLC is a suitable way to measure the ratios between the ring-open and closed forms of photochromic compounds. The ratio between the ring-open and closed forms of compound **2** can be obtained as 1.0:0.42 from the ratio of the integrated area of HPLC peaks. Similarly, the ratio between the ring-open and closed forms of compound **3** was 1.0:0.37. But the ratio between the ring-open and closed forms of compounds **4**–**9** have not been obtained because their ring-open and closed forms are difficult to be separated by HPLC.

The photocyclization and photocycloreversion quantum yields were measured for compounds **2**–**9** in dichloromethane (Table 2) according to a literature method [37]. The data in Table 2 show that their photocycloreversion quantum yields are higher than their photocyclization quantum yields, and the photocyclization and photocycloreversion quantum yields of compounds **6** and **7** are little higher than that of other compounds.

3. Conclusions

Compounds **2**–**9** display good photochromic behavior; further research efforts will focus on utilizing the excellent coordinative ability of the bis(phosphine) ligands to synthesize metallic complexes and explore their switching behavior.

4. Experimental

4.1. General procedures and starting materials

The manipulations were carried out at room temperature under an inert atmosphere of argon by using standard Schlenk techniques. The solvents were dried using standard procedures. 1,2-Bis-(5-chloro-2-methylthien-3-yl) cyclopentene was prepared according to literature [31]. All other chemicals were obtained from commercial sources without further purification. ^1H NMR (400 MHz), ^{13}C NMR (100.6 MHz) and ^{31}P NMR (121.5 MHz) spectra were collected on a Varian MERCURY Plus 400 spectrometer (400 MHz). ^1H and ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4.

Table 2
Photochemical quantum yields (Φ) of dithienylethene derivatives **2**–**9** in dichloromethane.

Compounds	$\Phi_{O\rightarrow C}$[a]	$\Phi_{C\rightarrow O}$[b]	Compounds	$\Phi_{O\rightarrow C}$[a]	$\Phi_{C\rightarrow O}$[b]
2	0.15	0.84	**3**	0.14	0.81
4	0.14	0.85	**5**	0.13	0.82
6	0.19	0.90	**7**	0.18	0.88
8	0.16	0.86	**9**	0.15	0.85

[a] Irradiation with 254 nm light.
[b] Irradiation with 510 nm light.

UV/vis spectra were recorded with Shimadzu UV-2550 spectrometer. Photoisomerization measurements were carried out under a PHK 125-W mercury lamp as an irradiation source. The ring-opening reactions were carried out using the light of a 200-W tungsten source that was passed through the appropriate cutoff filter to eliminate higher energy light. The distance between the sample and the lamp is 10 cm. HPLC analyses were determined by Agilen 1100.

*4.2. Bis(phosphine) ligand (**2**)*

n-Butyllithium (2.4 mL, 6.0 mmol, 2.5 M in hexane solution) was added dropwise to a solution of compound **1** (0.66 g, 2 mm) in anhydrous diethyl ether (60 mL) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h, then it was treated with PPh_2Cl (0.81 mL, 4.5 mm) in one portion *via* a syringe. Then the mixture was stirred for another 14 h. The solution was concentrated to dry *in vacuo*. The crude product was purified by column chromatography (silica gel, eluent: petroleum ether/CH_2Cl_2, 2:1) to give a white solid in a yield of 85%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.94 (s, 6H, CH_3), 2.01–2.04 (m, 2H, CH_2), 2.74 (t, $J = 7.2$ Hz, 4H, CH_2), 7.01 (d, $J = 6.4$ Hz, 2H, thienyl-H), 7.25–7.36 (m, 20H, Ph). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ −20.03 (s, PPh_2). Anal. calcd for $C_{39}H_{34}P_2S_2$: C, 74.50; H, 5.45; S, 10.20. Found: C, 74.77; H, 5.29; S, 10.32.

*4.3. Bis(phosphine) ligand **3***

The method was the same with compound **2** to give a white solid in a yield of 82%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.12–1.97 (m, 44H, Cy), 1.91 (s, 6H, CH_3), 2.01–2.04 (m, 2H, CH_2), 2.80 (t, $J = 7.2$ Hz, 4H, CH_2), 6.92 (d, $J = 6.4$ Hz, 2H, thienyl-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.53 (s, CH_3), 22.95 (s, CH_2), 24.50 (s, Cy), 25.57 (d, $J = 60.06$ Hz, Cy), 26.24 (d, $J = 11.87$ Hz, Cy), 26.88 (s, Cy), 38.44 (s, CH_2), 124.96, 134.55, 135.17, 137.10, 142.07 (s, thiophene, ethene). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ −9.10 (s, PCy_2). Anal. calcd for $C_{39}H_{58}P_2S_2$: C, 71.74; H, 8.95; S, 9.82. Found: C, 72.01; H, 8.83; S, 9.90.

Table 1
The absorption maximum (λ_{max}) of dithienylethene derivatives **2**–**9**.

Compounds	λ_{max}/nm ($\epsilon/10^4$, CH_2Cl_2) (open)	λ_{max}/nm ($\epsilon/10^4$, CH_2Cl_2) (PSS)	Compounds	λ_{max}/nm ($\epsilon/10^4$, CH_2Cl_2) (open)	λ_{max}/nm ($\epsilon/10^4$, CH_2Cl_2) (PSS)
2	228 (10.0)	505 (0.8)	**3**	233 (7.8)	497 (0.7)
4	226 (4.2)	512 (0.2)	**5**	240 (3.0)	497 (0.4)
6	226 (3.0)	513 (0.4)	**7**	241 (2.4)	505 (0.6)
8	226 (3.2)	514 (0.2)	**9**	242 (2.7)	510 (0.6)

Compound 4: a solution of compound **2** (94 mg, 0.15 mm) in $CHCl_3$ (20 mL) was treated with H_2O_2 (1 mL). The resulting solution was heated to reflux for 4 h, and the reaction mixture was slowly cooled to room temperature. The reaction mixture was extracted with $CHCl_3$ (3 × 20 mL), and dried by Na_2SO_4. The crude product was purified by column chromatography (silica gel, eluent: acetone/CH_2Cl_2, 1:3) to give a white solid in a yield of 72%. ^1H NMR (400 MHz, $CDCl_3$): δ 2.00 (s, 6H, CH_3), 1.92–2.03 (m, 2H, CH_2), 2.72 (t, $J = 7.2$ Hz, 4H, CH_2), 7.09 (d, $J = 8.0$ Hz, 2H, thienyl-H), 7.41–7.68 (m, 20H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.50 (s, CH_3), 22.83 (s, CH_2), 38.21 (s, CH_2), 128.50, 129.96, 131.58, 132.17, 133.37, 134.92, 137.23, 137.98, 143.89 (s, thiophene, ethane, Ph). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 19.75 (s, PPh_2). Anal. calcd for $C_{39}H_{34}O_2P_2S_2$: C, 70.89; H, 5.19; S, 9.71. Found: C, 70.95; H, 5.01; S, 9.89.

The method of other derivatives was similar to compound **4**.

Compound 5: white solid in the yield of 58%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.14–1.95 (m, 44H, Cy), 1.98 (s, 6 H, CH_3), 2.00–2.06 (m, 2H, CH_2), 2.80 (t, $J = 7.2$ Hz, 4H, CH_2), 7.18 (d, $J = 7.2$ Hz, 2H, thiophene-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.53 (s, CH_3), 22.90 (s, CH_2), 23.48 (s, Cy), 24.78 (d, $J = 59.35$ Hz, Cy), 25.54 (d, $J = 58.65$ Hz, Cy), 26.29 (s, Cy), 38.76 (s, CH_2), 124.63, 127.73, 134.79, 137.13, 142.46 (s, thiophene, ethene). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 44.82 (s, PCy_2). Anal. calcd for $C_{39}H_{58}O_2P_2S_2$: C, 68.39; H, 8.53; S, 9.36. Found: C, 68.27; H, 8.81; S, 9.45.

Compound 6: white solid in the yield of 90%. ^1H NMR (400 MHz, $CDCl_3$): δ 2.00 (s, 6H, CH_3), 1.99–2.03 (m, 2H, CH_2), 2.72 (t, $J = 7.2$ Hz, 4H, CH_2), 7.09 (d, $J = 8.0$ Hz, 2H, thienyl-H), 7.41–7.72 (m, 20H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.59 (s, CH_3), 22.87 (s, CH_2), 38.05 (s, CH_2), 128.47, 130.05, 131.59, 133.50, 133.94, 135.01, 137.30, 138.26, 144.36 (s, thiophene, ethane, Ph). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 31.56 (s, PPh_2). Anal. calcd for $C_{39}H_{34}P_2S_4$: C, 67.60; H, 4.95; S, 18.51. Found: C, 67.92; H, 4.76; S, 18.45.

Compound 7: white solid in the yield of 88%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.27–1.90 (m, 44H, Cy), 1.97 (s, 6H, CH_3), 1.99–2.06 (m, 2H, CH_2), 2.81 (t, $J = 7.2$ Hz, 4H, CH_2), 7.22 (d, $J = 7.2$ Hz, 2H, thiophene-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.57 (s, CH_3), 22.95 (s, CH_2), 25.00 (s, Cy), 25.78 (d, $J = 8.05$ Hz, Cy), 26.18 (d, $J = 13.28$ Hz, Cy), 26.36 (s, Cy), 38.52 (s, CH_2), 125.72, 126.45, 134.63, 137.53, 142.77 (s, thiophene, ethene). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 53.68 (s, PCy_2). Anal. calcd for $C_{39}H_{58}P_2S_4$: C, 65.32; H, 8.15; S, 17.89. Found: C, 65.54; H, 8.02; S, 18.03.

Compound 8: white solid in the yield of 92%. ^1H NMR (400 MHz, $CDCl_3$): δ 2.00 (s, 6H, CH_3), 1.99–2.03 (m, 2H, CH_2), 2.72 (t, $J = 7.2$ Hz, 4H, CH_2), 7.11 (d, $J = 9.2$ Hz, 2H, thienyl-H), 7.38–7.73 (m, 20H, Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.66 (s, CH_3), 22.89 (s, CH_2), 38.10 (s, CH_2), 128.51, 129.62, 131.70, 131.96, 132.87, 135.07, 137.41, 138.89, 144.73 (s, thiophene, ethane, Ph). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 20.97 (s, PPh_2). Anal. calcd for $C_{39}H_{34}P_2S_2Se_2$: C, 59.54; H, 4.36; S, 8.15. Found: C, 59.79; H, 4.15; S, 8.33.

Compound 9: white solid in the yield of 91%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.19–1.84 (m, 44H, Cy), 1.96 (s, 6H, CH_3), 1.99–2.06 (m, 2H, CH_2), 2.81 (t, $J = 7.2$ Hz, 4H, CH_2), 7.28 (d, $J = 7.2$ Hz, 2H, thiophene-H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 14.62 (s, CH_3), 22.92 (s, CH_2), 25.75, 26.05, 26.19, 26.31 (s, Cy), 38.44 (s, CH_2), 123.87, 124.51, 134.65, 138.63, 143.11 (s, thiophene, ethene). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 45.76 (s, PCy_2). Anal. calcd for $C_{39}H_{58}P_2S_2Se_2$: C, 57.77; H, 7.21; S, 7.91. Found: C, 58.01; H, 7.06; S, 8.14.

Acknowledgment

We gratefully acknowledge financial support from National Natural Science Foundation of China (No. 20572029, 20772039), the Science Foundation of Ministry of Education for the New Teacher at the University of China (No. 20070511006).

References

[1] Tsivgouils GM, Lehn J-M. Angew Chem Int Ed Engl 1995;34:1119–22.

[2] Tsivgouils GM, Lehn J-M. Chem Eur J 1996;2:1399–406.

[3] Seibold H, Port H. Chem Phys Lett 1996;252:135–40.

[4] Stallacci F, Bertarelli C, Toscano F, Gallazzi MC, Zerbi G. Chem Phys Lett 1999;302:563–70.

[5] Feringa BL, editor. Molecular switches. Weinheim, Germany: Wiley-Vch; 2001. p. 37–62.

[6] Raymo FM. Adv Mater 2002;14:401–14.

[7] Andreasson J, Kodis G, Terazono Y, Liddell PLA, Bandyopadhyay S, Mitchell RH, et al. J Am Chem Soc 2004;126:15926–7.

[8] Yuan W, Sun L, Huang W, Tang H, Wen Y, Jiang G, et al. Adv Mater 2005;17:156–60.

[9] Pu S, Xu J, Shen L, Xiao Q, Yang T, Liu G. Tetrahedron Lett. 2005;46:871–5.

[10] Zeng DX, Chen Y. Chin J Chem 2006;24:264–8.

[11] Kim E, Choi K, Rhee SB. Macromolecules 1998;31:5726–33.

[12] Lucas LN, Esch JV, Kellogg RM, Feringa BL. Chem Commun 2001:759–60.

[13] Murguly E, Norsten TB, Branda NR. Angew Chem Int Ed 2001;40:1752–5.

[14] Irie M, Fukaminato T, Sasaki T, Tamai N, Kawai T. Nature 2002;420:759–60.

[15] Mulder A, Jukovie A, Lucas LN, Esch JV, Feringa BL, Huskens J, et al. Chem Commun 2002:2734–5.

[16] Tian H, Chen BZ, Tu HY, Müllen K. Adv Mater 2002;14:918–23.

[17] Mitchell RH, Bandyopadhyay S. Org Lett 2004;6:1729–32.

[18] Chen Y, Zeng DX. J Org Chem 2004;69:5037–40.

[19] Morimoto M, Irie M. Chem Commun 2005:3895–905.

[20] Pu S, Xiao Q, Xu J-K, Shen L, Li G-Z, Chen B. Chin J Chem 2006;24:463–7.

[21] Irie M, Uchida K. Bull Chem Soc Jpn 1998;71:985–6.

[22] Irie M. Chem Rev 2000;100:1685–716.

[23] Kawata S, Kawata Y. Chem Rev 2000;100:1777–88.

[24] Myles AJ, Branda NR. Adv Funct Mater 2002;12:167–73.

[25] Tian H, Yang S. Chem Soc Rev 2004;33:85–97.

[26] Matsuda K, Irie M. J Photochem Photobio C Photochem Rev 2004;5:169–82.

[27] Raymo FM, Tomasulo M. Chem Soc Rev 2005;34:327–36.

[28] Nakatsuji S. Chem Soc Rev 2004;33:348–53.

[29] Feng YL, Zhang Q, Tan WJ, Zhang DQ, Tu YQ, Agren H, et al. Chem Phys Lett 2008;455(4-6):256–60.

[30] Tian H, Feng YL. J Mater Chem 2008;18:1617–22.

[31] Tian H, Wang S. Chem Commun 2007:781–92.

[32] Feng YL, Shen W, Huang W, Tan WJ, Lu CG, Cui YP, et al. J Phys Org Chem 2007;20:968–74.

[33] Wang S, Shen W, Feng YL, Tian H. Chem Commun 2006:1497–9.

[34] Feng YL, Yan YL, Wang S, Zhu WH, Qian SX, Tian H. J Mater Chem 2006;16:3685–92.

[35] Sud D, McDonald R, Branda NR. Inorg Chem 2005;44:5960–2.

[36] Lucas LN, de Jong JJD, van Esch JH, Kellogg RM, Feringa BL. Eur J Org Chem 2003:155–66.

[37] Yokoyama Y, Goto T, Inoue T, Yokoyama M, Kurita Y. Chem Lett 1988:1049–52.