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PAPER

Synthesis, structures and optical properties of trisilasumanene and its related compounds†

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Novel trisilasumanenes that have no substituents on the *exo* carbon atoms, silicon analogues of sumanene, were prepared *via* repetitive lithiations of triphenylene followed by introduction of silicon functionalities. The optical properties of these trisilasumanenes and their related compounds were investigated by UV–vis and fluorescence spectroscopy.

Introduction

Sumanene, which was synthesized by Sakurai and Hirao *et al.* in 2003,[1] has received considerable recent attention as a novel partial structure of C_{60}. This beautiful bowl-shaped molecule reveals bowl-to-bowl inversion, and is applied to electrical materials such as OFET.[2] Meanwhile, substitution of carbon atoms in π-frameworks by heteroatoms is also of current interest. From this viewpoint, much attention has been focused on 9-heterafluorenes because of their unique electronic properties, which are dependent on the central heteroatoms on the 9-position,[3] so that they are utilized as central skeletons of such intelligent materials as fluorescent polymers[4] and chemical sensors.[5] With this in mind, heterasumanenes, which are bridged by heteroatom functionalities at the three bay regions of triphenylene, are fascinating species. While theoretical calculations about these compounds have extensively been carried out,[6] synthetic research has been less explored. Otsubo *et al.* have succeeded in the synthesis of trithiasumanene, which is the first example of a heterasumanene. However, in their synthetic process, the severe reaction conditions of flash vacuum pyrolysis are necessary.[7] Most recently, Kawashima *et al.* have reported on the synthesis of trisilasumanene, each *exo* carbon of which has a butoxy group, *via* their original sila-Friedel–Crafts reaction.[8] The electronic property of this compound is thought to be strongly perturbed by the six butoxy groups, compared to that of the parent trisilasumanene. In the same year, we reported on the synthesis of novel heterasumanenes having different heteroatom functionalities *via* stepwise functionalization of triphenylenothiophene, which would enable us to prepare a wide variety of heterasumanenes.[9] We discovered the intermolecular CH–π interactions between the trimethylsilyl groups and the three benzene rings of the triphenylene framework.[9] These results prompted us to create a novel trisilasumanene without any substituents on the benzene rings to investigate the intrinsic nature of a trisilasumanene framework. We herein report on the synthesis and optical properties of trisilasumanene **1** that has no substituents on the benzene rings, and its precursors, triphenylenosilole **2** and triphenylenodisilole **3**.

Results and discussion

1,12-Dilithiotriphenylene (**4**) was prepared from triphenylene with 4 equiv. of butyllithium and TMEDA at 60 °C for 3 h as reported previously.[10] Treatment of **4** with 2 equiv. of dichlorodimethylsilane afforded triphenyleno[1,12-*bcd*]silole **2** in 50% yield (Scheme 1). For further functionalization of **2**, first, lithiation of **2** was carried out by the treatment with 6 equiv. of butyllithium and TMEDA at 60 °C for 3 h, and then the reaction was quenched with 6 equiv. of chlorotrimethylsilane[11] to afford triphenyleno[1,12-*bcd*:4,5-*b′c′d′*]disilole **3** in 46% yield. Since 9,9-dimethyl-9-silafluorene reacted with butyllithium to give 9,9-dibutyl-9-silafluorene,[12] the introduction of two butyl groups onto the silicon atom of **3** through this reaction is quite reasonable. The final step of the synthesis of a trisilasumanene from compound **3** was to bridge the remaining bay region by a silylene unit. After treatment of triphenyleno[1,12-*bcd*:4,5-*b′c′d′*]disilole **3** with butyllithium, the reaction was quenched by dichlorodimethylsilane to afford novel trisilasumanene **5** in 15% yield, which is the first example of a trisilasumanene without any functional groups on the benzene rings. Moreover, treatment of **5** with butyllithium afforded hexabutyltrisilasumanene **1** bearing a C_3 axis in 31% yield with butyl groups on the three silicon atoms.

The *ORTEP* drawing of triphenylenosilole **2** is shown in Fig. 1.[13] The C–C bonds in the central six-membered ring slightly alternate from 1.404 Å to 1.471 Å, and the degree of alternation in **2** is larger than those found in the parent triphenylene (1.411–1.470 Å)[13] and sumanene (1.38–1.431 Å),[2] but is smaller than that

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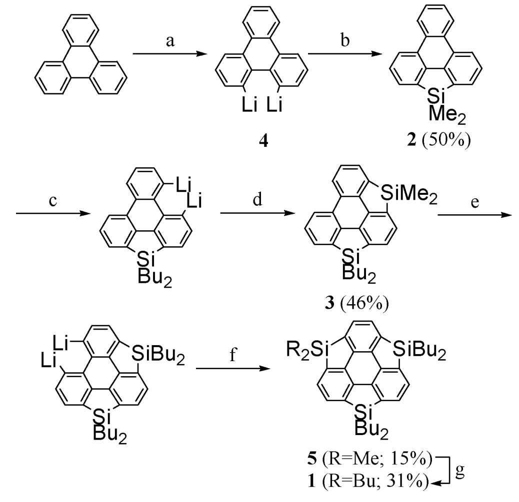
† Electronic supplementary information (ESI) available: The NMR and mass spectroscopic charts of compounds **1**, **2**, **3** and **5**. The Cartesian coordinates of the optimized geometries for compounds **1**, **2**, **3** and **B**. CCDC reference numbers 792994. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ob00987c



Scheme 1 *Reagents and Conditions*: a) 4 equiv. BuLi, 4 equiv. TMEDA, hexane, 60 °C for 3 h; b) 2 equiv. Me_2SiCl_2, 0.1 equiv. CuCN, THF, r. t. for 14 h; c) 6 equiv. BuLi, 6 equiv. TMEDA, hexane, 60 °C for 3 h; d) 6 equiv. Me_3SiCl, THF, −78 °C to r. t. for 13 h; e) 10 equiv. BuLi, 10 equiv. TMEDA, hexane, 60 °C for 3 h; f) 10 equiv. Me_2SiCl_2, 0.6 equiv. CuCN, THF, −88 °C to r. t. for 13 h; g) 10 equiv. BuLi, THF, −72 °C to r. t. for 1.5 h. TMEDA = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine.

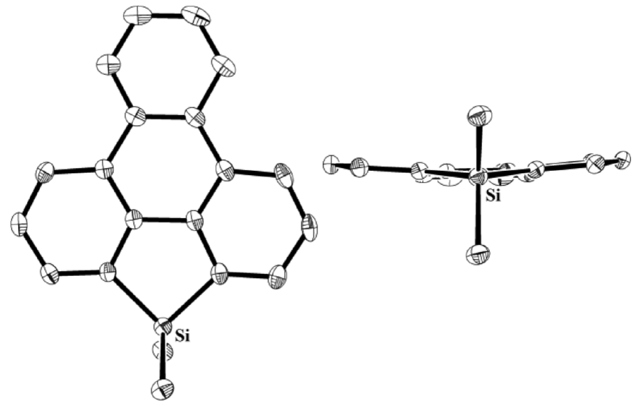


Fig. 1 *ORTEP* drawings of **2** with thermal ellipsoids plots (40% probability for no-hydrogen atoms). Top view (left) and side view (right). All hydrogen atoms were omitted for clarity.

of triphenylenothiophene (1.375–1.467 Å).[14] The π-framework of **2** is almost planar. In the packing structure of **2**, there are no significant intermolecular interactions.

The optical properties of compounds **1**, **2** and **3** were investigated. Electronic absorption spectra of **1**, **2** and **3** are shown in Fig. 2. Comparison of the spectra of the parent triphenylene and triphenylenosilole **2** shows that each of the characteristic absorption maxima of the parent triphenylene (258, 275, and 286 nm) are quite similar to that of **2** (254, 262, and 289 nm). However, after introduction of the silylene unit into triphenylenosilole **2** leading to **3**, each absorption maximum (258, 267, and 291 nm) is red-shifted (4, 5, and 2 nm from **2**). Moreover, after introduction of the silylene unit into triphenylenodisilole **3** leading to **1**, each absorption maximum (260, 270, and 294 nm) is further red-shifted (2, 3, and 3 nm from **3**). The intense absorption band of **1** at 270 nm is slightly blue-shifted from that of sumanene (278 nm)[2] and substantially blue-shifted compared to that of Kawashima's hexabutoxytrisilasumanene **A** (299 nm) (Chart 1).[8]

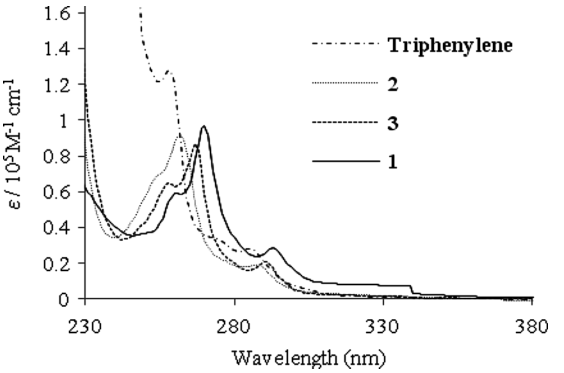


Fig. 2 UV–vis absorption spectra of triphenylene, **1**, **2** and **3** in CH_2Cl_2.

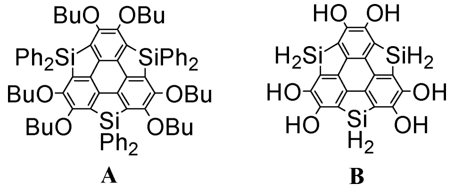


Chart 1 Model compound **B** of Kawashima's hexabutoxytrisilasumanene **A**.

To understand the electronic absorption spectra observed for **1**, **2** and **3**, theoretical calculations of **1**, **2**, **3**, and a model compound **B** (Chart 1) of Kawashima's hexabutoxytrisilasumanene **A** that has six OH groups instead of six butoxy groups and hydrogen atoms on the silicon atoms, were carried out with hybrid density functional theory at the B3LYP level using the Gaussian 03 program (Fig. 3).[15] The geometry optimization was performed using the 6-311+G(2df) basis set for the Si atom and 6-31G* for other atoms. The UV–vis absorption spectra of the optimized geometries were calculated with the time dependent (TD) B3LYP method. All the optimized structures of **1**, **2** and **3** were found to have planar π-framworks, as in the X-ray crystal structure of **2** and the calculation of trisilasumanene.[6] The structure optimized for the model compound **B** also agreed well with the X-ray crystal structure of compound **A**.[8] The HOMO and LUMO of triphenylene are π-orbital and π*-orbital, respectively. The HOMOs of **1**, **2** and **3** consist mainly of the π-orbital of triphenylene, while the LUMOs of **1**, **2** and **3** are derived from conjugation of σ*(Si–C) and π*(LUMO+2 of triphenylene), even though contribution of the π*-orbitals to the LUMOs is predominant. The longest absorptions at 289, 291, and 294 nm observed for **2**, **3**, and **1**, respectively, can be therefore assigned to the π–π* transitions (Table 1). In contrast, calculations of **B** show that the lone pairs of the oxygen atoms strongly contribute toward raising the HOMO level and making the HOMO–LUMO gap decrease to 3.76 eV (Table 1). As a result, the longest absorption of **B** was calculated to be considerably red-shifted to 386 nm. This value agrees reasonably well with the value (>350 nm) observed for **A**,[8] which is the most red-shifted among those of **1**, **2**, **3** and **A**. It can be concluded that butoxy groups on the *exo* carbon atoms of the trisilasumanene framework strongly perturb the intrinsic electronic nature of a trisilasumanene skeleton.

Table 1 HOMO–LUMO gaps and maximum absorption wavelengths calculated for **1**, **2**, **3** and **B**

	calculated HOMO–LUMO gap (eV)	calculated λ_{max} (nm)	oscillator strengths (gas phase)	oscillator strengths (in solution)[18]	experimental λ_{max} (nm)
2	4.77	302	0.014	0.024	289
3	4.53	321	0.007	0.011	291
1	4.35	333	0.000	0.0001	294
B	3.76	386			
A					>350

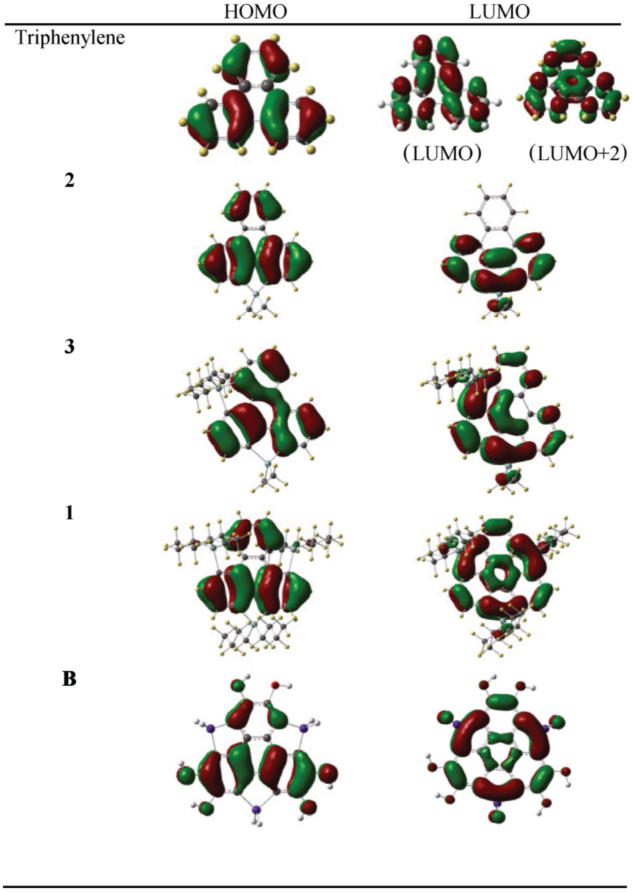


Fig. 3 HOMO and LUMO calculated for triphenylene, **1**, **2**, **3** and **B**.

The fluorescence spectra of obtained triphenylenosilole **2**, triphenylenodisilole **3**, and trisilasumanene **1** were also measured (Fig. 4). In each of the spectra, three main fluorescence maxima were observed. Each of the three fluorescence maxima of **2** is blue-shifted compared to those of triphenylene, reflecting the introduction of the silicon functionality. However, as the number of silylene units increases from compound **2** to **1**, each of the three fluorescence maxima is further red-shifted. Such red shifts have already been reported by Tamao and Yamaguchi,[16] even though the reason for the blue-shift from triphenylene to **2** is still difficult to elucidate. The intense fluorescence band of **1** at 380 nm is slightly red-shifted from that of sumanene (376 nm)[2] and substantially blue-shifted compared to that of hexabutoxytrisilasumanene **A** (427 nm).[8] Comparing the optical properties of the present novel trisilasumanene **1** with hexabutoxytriphenylene **A**, it can be seen that both absorption and fluorescence spectra of trisilasumanene **1** are drastically blue-shifted compared to those of hexabutoxytriphenylene **A**, showing the intrinsic electronic nature of a trisilasumanene framework.[17] It is therefore concluded that substituents on the *exo* carbon atoms of a triphenylene framework can strongly perturb optical properties of trisilasumanenes.

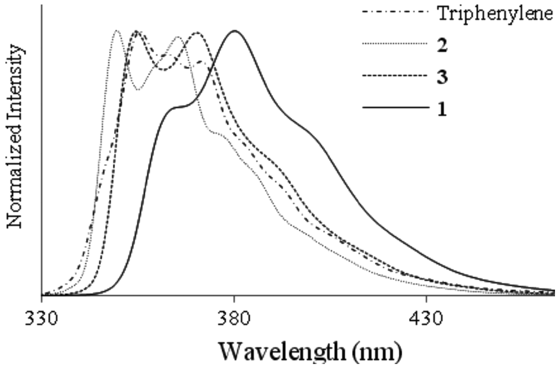


Fig. 4 Fluorescence spectra of triphenylene, **1**, **2** and **3** in CH_2Cl_2.

Conclusion

In summary, we succeeded in the synthesis of novel trisilasumanenes **1** and **5** from triphenylene under mild reaction conditions without using pyrolysis method, and the optical properties of these compounds were investigated. The UV–vis absorption and fluorescence spectra of trisilasumanenes **1** and **5** revealed the intrinsic electronic nature of a trisilasumanene framework, and substituents on the *exo* carbon atoms were found to strongly perturb the electronic nature of the trisilasumanene framework. Investigation of the reactivity of these novel trisilasumanenes and the synthesis of heterasumanenes bearing other heteroatom functionalities are currently in progress.

Experimental

General procedures

THF, hexane were distilled over sodium/benzophenone. ^1H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{29}Si NMR (99 MHz) spectra were recorded on a Bruker DRX-400 or a Bruker AVANCE III-500 spectrometer in $CDCl_3$. The multiplicities of signals in ^{13}C NMR given in parentheses were deduced from DEPT spectra. Wet column chromatography (WCC) and preparative thin layer chromatography (PTLC) were carried out with Kanto silica gel 60 N and Merck silica gel 60, respectively. Preparative gel permeation chromatography (GPC) 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 Hitachi NanoFrontier eLD 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.

Preparation of 4,4-dimethyltriphenyleno[1,12-*bcd*]silole (2)

To a hexane (4 mL) solution of triphenylene (45.8 mg, 2.01 mmol) was added TMEDA (1.20 mL, 8.06 mmol) and butyllithium

(2.69 M in hexane; 3.0 mL, 8.07 mmol) at room temperature. The resulting mixture was heated at 60 °C for 3 h. After the reaction mixture was cooled to room temperature, hexane was evaporated, and THF (4 mL) was then added to the residue, which was treated with a THF (10 mL) suspension of dichlorodimethylsilane (0.48 mL, 4.02 mmol) and copper cyanide (17.7 mg, 0.20 mmol). After the mixture was warmed to room temperature over 14 h, to the mixture was added saturated NH_4Cl_{aq}. The organic layer was extracted with ethyl acetate (2×20 mL) and dried over anhydrous magnesium sulfate. After removal of volatile substances, the residue (757.4 mg) was subjected to GPC to afford 4,4-dimethyltriphenyleno[1,12-*bcd*]silole (**2**) (261.2 mg, conversion yield 50%) and triphenylene (25.8 mg, 6%). **2**: mp 97–105 °C (ethanol). ^{1}H NMR: δ 0.56 (s, 6H), 7.64–7.69 (m, 4H), 7.87 (d, $J = 7$ Hz, 2H), 8.54 (d, $J = 8$ Hz, 2H), 8.65 (dd, $J = 3, 6$ Hz, 2H); ^{13}C NMR: δ –2.97 (q), 123.41 (d), 123.46 (d), 126.97 (d), 127.31 (d), 127.69 (s), 130.14 (s), 131.13 (d), 138.05 (d), 141.22 (s). ^{29}Si NMR: δ 1.14. Anal. Calcd for $C_{20}H_{16}Si$: C, 84.46; H, 5.67. Found: C, 84.54; H, 5.63. HRMS (ESI): Calcd for $C_{20}H_{16}SiNa$, [M+Na]: 307.0914. Found: 307.0911.

Preparation of 3,3-dibutyl-10,10-dimethyltriphenyleno[1,12-*bcd*:4,5-*b′c′d′*]disilole (3)

To 4,4-dimethyltriphenyleno[1,12-*bcd*]silole (**2**) (2.2787 g, 8.01 mmol) was added TMEDA (7.20 mL, 48.33 mmol) and butyllithium (2.76 M in hexane; 17.5 mL, 48.3 mmol) at room temperature. The resulting mixture was heated at 60 °C for 3 h. After the reaction mixture was cooled to room temperature, hexane was evaporated, and THF (100 mL) was added to the residue, which was then treated with chlorotrimethylsilane (6.2 mL, 49.08 mmol) at –78 °C. After the mixture was warmed to room temperature over 13 h, to the mixture was added saturated NH_4Cl_{aq}. The organic layer was extracted with ethyl acetate (2×100 mL) and dried over anhydrous magnesium sulfate. After removal of volatile substances, the residue (5.61 g) was subjected to WCC (eluent: hexane) to afford pale brown oil (3.48 g). An aliquot (3.17 g) of the crude oil was subjected to GPC to afford 3,3-dibutyl-10,10-dimethyltriphenyleno[1,12-*bcd*:4,5-*b′c′d′*]disilole (**3**) (1.43 g, 42%, conversion yield 46%). **3**: ^{1}H NMR: δ 0.59 (s, 6H), 0.84 (t, $J = 7$ Hz, 6H), 1.08–1.12 (m, 4H), 1.34 (q, $J = 7$ Hz, 4H), 1.41–1.47 (m, 4H), 7.64–7.69 (m, 2H), 7.85–7.88 (m, 4H), 8.51 (d, $J = 8$ Hz, 2H); ^{13}C NMR: δ –2.75 (q), 12.38 (t), 13.67 (q), 26.22 (t), 26.42 (t), 123.56 (d), 123.68 (d), 127.04 (d), 127.17 (d), 127.77 (s), 127.81 (s), 130.72 (d), 130.80 (d), 131.44 (d), 131.48 (d), 136.92 (s), 137.54 (s), 137.60 (s), 138.56 (s), 138.68 (s), 139.27 (s), 141.34 (s), 141.83 (s). ^{29}Si NMR: δ 3.38, 6.37. Anal. Calcd for $C_{28}H_{32}Si_2$: C, 79.18; H, 7.59. Found: C, 79.08; H, 7.62. HRMS (ESI): Calcd for $C_{28}H_{32}Si_2Na$, [M+Na]: 447.1935. Found: 447.1938.

Preparation of 3,3,6,6-tetrabutyl-9,9-dimethyltriphenyleno-[1,12-*bcd*:4,5-*b′c′d′*:8,9-*b″c″d″*]trisilole (5)

To a hexane (8 mL) solution of 3,3-dibutyl-10,10-dimethyltriphenyleno[1,12-*bcd*:4,5-*b′c′d′*]disilole (**3**) (116.2 mg, 0.27 mmol) was added TMEDA (0.41 mL, 2.75 mmol) and butyllithium (2.76 M in hexane; 1.0 mL, 2.76 mmol) at room temperature. The resulting mixture was heated at 60 °C for 3 h. After being cooled to room temperature, hexane was evaporated. After the evaporation, the mixture was treated with a THF suspension (8 mL) of dichlorodimethylsilane (0.34 mL, 2.85 mmol) and copper cyanide (13.2 mg, 0.15 mmol) at –88 °C. After being stirred for 10 min at –88 °C, and the mixture allowed to warm to room temperature for 13 h, saturated NH_4Cl_{aq} and water was poured into the mixture. The organic layer was extracted with ethyl acetate (2×20 mL) and dried over anhydrous magnesium sulfate. After removal of volatile substances, the residue (281.2 mg) was subjected to WCC (eluent: hexane : ethyl acetate = 10 : 1) to afford yellow oil (56.2 g). The obtained oil gel was subjected to GPC followed by PTLC to afford 3,3,6,6-tetrabutyl-9,9-dimethyltriphenyleno[1,12-*bcd*:4,5-*b′c′d′*:8,9-*b″c″d″*]trisilole (**5**) (23.4 mg, 15%). **5**: ^{1}H NMR: δ 0.60 (s, 6H), 0.84 (t, $J = 7$ Hz, 12H), 1.06–1.11 (m, 8H), 1.34 (q, $J = 7$ Hz, 8H), 1.43–1.51 (m, 8H), 7.82 (d, $J = 8$ Hz, 4H), 7.83 (s, 2H); ^{13}C NMR: δ –2.44 (s), 12.55 (t), 13.72 (q), 26.32 (t), 26.46 (t), 130.52 (d), 131.21 (d), 131.36 (d), 137.21 (s), 137.44 (s), 138.08 (s), 138.31 (s), 138.79 (s), 138.87 (s); ^{29}Si NMR: δ 6.41, 9.70. Anal. Calcd for $C_{36}H_{48}Si_3$: C, 76.53; H, 8.56. Found: C, 76.57; H, 8.70. HRMS (ESI): Calcd for $C_{36}H_{48}Si_3Na$, [M+Na]: 587.2956. Found: 587.2958.

Preparation of 3,3,6,6,9,9-hexabutyltriphenyleno-[1,12-*bcd*:4,5-*b′c′d′*:8,9-*b″c″d″*]trisilole (1)

To a THF (4 mL) solution of 3,3,6,6-tetrabutyl-9,9-dimethyltriphenyleno[1,12-*bcd*:4,5-*b′c′d′*:8,9-*b″c″d″*]trisilole (**5**) (15.5 mg, 0.027 mmol) was added butyllithium (2.76 M in hexane; 0.1 mL, 0.28 mmol) at –72 °C. The resulting mixture was heated at –72 °C for 5 min. After being warmed to room temperature, the mixture was stirred for 1.5 h. After the stirring, it was treated with water. The mixture was extracted by ethyl acetate (2×20 mL) and dried over anhydrous magnesium sulfate. After removal of volatile substances, the residue (23.9 mg) was subjected to PTLC to afford 3,3,6,6,9,9-hexabutyltriphenyleno[1,12-*bcd*:4,5-*b′c′d′*:8,9-*b″c″d″*]trisilole (**1**) (5.5 mg, 31%). **1**: ^{1}H NMR: δ 0.85 (t, $J = 7$ Hz, 18H), 1.07–1.11 (m, 12H), 1.35 (q, $J = 7$ Hz, 12H), 1.45–1.51 (m, 12H), 7.81 (s, 6H); ^{13}C NMR δ 12.58 (t), 13.71 (q), 26.35 (t), 26.47 (t), 131.20 (d), 137.23 (s), 138.84 (s); ^{29}Si NMR δ 9.47. Anal. Calcd for $C_{42}H_{60}Si_3$: C, 77.71; H, 9.32. Found: C, 77.31.; H, 9.79. HRMS (ESI): Calcd for $C_{42}H_{60}Si_3Na$, [M+Na]: 671.3895. Found: 671.3897.

X-ray diffraction analysis of triphenylenosilole 2

Crystal suitable for X-ray diffraction were obtained by recrystallization in EtOH solution of **2** at –20 °C. The intensity data were collected at –173 °C on a Bruker SMART APEX equipped with a CCD area detector with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and graphite monochromater. Formula $C_{20}H_{16}Si_1$, FW = 284.42, crystal dimensions $0.60 \times 0.40 \times 0.30$ nm, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 8.3831(10)$ Å, $b = 11.7677(15)$ Å, $c = 15.0120(19)$ Å, $V = 1480.9(3)$ Å^3, $D_c = 1.276$ g cm^{-3}, $R_1 = 0.0381$ ($I > 2\sigma(I)$, 3356 reflections), $_wR_2 = 0.1005$ (for all reflections) for 3549 reflections and 192 parameters, GOF = 1.057. CCDC-792994 contains the supplementary crystallographic data for compound **2**.† These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk)

Theoretical calculations

All calculations were carried out using the Gaussian 03 program.[15] Geometries were fully optimized with density functional theory at the M05-2x level by using the 6-311+G(2df) basis set for Si and the 6-31G** basis set for all other atoms. The Cartesian coordinates of the optimized geometries for compounds **1**, **2**, **3** and **B** are shown in electronic supplementary information.†

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