ORGANIC LETTERS

2007
Vol. 9, No. 23
4877−4879

Synthesis of Novel Ladder Bis-Silicon-Bridged *p*-Terphenyls

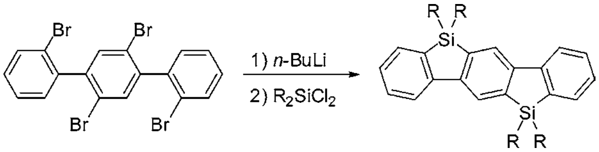
Liangchun Li, Junfeng Xiang, and Caihong Xu*

Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

caihong@iccas.ac.cn

Received September 10, 2007

ABSTRACT



The tetralithiation reaction of 2,2′,5′,2″-tetrabromo-*p*-terphenyl followed by a double silacyclization produces bis-silicon-bridged *p*-terphenyls. On the basis of this convenient method, a series of new ladder-type *p*-terphenyl derivatives have been synthesized. Their crystal structures and photophysical properties are described.

Ladder π-conjugated molecules have attracted considerable attention in the past decades, due to their fascinating properties relating to organic electronics and optoelectronics.[1] As a representative example, ladder-type oligo- or poly(*p*-phenylene)s with carbon[2] or heteroatom bridges[3] have been extensively studied, and their significant potentials for applications have been proven by recent research. On the other hand, incorporation of the silole unit into π-conjugated molecules has also received keen interest.[4] The $\sigma^*-\pi^*$ conjugation in the silole ring effectively decreases the LUMO level and makes this ring attractive as a building unit for new π-systems.[5]

Significant progress has recently been made in the synthesis of ladder π-conjugated molecules containing silole units.[6] However, little attention has been paid to the silicon-bridged ladder oligo- or poly(*p*-phenylene)s. Until very recently, the first example of a bis-silicon-bridged *p*-terphenyl had been synthesized by Murakami and co-workers on the basis of the elegant iridium(I)-catalyzed double [2 + 2 + 2] cycloaddition.[7]

---

(1) For recent reviews, see: (a) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350. (b) Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1853. (c) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267. (d) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359. (e) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891.

(2) (a) Scherf, U.; Müllen, K. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 489. (b) Grimme, J.; Kreyenschmidt, M.; Uckert, F.; Müllen, K.; Scherf, U. *Adv. Mater.* **1995**, *7*, 292. (c) Grimme, J.; Scherf, U. *Macromol. Chem. Phys.* **1996**, *197*, 2297. (d) Setayesh, S.; Marsitzky, D.; Müllen, K. *Macromolecules* **2000**, *33*, 2016. (e) Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34*, 6922. (f) Jacob, J.; Zhang, J.; Grimsdale, A. C.; Müllen, K.; Gaal, M.; List, E. J. W. *Macromolecules* **2003**, *36*, 8240. (g) Qiu, S.; Lu, P.; Liu, X.; Shen, F.; Liu, L.; Ma, Y.; Shen, J. *Macromolecules* **2003**, *36*, 9823. (h) Jacob, J.; Sax, S.; Piok, T.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 6987. (i) Wong, K.-T.; Chi, L.-C.; Huang, S.-C.; Liao, Y.-L.; Liu, Y.-H.; Wang, Y. *Org. Lett.* **2006**, *8*, 5029.

(3) (a) Haryono, A.; Miyatake, K.; Natori, J.; Tsuchida, E. *Macromolecules* **1999**, *32*, 3146. (b) Patil, S. A.; Scherf, U.; Kadashchuk, A. *Adv. Funct. Mater.* **2003**, *13*, 609. (c) Wakim, S.; Bouchard, J.; Blouin, N.; Michaud, A.; Leclerc, M. *Org. Lett.* **2004**, *6*, 3413.

(4) For recent silicon-containing π-electron compounds applicable to organic LEDs, see for instance: (a) Yamaguchi, S.; Tamao, K. *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: Chichester, UK, 2001; pp 641−694 and references therein. (b) Murata, H.; Kafafi, Z. H.; Uchida, M. *Appl. Phys. Lett.* **2002**, *80*, 189. (c) Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.;Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *Chem. Commun.* **2001**, 1740. (d) Liu, M. S.; Luo, J.; Jen, A. K.-Y. *Chem. Mater.* **2003**, *15*, 3496. (e) Lee, J.; Yuan, Y.-Y.; Kang, Y.; Jia, W.-L.; Lu, Z.-H.; Wang, S. *Adv. Funct. Mater.* **2006**, *16*, 681. (f) Chan, K. L.; McKiernan, M. J.; Towns, C. R.; Holmes, A. B. *J. Am. Chem. Soc.* **2005**, *127*, 7662. (g) Usta, H.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9034. (h) Mo, Y.; Tian, R.; Shi, W.; Cao, Y. *Chem. Commun.* **2005**, 4925. (i) Wang, E.; Li, C.; Mo, Y.; Zhang, Y.; Ma, G.; Shi, W.; Peng, J.; Yang, W.; Cao, Y. *J. Mater. Chem.* **2006**, *16*, 4133. (j) Chan, K. L.; Watkins, S. E.; Mak, C. S.; Mckiernan, M. J.; Towns, C. R.; Pascu, S. I.; Holmes, A. B. *Chem. Commun.* **2005**, 5766. (k) Lee, S. H.; Jang, B.-B.; Kafafi, Z. H. *J. Am. Chem. Soc.* **2005**, *127*, 9071.

(5) (a) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans.* **1998**, 3693. (b) Yamaguchi, S.; Tamao, K. *J. Organomet. Chem.* **2002**, *653*, 223. (c) Yamaguchi, S.; Tamao, K. *Chem. Lett.* **2005**, *34*, 2.

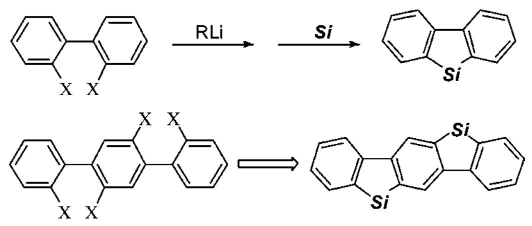
(6) (a) Ma, Z.; Ijadi-Maghsoodi, S.; Barton, T. J. *Polym. Prepr.* **1997**, *38*, 249. (b) Yamaguchi, S.; Xu, C.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 13662. (c) Xu, C.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2004**, *6*, 3707. (d) Xu, C.; Wakamiya, A.; Yamaguchi, S. *J. Am. Chem. Soc.* **2005**, *127*, 1638. (e) Xu, C.; Yamada, H.; Wakamiya, A.; Yamaguchi, S.; Tamao, K. *Macromolecules* **2004**, *37*, 8978. (f) Yamaguchi, S.; Xu, C.; Okamoto, T. *Pure Appl. Chem.* **2006**, *78*, 721. (g) Mouri, K.; Wakamiya, A.; Yamada, H.; Kajiwara, T.; Yamaguchi, S. *Org. Lett.* **2007**, *9*, 93.

10.1021/ol702215m CCC: $37.00

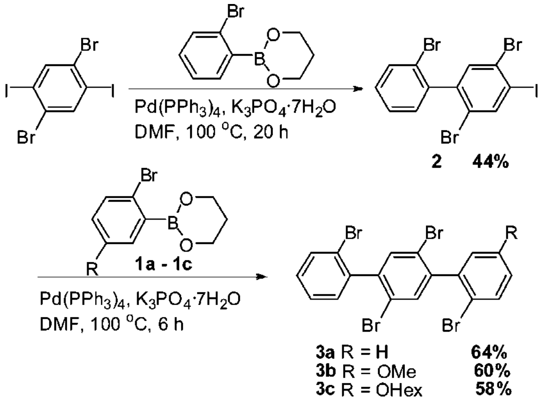
In this paper, we disclose a new entry into this class of molecules formed by a sequential tetralithiation and double silacyclization reactions. Crystal structures and fundamental photophysical properties of the new molecules will also be reported.

The reaction of dichlorosilanes with 2,2′-dilithiodiphenyl generated from biaryl halide has been a common method for the preparation of silafluorenes, for example, dibenzosilole derivatives.[4,8] We envisioned that bis-silicon-bridged *p*-terphenyl could be synthesized in a similar way by the reaction of dichlorosilane with 2,2′,5′,2″-tetralithio-*p*-terphenyl (Scheme 1). As the lithium−halogen exchange reaction of aryl bromide with organolithium conveniently produces aryllithiums,[9] the key point for this synthetic route is the preparation of 2,2′,5′,2″-tetrabromo-*p*-terphenyl.

Scheme 1



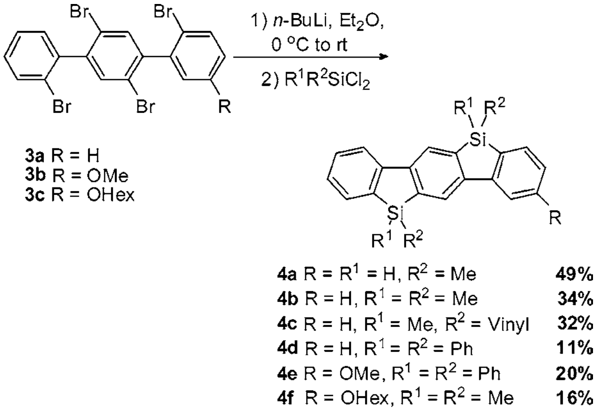
Scheme 2. Synthesis of 2,2′,5′,2″-Tetrabromo-*p*-terphenyls

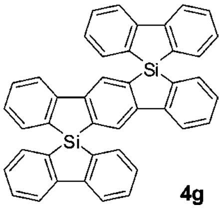


Scheme 2 depicts the synthetic route to 2,2′,5′,2″-tetrabromo-*p*-terphenyls. The palladium-catalyzed Suzuki−Miyaura cross-coupling reaction of 1,4-dibromo-2,5-diiodobenzene with 2-(2-bromophenyl)-1,3,2-dioxaborinane in the presence of K_3PO_4•$7H_2O$ in DMF produces 2,5,2′-tribromo-4-iodobiphenyl **2** in an isolated yield of 44%. Then another coupling reaction between **2** and the boronic esters **1a**−**1c** successfully produces the target 2,2′,5′,2″-tetrabromo-*p*-terphenyls **3a**−**3c** in moderate (58−64%) yields. The flexibility of this synthetic sequence allowed us to introduce different substituents at the 5,5″ positions of *p*-terphenyl and thus prepare symmetrical or unsymmetrical tetrabromo-*p*-terphenyls. In addition, **3a** was also prepared in a one-step procedure by selective double cross-coupling of **1a** and 1,4-dibromo-2,5-diiodobenzene in 87% yield.

With the 2,2′,5′,2″-tetrabromo-*p*-terphenyls in hand, we then carried out the synthesis of bis-silicon-bridged *p*-terphenyls by sequential tetralithiation and double silacyclization reactions. We first examined the tetralithiation of 2,2′,5′,2″-tetrabromo-*p*-terphenyl **3a**. The initial attempt to react **3a** with *n*-BuLi in THF failed, and an unidentified material was obtained, although the tetralithiation proceeded well in diethyl ether. *p*-Terphenyl was formed in high yield when the mixture was quenched with water. The reaction of **3** with 4 molar amounts of *n*-BuLi, followed by addition of the resulting mixture to a solution of dichlorosilane in diethyl ether, produces bis-silicon-bridged *p*-terphenyl **4** in moderate yield (Scheme 3). The substituents R^1 and R^2 in dichlorosilane have a substantial effect on the yield of **4**. The use of $HMeSiCl_2$ produces **4a** in 49% yield, and the use of Me_2SiCl_2 and $MeViSiCl_2$ produce **4b** and **4c** with yields of 34 and 32%, respectively. Lower yields were found for the preparation of **4d** and **4e**, in which Ph_2SiCl_2 was used. The double silacyclization was presumably affected due to the increase of steric hindrance when moving from H, Me, vinyl to the Ph group. When 5,5-dichlorodibenzosilole was allowed to react with the tetralithiated intermediate, the bis-silicon-bridged bispiro *p*-terphenyl **4g** was obtained in 33% yield.

Scheme 3. Synthesis of Bis-Silicon-Bridged *p*-Terphenyls





4g

---

[7] Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. *Org. Lett.* **2007**, *9*, 133.

[8] See for example: (a) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1955**, *77*, 6380. (b) Chen, R.-F.; Fan, Q.-L.; Zheng, C.; Huang, W. *Org. Lett.* **2006**, *8*, 203. (c) Kim, D.-H.; Oshita, J.; Lee, K.-H.; Kunugi, Y.; Kunai, A. *Organometallics* **2006**, *25*, 1511.

[9] Clayden, J. *Tetrahedron Organic Chemistry Series*, 1st ed.; Pergamon: Oxford, 2002; Vol. 23, Chapter 3.

[10] Merlet, S.; Birau, M.; Wang, Z. Y. *Org. Lett.* **2002**, *4*, 2157.

Among the new π-electron systems produced, the structures of compound **4b** and **4d** have been determined by X-ray crystallography, as shown in Figure 1. Both compounds have highly coplanar π-conjugated frameworks due to the silicon bridges. The dihedral angles between the central and the outer benzene rings are only 1.93° for **4b** and 2.31° for **4d**. These results suggest that the π-conjugation is effectively extended over the entire molecules. Substituents attached to the silicon atoms strongly influence the crystal packing. **4b** arranges into a herringbone motif along the *a*-axis with an angle of 66° between the adjacent disilaindenofluorene backbones, while in the packing of **4d**, each molecule stacks in a parallel fashion (see Supporting Information).

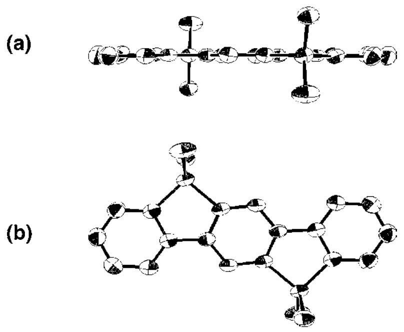


Figure 1. ORTEP drawings of compound **4b**: (a) side view and (b) top view.

The fluorescence spectra of the ladder-type silicon-bridged *p*-terphenyl in dichloromethane solution are shown in Figure 2, and their photophysical data are summarized in Table 1, together with the data of **5** and **6** for comparison. All compounds exhibit absorption maxima at 322−334 nm, while the emission maxima of the silicon-bridged compounds **4a**−**4f** are at longer wavelength (by more than 20 nm) compared with the indenofluorene analogues **5** and **6**. These phenomena are different from those of the bridged stilbene homologues. In the latter, the silicon bridge significantly shifts both the absorption and emission maxima to a longer wavelength.[6b] It is also noteworthy that all silicon-bridged compounds have comparable fluorescence efficiency to that of the carbon-bridged *p*-terphenyls. This fact is in accordance with the result that the incorporation of the silicon moieties does not necessarily decrease the quantum yield in ladder π-electron materials.[6f]

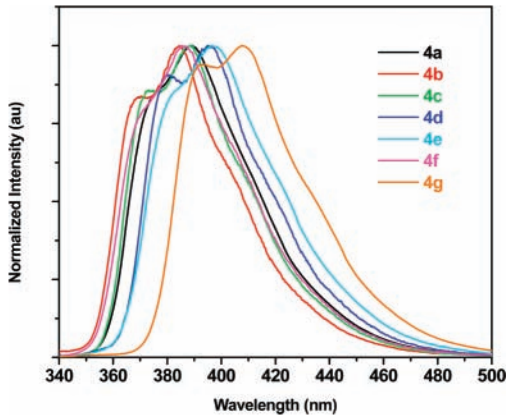
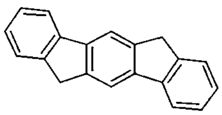


Figure 2. Normalized fluorescence spectra of compounds **4a**, **4b**, **4c**, **4d**, **4e**, **4f**, and **4g** in dichloromethane.

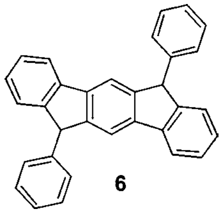
Table 1. Photophysical Properties of Bis-Silicon-Bridged *p*-Terphenyls and Related Compounds

	UV−vis absorption^{a}		fluorescence^{a}	
compd	λ_{max}/nm^{b}	log ϵ	λ_{max}/nm^{c}	$\Phi_F{}^{d}$
4a	324	4.30	389	0.50
4b	322	4.25	370, 384	0.45
4c	325	4.55	373, 389	0.50
4d	328	4.03	380, 395	0.56
4e	334	4.38	397	0.40
4f	327	4.50	387	0.51
4g	329	4.04	394, 408	0.59
5^{e}	333	4.83	340, 356	0.73
6^{f}	328		345, 360	0.36

^{a} In dichloromethane. ^{b} All compounds show vibronic absorption spectra. Only the longest absorption maxima are listed. ^{c} Excited at 324 nm. ^{d} Determined with anthracene as a standard. The Φ_F is the average values of repeated measurements within ±5% errors. ^{e} From ref 10. ^{f} From ref 2e.



5



6

In summary, we have developed a new synthetic route to ladder bis-silicon-bridged *p*-terphenyls by a sequential tetralithiation and double silacyclization reactions. This convenient route allows us to synthesize a series of new fluorescent bis-silicon-bridged *p*-terphenyls. The ease of structural modification of both the silicon moiety and the aromatic backbone provides the possibility to construct various new π-conjugated systems based on bis-silicon-bridged *p*-terphenyls. Further studies on the electronic properties of the present compounds as well as the incorporation of the ladder units into π-conjugated polymers are underway in our laboratory.

Acknowledgment. We gratefully acknowledge the National Science Foundation of China (NSFC, No. 50673094) for financial support.

Supporting Information Available: Experimental details, spectral data for all new compounds, and crystallographic data in CIF format and crystal packing of **4b** and **4d**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL702215M