Arching a bay area of triphenyleno[1,12-*bcd*]thiophene with group 14 functionalities: Synthesis of the first triphenylene derivatives having thiophene and metallafluorene moieties

Masaichi Saito [a,*], Tomoharu Tanikawa [a], Tomoyuki Tajima [a], Jing Dong Guo [b], Shigeru Nagase [b]

[a] *Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-okubo, Sakura-ku, Saitama-city, Saitama 338-8570, Japan*
[b] *Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8585, Japan*

ABSTRACT

Arching a bay area of triphenyleno[1,12-*bcd*]thiophene with group 14 functionalities gave the first triphenylene derivatives whose two pairs of bay carbons are connected by two different heteroatom functionalities. Triphenyleno[1,12-*bcd*:4,5-*b′c′d′*]dithiophene, which had been only accessible through the very severe reaction conditions, was synthesized under the mild reaction conditions. Photophysical properties of newly-obtained heterolotriphenylene derivatives are discussed with theoretical calculations.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Fluorene has long intensively been investigated from the viewpoint of its fluorescent nature [1], synthetic utility as a ligand and a spacer of transition metal complexes [2], and aromaticity of its anionic species [3]. On the other hand, 9-heterafluorenes have also received considerable attention in terms of their unique electronic properties dependent on the central heteroatoms on the 9-position [4], applied in the synthesis of such intelligent materials as fluorescent polymers [5] and chemical sensors [6]. Attention has been next paid to extension of their π-framework to develop novel properties. Arching two bay areas of an *o*-terphenyl with heteroatom functionalities have already been reported [7]. Triphenylene **1**, more rigid than *m*-terphenyl, is one of the attractive platforms to extend 9-heterafluorene frameworks because it has three bay regions in a molecule. To the best of our knowledge, however, a triphenyleno[1,12-*bcd*:4,5-*b′c′d′*]dithiophene **2** (Chart 1) is only one example of triphenylene derivatives whose two bay areas are arched with heteroatom functionalities and it was synthesized under very severe conditions using a catalyst at 500 °C [8]. Therefore, we became interested in development of novel synthetic methods, milder and more versatile than the previous method, for the synthesis of triphenylene derivatives **3** whose two bay areas are

arched with heteroatom functionalities (Chart 1). We report herein the first synthesis of triphenylene derivatives whose two pairs of bay carbons are connected by two different heteroatom functionalities and their structures and optical properties.

2. Results and discussion

2.1. Synthesis of heterolotriphenylenothiophenes

We chose triphenyleno[1,12-*bcd*]thiophene [9] as a starting compound. Because abstraction of the bay protons of triphenylene is known to proceed easily, direct abstraction of the bay protons of triphenyleno[1,12-*bcd*]thiophene (**4**) was first attempted. After treatment of **4** with four equivalents of butyllithium in hexane-TMEDA at 60 °C for 3 h [9], the reaction was quenched by D_2O to afford 3,5-dideuteriated compound **5** in 80% yield (Scheme 1). Protons on the α-carbons of the dibenzothiophene moiety were abstracted more easily than bay protons to afford dilithio derivative **6**. Thus, for further fuctionalization of a bay area of **4**, the α-carbons of the dibenzothiophene moiety were protected by trimethylsilyl groups to give bis(trimethylsilyl) derivative **7** [10] in 71% yield together with mono-substituted **8** in 8% yield (Scheme 1).

To functionalize **7**, first, lithiation of **7** was examined. After treatment of **7** with four equivalents of butyllithium in hexane-TMEDA at 60 °C for 3 h, the reaction was quenched by D_2O. A ^{1}H NMR spectrum of the crude mixture revealed the formation of

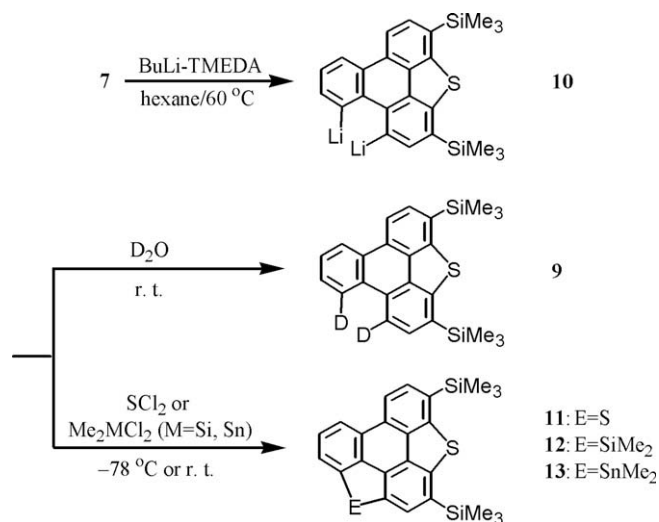* Corresponding author. Tel.: +81 48 858 9029; fax: +81 48 858 3698.
E-mail address: masaichi@chem.saitama-u.ac.jp (M. Saito).
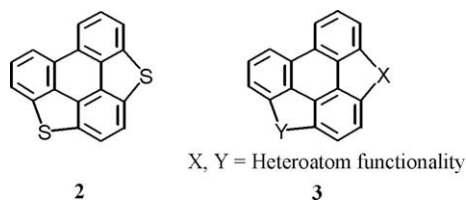
Chart 1. Triphenylene derivatives whose two pairs of bay carbons are connected by heteroatom functionalities.
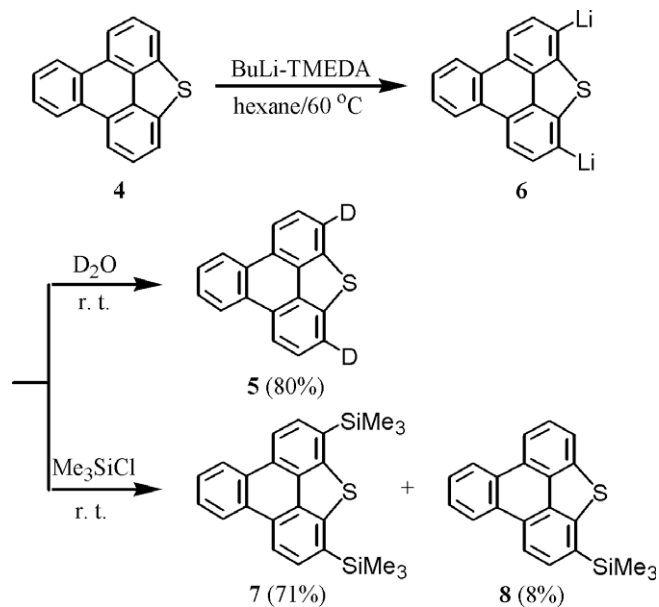

Scheme 1. Lithiation and silylation of **4**.

Scheme 2. Preparation of heterolotriphenylenothiophenes **11–13**.

dideuterated compound **9**, the yield of which was estimated to be about 20% (Scheme 2). Thus, lithiated compound **10** was generated [11]. Second, arching of a bay area of **7** with a heteroatom functionality was carried out. Treatment of a solution of **10** with sulfur dichloride gave triphenyleno[1,12-*bcd*:4,5-*b'c'd'*]dithiophene **11** in 12% yield (Scheme 2). Consequently, the present reaction conditions, milder than that reported previously [8], enable us to
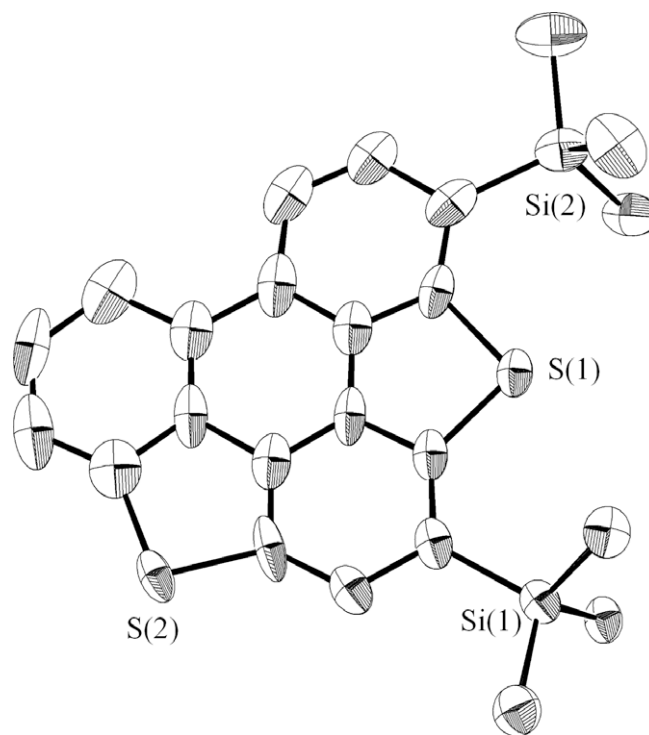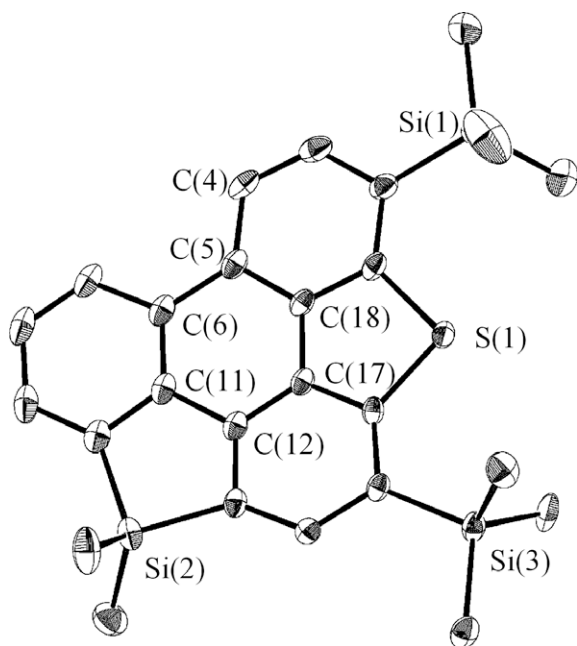

Fig. 1. ORTEP drawings of **11** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogen atoms were omitted for clarity.

construct a triphenyleno[1,12-*bcd*:4,5-*b'c'd'*]dithiophene skeleton. Third, introduction of a group 14 functionality into **7** was investigated because 9-metallafluorenes of group 14 atoms exhibit such unique optical properties as long absorptions. Treatment of **10** with dichlorodimethylsilane afforded novel 10,10-dimethyl-10*H*-silolo[2',3',4',5':4,5]triphenyleno[1,12-*bcd*]thiophene **12** in 27% yield (Scheme 2) [12]. When dilithio derivative **10** was treated with dichlorodimethylstannane, novel 10,10-dimethyl-10*H*-stannolo[2',3',4',5':4,5]triphenyleno[1,12-*bcd*]thiophene **13** in 13% yield. When lithiation of **7** was carried out using 10 equivalents of butyllithium, the ratio of dideuterated compound **9** in a crude mixture was improved to be 70%, even though the possibility of the formation of more lithiated compounds cannot be neglected [13]. The yield of **12** (1%) in the reaction using 10 equivalents of butyllithium were lower than that in the reaction using four equivalents of butyllithium, because the formation of polymeric materials derived from dichlorometallanes made it difficult to isolate the compounds from the crude mixtures [13]. However, the present methods are worthy of note from the standpoint of experimental procedures which are obviously simpler than the previous ones.

2.2. Structures of heterolotriphenylenothiophenes

We succeeded in the first X-ray characterization of **11** and **12** (Figs. 1 and 2). Triphenylenodithiophene **11** has a planar structure, although bond lengths and angles of **11** cannot be discussed, as 2:1 disorder about location of a sulfur atom was found in **11**. Silolotriphenylenothiophene **12** is also almost planar, although vectors of bonds between the carbon and the silicon atoms of the trimethylsilyl groups slightly deviate from the plane of the triphenylene skeleton. The C—C bonds in the central six-membered ring slightly alter from 1.375 to 1.475 Å, compared with those found in the parent triphenylene (1.411–1.470 Å) [14]. As the two heteroatoms in the five-membered rings tether the adjacent π-frameworks to each other, large deviation from the ideal sp^2 geometry is found at the

Fig. 2. ORTEP drawings of **12** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°), C(5)–C(6), 1.472(4); C(6)–C(11), 1.409(4); C(11)–C(12), 1.450(3); C(12)–C(17), 1.378(4); C(17)–C(18), 1.405(4); C(18)–C(5), 1.405(3); C(4)–(5)–C(6), 128.2(2), C(4)–(5)–C(18), 115.4(2).

C(5) position. The bond angles of C(4)–C(5)–C(18) and C(4)–C(5)–C(6) are 115.4(2)° and 128.2(2)°, respectively, even though the bond lengths around the C(5) atom are normal.

2.3. Photophysical properties of heterolotriphenylenothiophenes

Optical properties of newly-obtained heterolotriphenylenothiophenes **11–13** were investigated. Electronic absorption spectra of **1**, **4**, **7**, and **11–13** are shown in Fig. 3. Comparison of the spectra of the parent triphenylene **1** and triphenylenothiophene **4** shows that each of the characteristic absorption maxima of triphenylene (258, 275, and 286 nm) is red-shifted (266, 282, 318 nm). After introduction of the two trimethylsilyl groups into triphenylenothiophene **4** leading to **7**, each absorption maximum (269, 292, and 332 nm) is further red-shifted. However, after introduction of the

second bridge of the silylene and the stannylene units leading to **12** and **13**, the spectra of each metallolotriphenylene are quite similar to that of **4** (273, 293, and 333 nm for **12**; 273, 296, and 336 nm for **13**). Hence, the effect of the two trimethylsilyl groups on the electronic properties of these compounds may dominate, while the second bridge of group 14 functionality has only a small effect on the electronic properties of these compounds. In contrast, the electronic spectrum of triphenylenodithiophene **11** is slightly different from those of **12** and **13**. Its characteristic absorption maxima are observed at 296, 306, and 345 nm, and each of them is further red-shifted, compared with those observed in **12** and **13**. To understand the electronic absorption spectra, theoretical calculations about **1**, **4**, **7**, and **11–13** were carried out (Fig. 4). The optimized geometries of all the compounds are consistent with those found in the solid state. Expectedly, the HOMO of the parent triphenylene **1** is π-orbital, while the LUMO of **1** is π*-orbital, and the longest absorption observed at 287 nm can be assigned to the π–π* transition. The HOMO of triphenylenothiophene **4** consists of π-orbital derived from the triphenylene moiety and the two lone pairs of the sulfur atom, while the LUMO of **4** is quite similar to that of **1**, and the longest absorption observed at 319 nm therefore can be assigned to the π–π* transition. The HOMO of **7** is similar to that for **1** and **4**, and hence introduction of the two silyl group does not have any considerable effects on the HOMO. However, the LUMO of **7** is extended to the silicon atoms, leading to lowering the LUMO level, which causes longer absorption of **7** (332 nm) than that of **4** (318 nm). As there is no contribution of the second bridges of group 14 functionalities to the HOMO and the LUMO in **12** and **13**, both of the HOMO and the LUMO of **12** and **13** are quite similar, resulting in similar absorption maxima of **7**, **12**, and **13**. In the HOMO of **11**, contribution of two lone pairs of the two sulfur atoms is observed and hence the HOMO level of **11** is higher than those of **7**, **12**, and **13**, leading to the absorption (345 nm) longer than those for **7**, **12**, and **13** (332–336 nm). The contributions of HOMO–LUMO transitions to the oscillator strengths of the longest absorptions for **7**, **11**, **12**, and **13** are calculated to be 80%, 84%, 72%, and 81%, respectively. Although the shorter absorptions of **4**, **7**, **11**, **12**, and **13** can be partially assigned to π–π* transitions, contribution of orbitals to the transitions is quite complicated.

The fluorescence spectra of newly-obtained triphenylenothiophene **7**, and heterolotriphenylenothiophenes **11** and **12** were also measured (Fig. 5). In the spectra of **4**, **7**, **11**, and **12**, three main fluorescence maxima were observed. As observed in the absorption spectra, the fluorescence maxima are successively red-shifted by
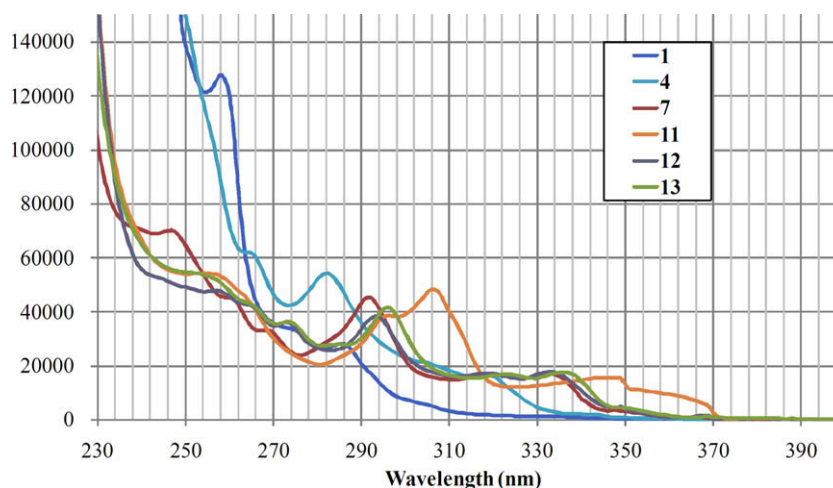
Fig. 3. UV–Vis spectra of **1**, **4**, **7**, **11**, **12**, and **13** in dichloromethane.
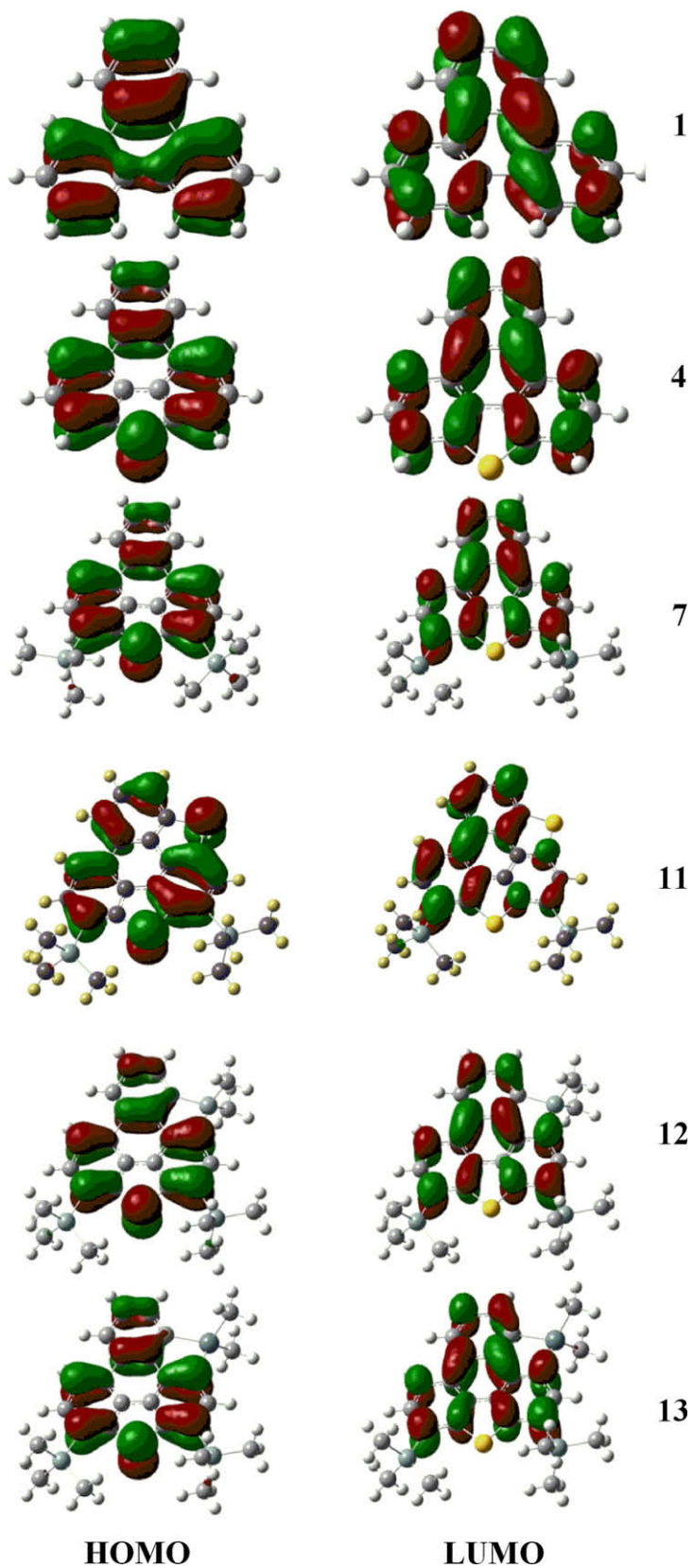
Fig. 4. HOMO and LUMO diagrams of **1**, **4**, **7**, **11**, **12**, and **13**.

the introduction of a sulfur atom followed by two trimethylsilyl groups into the parent triphenylene **1**. The fluorescence spectrum of silolotriphenylenothiophene **12** is quite similar to that of **7**, and hence the second bridge of group 14 functionality does not affect strongly the fluorescent nature of these compounds. However, each of the three fluorescence maxima of **11** is about 15 nm
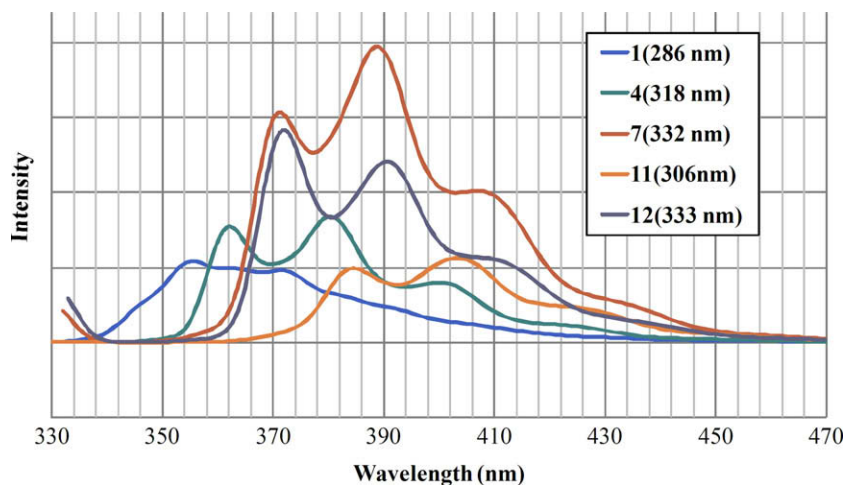
Fig. 5. Fluorescence spectra of **1**, **4**, **7**, **11**, and **12**. The excited wavelengths are shown in parentheses.

Table 1
Calculated HOMO and LUMO energies.

	HOMO (au)	LUMO (au)	Gap (eV)
1	−0.21491	−0.03417	4.92
4	−0.20572	−0.04327	4.42
7	−0.20120	−0.04548	4.24
11	−0.19912	−0.05051	4.04
12	−0.19967	−0.04364	4.25
13	−0.19883	−0.04441	4.20

red-shifted, compared with the corresponding fluorescence maxima of **7** and **12**, probably because the two sulfur lone pairs of **11** affect the excited state, as they affect the HOMO (Table 1). Among the compounds described here, the HOMO of **11** is the second highest, while the LUMO is the lowest, and the HOMO–LUMO gap is calculated to be 4.04 eV, even though the reason for it cannot be elucidated from the pictures of HOMO and LUMO orbitals.

3. Conclusion

Starting from triphenyleno[1,12-*bcd*]thiophene **4**, we synthesized heterolotriphenylenothiophenes **11–13**, whose two pairs of bay carbons in the triphenylene skeleton are connected by heteroatom functionalities. Heterolotriphenylenothiophenes **12** and **13** are worthy of note from the standpoint of the first examples of heterolotriphenylene derivatives which have different heteroatom functionalities. Comparison of electronic absorption and fluorescence spectra of **7**, **12**, and **13** reveals that the two trimethylsilyl groups outside the π-frameworks affect mainly their photophysical properties, while group 14 functionalities in the π-frameworks do not perturb the properties strongly. In contrast, the interaction between the two sulfur lone pairs and π-framework in **11** enhances slightly the HOMO level and hence both of the absorption and the fluorescence maxima of **11** are red-shifted. These results clearly show that introduction of different heteroatom functionalities into the π-frameworks can lead to novel photophysical properties and is of considerable interest.

4. Experimental

4.1. General procedures

Diethyl ether (Et$_2$O) and THF were distilled over sodium/benzophenone. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{119}Sn NMR (149 MHz) spectra were recorded on a Bruker DRX-400 or a Bruker DPX-400 spectrometer in CDCl$_3$. The multiplicities of signals in ^{13}C NMR given in parentheses were deduced from DEPT spectra. Wet column chromatography and preparative thin layer chromatography were carried out with Kanto silica gel 60 N and Merck silica gel 60, respectively. Preparative gel permeation chromatography was carried out on an LC-918 (Japan Analytical Ind. Co., Ltd.) with JAIGEL-1H and -2H columns with chloroform (CHCl$_3$) as the eluant. High-resolution mass spectra were recorded on a JEOL JMX-700AM mass spectrometer. All the melting points were determined on a Mitamura Riken Kogyo MEL-TEMP apparatus and were uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of Molecular Analysis and Life Science Center, Saitama University.

4.2. Protection of the α-carbons of triphenyleno[1,12-bcd]thiophene (4) by trimethylsilyl groups

To a hexane (4 mL) solution of triphenyleno[1,12-*bcd*]thiophene (**4**) (51.6 mg, 0.20 mmol) was added TMEDA (0.12 mL, 0.81 mmol) and butyllithium (1.58 M in hexane; 0.51 mL, 0.80 mmol) at room temperature. The resulting mixture was heated at 60 °C for 3 h. After being cooled to room temperature, THF (25 mL) was added to the mixture, which was treated with chlorotrimethylsilane (0.10 mL, 0.80 mmol). After being stirred for 12 h at room temperature, the mixture was poured into water (50 mL). The organic layer was extracted with chloroform and dried over anhydrous magnesium sulfate. After removal of volatile substances, the residue (88.7 mg) was subjected to gel permeation chromatography to afford 3,5-bis(trimethylsilyl)triphenyleno[1,12-*bcd*]thiophene (**7**) (57.3 mg, 71%) and 3-trimethylsilyltriphenyleno[1,12-*bcd*]thiophene (**8**) (5.0 mg, 8%). **7**: mp 204-205 °C (chloroform + ethanol). ^{1}H NMR: δ 0.56(s, 18H), 7.74(dd, *J* = 3, 6 Hz, 2H), 7.98(d, *J* = 8 Hz, 2H), 8.45(d, *J* = 8 Hz, 2H), 8.74(dd, *J* = 3, 6 Hz, 2H); ^{13}C NMR: δ −1.04(q), 116.41(d), 124.15(d), 127.56(d), 129.28(s), 129.64(s), 130.62(s), 131.44(s), 132.15(d), 145.25(s). Anal. Calc. for C$_{24}$H$_{26}$SSi$_2$: C, 71.58; H, 6.51. Found: C, 71.45; H, 6.49%. **8**: mp 120–121 °C (chloroform + ethanol). ^{1}H NMR: δ 0.55(s, 9H), 7.75–7.77(m, 2H), 7.87(dd, *J* = 8, 8 Hz, 1H), 7.99(d, *J* = 8 Hz, 1H), 8.07(d, *J* = 8 Hz, 1H), 8.45–8.48(m, 2H), 8.70–8.76(m, 2H); ^{13}C NMR: δ −1.12(q), 116.52(d), 116.98(d), 119.82(d), 124.12(d), 124.24(d), 126.87(d), 127.49(d), 127.63(d), 128.65(s), 129.35(s), 129.92(s), 130.53(s), 130.57(s), 130.63(s), 131.68(s), 132.30(d), 138.85(s), 145.35(s). Anal. Calc. for C$_{21}$H$_{18}$SSi: C, 76.31; H, 5.49. Found: C, 75.83; H, 5.47%.

4.3. Preparation of triphenyleno[1,12-bcd:4,5-b′c′d′]dithiophene 11

To a hexane (7 mL) solution of 3,5-bis(trimethylsilyl)triphenyleno[1,12-*bcd*]thiophene (**7**) (450.2 mg, 1.12 mmol) was added TMEDA (0.67 mL, 4.50 mmol) and butyllithium (2.64 M in hexane; 1.70 mL, 4.49 mmol) at room temperature. The resulting mixture was heated at 60 °C for 3 h. After being cooled to −78 °C, to the resulting mixture was added THF (7 mL) followed by sulfur dichloride (0.29 mL, 4.56 mmol). After being warmed to room temperature overnight, the mixture was poured into water. The organic phase was extracted with chloroform and dried over anhydrous magnesium sulfate. After removal of volatile substances, the residue (623.7 mg) was subjected to column chromatography (eluant; hexane) followed by gel permeation chromatography to afford 3,5-bis(trimethylsilyl)triphenyleno[1,12-*bcd*:4,5-*b′c′d′*]dithiophene (**11**) (58.1 mg, 12%). **11**: mp 208–210 °C (chloroform). ^{1}H NMR δ 0.58(s, 9H), 0.60(s, 9H), 7.88(dd, J = 8, 8 Hz, 1H), 8.01(d, J = 8 Hz, 1H), 8.10(d, J = 8 Hz, 1H), 8.27(s), 8.47(d, J = 8 Hz, 1H), 8.48(d, J = 8 Hz, 1H); ^{13}C NMR δ −1.05(q), −0.81(q), 118.51(d), 119.11(d), 121.22(d), 124.63(d), 127.93(d), 128.93(s),129.88(s), 130.40(s), 130.61(s), 130.65(s), 132.12(s), 132.58(s), 132.97(d), 133.08(s), 133.54(s), 138.50(s), 142.81(s), 149.33(s). High-resolution MS (EI/70 eV) Calc. for $C_{24}H_{24}S_2Si_2$: 432.0858. Found: 432.0860.

4.4. Preparation of silolo[2′,3′,4′,5′:4,5]triphenyleno[1,12-bcd]thiophene 12

To a hexane (6 mL) solution of 3,5-bis(trimethylsilyl)triphenyleno[1,12-*bcd*]thiophene (**7**) (80.7 mg, 0.20 mmol) was added TMEDA (0.12 mL, 0.8 mmol) and butyllithium (1.58 M in hexane; 0.51 mL, 0.80 mmol) at room temperature. The resulting mixture was heated at 60 °C for 3.5 h. After being cooled to −78 °C, the resulting mixture was treated with dichlorodimethylsilane (0.10 mL, 0.84 mmol). After being warming to room temperature over 2 days, the mixture was poured into water (50 mL). The organic layer was extracted with chloroform and dried over anhydrous magnesium sulfate. After removal of volatile substances, the residue (134.5 mg) was subjected to gel permeation chromatography to afford the recovered **7** (5.0 mg, 6%) and 2,4-bis(trimethylsilyl)-10,10-dimethyl-10*H*-silolo[2′,3′,4′,5′:4,5]triphenyleno[1,12-*bcd*]thiophene (**12**) (23.5 mg, conv. 27%). **12**: mp 116–117 °C (chloroform + ethanol). ^{1}H NMR: δ 0.57(s, 9H), 0.58(s, 9H), 0.64(s, 6H), 7.73(dd, J = 7, 8 Hz, 1H), 7.92(dd, J = 1, 7 Hz, 1H), 7.98(d, J = 8 Hz, 1H), 8.16(s, 1H), 8.42(d, J = 8 Hz, 1H), 8.57(dd, J = 1, 8 Hz, 1H); ^{13}C NMR: δ −2.30(q), −1.02(q), −0.85(q), 117.30(d), 124.53(d), 127.55(s), 127.99(d), 128.06(s), 128.84(s), 129.71(s), 129.84(s), 131.34(s), 131.45(d), 131.89(s), 132.27(d), 135.29(d), 140.22(s), 140.94(s), 141.51(s), 145.95(s), 147.05(s). Anal. Calc. for $C_{26}H_{30}SSi_3$: C, 68.06; H, 6.59. Found: C, 67.99; H, 6.52%.

4.5. Preparation of stannolo[2′,3′,4′,5′:4,5]triphenyleno[1,12-bcd]thiophene 13

To a hexane (6 mL) solution of 3,5-bis(trimethylsilyl)triphenyleno[1,12-*bcd*]thiophene (**7**) (80.4 mg, 0.20 mmol) was added TMEDA (0.12 mL, 0.81 mmol) and butyllithium (1.57 M in hexane; 0.51 mL, 0.80 mmol) at room temperature. The resulting mixture was heated at 60 °C for 3 h. After being cooled to room temperature, the resulting mixture was treated with a diethyl ether (3 mL) solution of dichlorodimethylstannane (92.7 mg, 0.42 mmol). After being stirred at room temperature overnight, insoluble materials in dichloromethane were removed by filtration and the filtrate was concentrated. The residue (129.6 mg) was subjected to preparative thin layer chromatography (eluant; hexane) followed by gel permeation chromatography to afford 2,4-bis(tri-methylsilyl)-10,10-dimethyl-10*H*-stannolo[2′,3′,4′,5′:4,5]triphenyleno[1,12-*bcd*]thiophene (**13**) (10.7 mg, conv. 13%) as pale yellow oil. **13**: ^{1}H NMR δ 0.56(s, 9H), 0.58(s, 9H), 0.70(s, J(Sn–H) = 58, 60 Hz, 6H), 7.75(dd, J = 7, 8 Hz, 1H), 7.97(d, J = 8 Hz, 1H), 7.98(dd, J = 1, 7 Hz, 1H), 8.20(s, J(Sn–H) = 33 Hz, 1H), 8.44(d, J = 8 Hz, 1H), 8.63(d, J = 8 Hz, 1H); ^{13}C NMR δ −7.56(q, J(Sn–C) = 344, 360 Hz), −1.02(q), −0.90(q), 116.80(d), 123.95(d), 127.67(d, J(Sn–C) = 45 Hz), 129.58(s), 129.81(s), 129.91(s), 131.33(s), 131.39(s), 131.54(s), 132.20(s), 135.01 (d, J(Sn–C) = 46 Hz), 138.35(d, J(Sn–C) = 46 Hz), 141.64(s), 142.40(s), 142.63(s), 145.59(s), 145.93(s), 167.75(s); ^{119}Sn NMR δ −16.9. High-resolution MS (EI/70 eV) Calc. for $C_{26}H_{30}SSi_2Sn$: 550.0631. Found: 550.0630.

4.6. X-ray crystallographic analysis of 11 and 12

The intensity data were collected at −170 °C on a Bruker SMART APEX equipped with a CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. **11**: Formula $C_{24}H_{24}S_2Si_2$, FW = 432.73, crystal dimension $0.25 \times 0.05 \times 0.02$ mm, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 7.0715(7)$ Å, $b = 14.2054(13)$ Å, $c = 21.878(2)$ Å, $\beta = 93.870(2)°$, $V = 2192.8(4)$ Å^3, $D_{calcd} = 1.311$ g cm^{-3}, $R_1 = 0.085$ ($I > 2\sigma(I)$, 3007 reflections), $wR_2 = 0.217$ (for all reflections) for 3967 reflections and 263 parameters, Goodness-of-fit (GOF) = 1.145. **12**: Formula $C_{26}H_{30}SSi_3$, FW = 458.83, crystal dimension $0.40 \times 0.10 \times 0.10$ mm, hexagonal, space group $P6_1$, $Z = 6$, $a = 19.4016(9)$ Å, $c = 13.0559(12)$ Å, $V = 4256.1(5)$ Å^3, $D_{calcd} = 1.074$ g cm^{-3}, $R_1 = 0.053$ ($I > 2\sigma(I)$, 6149 reflections), $wR_2 = 0.135$ (for all reflections) for 6770 reflections and 279 parameters, GOF = 1.125.

4.7. Computational details

All calculations were carried out using the GAUSSIAN 03 program [15]. Geometry optimization was performed with hybrid density functional theory (DFT) at the B3LYP level, by using a double-ζ basis set (Lanl2dz) augmented by a d-type polarization function (d exponent 0.183) along with the effective core potential (Lanl2 ECP [16]) for Sn atom and 6-31G* basis set for all other atoms. The UV/Vis absorption spectra of optimized geometries were calculated with the time dependent (TD) DFT method.

Appendix A. Supplementary material

CCDC 749877 and 745674 contain the supplementary crystallographic data for **11** and **12**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.11.039.

References

[1] (a) For examples of recent reviews, see: A. Monkman, C. Rothe, S. King, F. Dias, Adv. Polym. Sci. 212 (2008) 187;
(b) E. Da Como, K. Becker, J.M. Lupton, Adv. Polym. Sci. 212 (2008) 293;
(c) K.D. Belfield, S. Yao, M.V. Bondar, Adv. Polym. Sci. 213 (2008) 97.

[2] (a) For recent examples, see: S. Gentil, M. Dietz, N. Pirio, P. Meunier, J.C. Gallucci, F. Gallou, L.A. Paquette, Organometallics 21 (2002) 5162;
(b) E. Kirillov, C.W. Lehmann, A. Razavi, J.-F. Carpentier, Eur. J. Inorg. Chem. (2004) 943.

[3] H. Jiao, P.v.R. Schleyer, Y. Mo, M.A. McAllister, T.T. Tidwell, J. Am. Chem. Soc. 119 (1997) 7075.

[4] R.-F. Chen, C. Zheng, Q.-L. Fan, W. Huang, J. Comput. Chem. 28 (2007) 2091.

[5] (a) For recent examples, see: J.C. Sanchez, S.A. Urbas, S.J. Toal, A.G. DiPaaquale, A.L. Rheingold, W.C. Trogler, Macromolecules 41 (2008) 1237;
(b) K. Tamura, M. Shiotsuki, N. Kobayashi, T. Masuda, F. Sanda, J. Polym. Sci., Part A: Polym. Chem. 47 (2009) 3506;
(c) S.M. King, I.I. Perepichka, I.F. Perepichka, F.B. Dias, M.R. Bryce, A.P. Monkman, Adv. Funct. Mater. 19 (2009) 586.

[6] (a) For recent examples, see: J. You, T. Yan, H. Zhao, Z. Sun, L. Xia, Y. Suo, Y. Li, Anal. Chim. Acta 636 (2009) 95;
(b) J.C. Sanchez, A.G. Di Pasquale, A.A. Mrse, W.C. Trogler, Anal. Bioanal. Chim. 395 (2009) 387.

[7] (a) E. Desarbre, J. Bergman, J. Chem. Soc., Perkin Trans. 1 (1998) 2009;
(b) H. Kudo, M.L. Tedjamulia, R.N. Castle, J. Heterocycl. Chem. 21 (1984) 185;
(c) J. Bergman, L. Engman, J. Am. Chem. Soc. 103 (1981) 5196.

[8] L.H. Klemm, E. Hall, L. Cousins, C.E. Klopfenstein, J. Heterocycl. Chem. 26 (1989) 345.

[9] A.J. Ashe III, J.W. Kampf, P.M. Savla, J. Org. Chem. 55 (1990) 5558.

[10] M. Saito, T. Tanikawa, T. Tajima, Acta Crystallogr. E 63 (2007) o2923.

[11] The neighboring two protons in a bay area are mainly abstracted in the lithiation of triphenylene, see Ref. [9].

[12] M. Saito, T. Tanikawa, T. Tajima, J.D. Guo, S. Nagase, Tetrahedron Lett., in press. doi:10.1016/j.tetlet.2009.11.102.

[13] The tetralithiated compound was probably also generated because 2,9-bis(trimethylsilyl)-4,4,7,7-tetramethyl-4,7-dihydrobissilolo[2′,3′,4′,5′:4,5;2′′, 3′′,4′′,5′′:8,9]triphenyleno[1,12-*bcd*]thiophene (**14**) was obtained in a very low yield (0.4%). This compound is categorized as a heterasumanene, which was introduced in ref. 12. Therefore, the reasons for the low yield in the reaction using 10 equivalents of butyllithium are very complicated. **14**: ^{1}H NMR δ 0.56(s, 18H), 0.65(s, 12H), 7.91(s, 2H), 8.13(s, 2H); ^{13}C NMR δ −2.29(q), −0.80(q), 127.62(s), 130.33(s), 131.54(d), 132.30(s), 135.49(d), 138.36(s), 139.90(s), 141.06(s), 148.26(s). High-resolution MS(EI/70 eV). Calc. for $C_{28}H_{34}SSi_4$: 514.1458. Found: 514.1456.

[14] K.K. Baldridge, J.S. Siegel, J. Am. Chem. Soc. 114 (1992) 9583.

[15] GAUSSIAN 03, Revision E. 01; Gaussian, Inc., Wallingford CT, 2004.

[16] W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284.