

Synthesis and characterisation of new oligoacetylenic silanes

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Synthetic routes to a series of novel oligoacetylenic silanes with or without (hetero)aromatic bridges have been developed. The compound $\text{Me}_3\text{SiC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CSiMe}_3$ was first prepared, which was selectively desilylated with CaCO_3 in methanol at room temperature to afford the mono-protected bis(alkynyl) silane $\text{Me}_3\text{SiC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CH}$ in moderate yield. Treatment of this mono-protected species with $n\text{BuLi}$, followed by silylation with Ph_2SiCl_2 , gives a good yield of $\text{Me}_3\text{SiC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CSiMe}_3$, with alternating silicon and acetylene units. A range of linear silicon-linked oligoalkynes containing phenylene, bithienylene and anthrylene rings, $\text{HC}\equiv\text{CRC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CH}$ and $\text{HC}\equiv\text{CRC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CH}$ ($\text{R} = 1,4\text{-phenylene}$, $5,5'\text{-bithienylene}$ or $9,10\text{-anthrylene}$), were synthesised by condensation reactions of Ph_2SiCl_2 with the components obtained *in situ* from a $\text{HC}\equiv\text{CRC}\equiv\text{CH}-n\text{BuLi}$ mixture in THF and the products were isolated by chromatography on silica. All these new compounds have been characterised by IR, ^1H and ^{13}C NMR and UV/VIS spectroscopies and mass spectrometry. The single-crystal X-ray structure of $\text{HC}\equiv\text{C}(p\text{-C}_6\text{H}_4)\text{C}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{C}(p\text{-C}_6\text{H}_4)\text{C}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{C}(p\text{-C}_6\text{H}_4)\text{C}\equiv\text{CH}$ has been determined, showing that two silicon atoms and six acetylene units constitute the backbone of the molecule.

The molecular design and synthesis of linear, cyclic or dendritic systems composed of silicon atoms and acetylene units has aroused considerable interest.^{1–5} These carbon-rich acetylene-based scaffolds have been demonstrated to exhibit intriguing electrical, electronic, optical and structural properties.^{1–5} The lower ionisation energy of the silicon atom compared with carbon is expected to enhance the through-bond interaction of ethynyl units along the backbone.^{6,7} In this context, the chemistry of linear inorganic polymers containing alternating arrangements of silylene and π -electron moieties represents an important area of current active research because they possess good potential as functional materials such as semiconductors,⁸ hole-transporting^{9–11} and heat-resistant materials,^{12–14} photoresists^{15,16} and ceramic precursors.^{1,17} The unusual electrical and optical properties associated with these materials are generally attributed to the delocalisation of electrons through the silylene linkages *via* π - d_{Si} interactions^{18,19} or σ - π conjugation.^{6,20} Among these, π -conjugated systems incorporating phenylene, anthrylene or oligothiophene bridges along with Si residues in the main chain have been extensively investigated regarding their applications to electro- and optical devices.^{21–28}

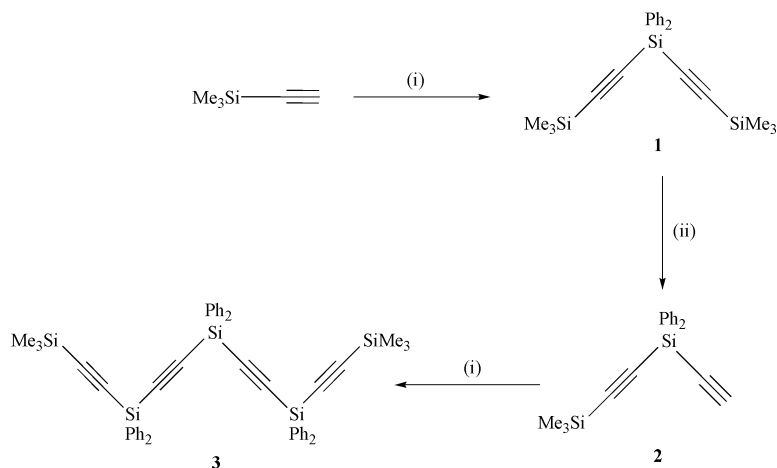
However, to our knowledge, reports on the synthesis of linear oligoacetylenic silanes have been scarce and related problems in this area remain relatively unexplored.^{5,29,30} Alkynylsilane-based short-chain oligomers are not only key intermediates in the preparation of their polymeric or cyclic compounds but also useful alternative materials with potentially enhanced performance by limiting the conjugation length of the polymer.^{31,32} In this respect, oligo(phenylene vinylene)s represent one of the best examples that have recently drawn considerable attention.^{31–33} Investigation of well-defined π -conjugated oligomers can provide an insight into the electronic, emissive and structural properties of the related polymeric materials.³¹ These oligoacetylenic silanes are also attractive building blocks for molecular architectures, but their

syntheses have been largely hampered by the limited availability of suitable difunctionalised silyl compounds by the ready polymerisation of the starting silylacetylene precursors.^{34–37} We have recently described a systematic approach to the synthesis of some oligoacetylenic sulfides,^{38,39} and the fruitful results prompted us to prepare a new series of linear oligoacetylenic silanes containing $\text{Ph}_2\text{SiC}\equiv\text{C}$ units. Based on our experience in the preparation of oligoacetylenic sulfides and related compounds in organic synthesis,⁴⁰ we report here the first synthesis of a novel class of well-defined oligo(alkynylsilane)s, with or without (hetero)aromatic groups, and a description of their spectroscopic, optical and structural properties is also presented.

Results and discussion

Syntheses

The preparation of the silylacetylene oligomer **3** starts with the synthesis of a mono-protected bis(alkynyl) silane **2**. Treatment of trimethylsilylacetylene with $n\text{BuLi}$ at -78°C yielded the corresponding lithium salt, which reacted *in situ* with Ph_2SiCl_2 to provide a white solid, $\text{Me}_3\text{SiC}\equiv\text{C}-\text{Si}(\text{Ph})_2\text{C}\equiv\text{CSiMe}_3$, **1**, in 72% yield based on $\text{Me}_3\text{SiC}\equiv\text{CH}$ (Scheme 1). The desired mono-protected bis(acetylene) silane **2** was obtained as a colourless liquid in moderate yield when **1** was desilylated with CaCO_3 in MeOH at room temperature. **2** was found to be slightly unstable in air, especially when concentrated, which precluded satisfactory elemental analysis. It is noteworthy that mono-desilylation of **1** to produce **2** did not occur under commonly used desilylation conditions (*e.g.*, $\text{K}_2\text{CO}_3\text{-MeOH}$ or KF-MeOH).^{38,39,41–43} Careful mono-desilylation of **1** with a $\text{CaCO}_3\text{-MeOH}$ mixture should be conducted under anhydrous condition and

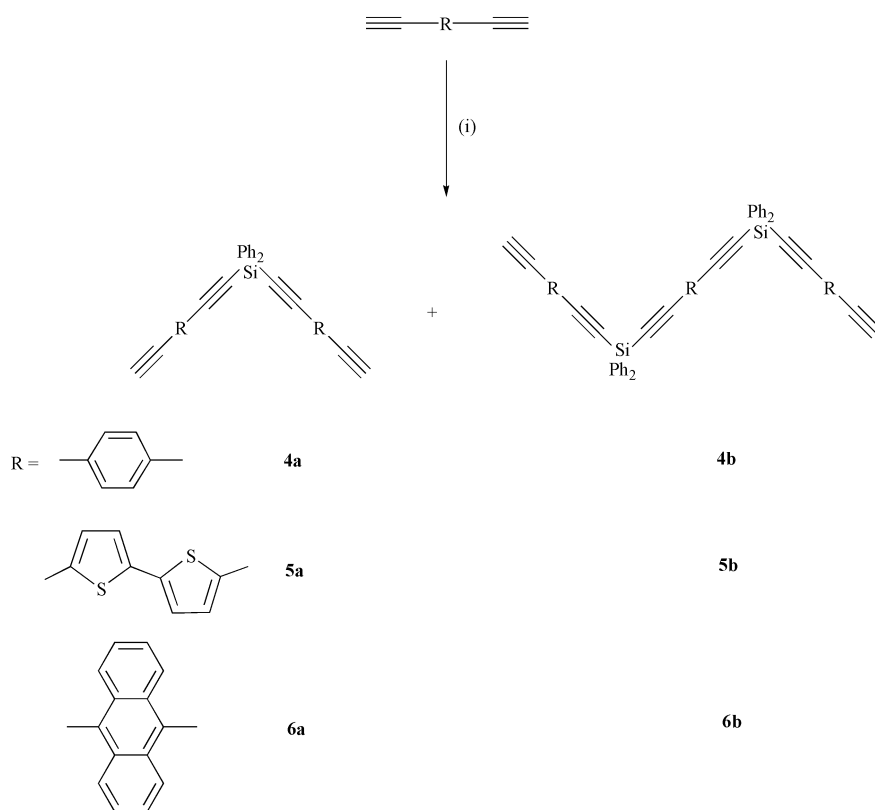


Scheme 1 (i) $n\text{BuLi}$, -20°C , Ph_2SiCl_2 , THF; (ii) $\text{CaCO}_3\text{--MeOH}$, r.t.

close monitoring with TLC. When $\text{HC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CH}$ started to appear, the reaction was quenched by water. Work-up and flash column chromatography gave **2** in 42% yield. Although the yield of **2** was not very high, the recovered **1** could be reused to prepare **2**. Freshly prepared **2** was then treated with $n\text{BuLi}$ followed by silylation with Ph_2SiCl_2 in THF to furnish, on chromatography, **3** as a colourless oily substance with a yield of 65%. The chain length was doubled in this synthetic procedure. Attempts have also been made to extend the chain length through further mono-desilylation of **3** followed by silylation with Ph_2SiCl_2 . Unfortunately, only a complicated mixture was obtained in this way.

In the pursuit of more stable oligoacetylenic silanes with tunable physical and optical properties, it seemed an attractive goal to us to synthesise new silylacetylene compounds containing a range of aromatic and heteroaromatic moieties along the backbone. The synthetic route leading to the target mole-

cules is outlined in Scheme 2. When $\text{HC}\equiv\text{CRC}\equiv\text{CH}$ was treated with 1 equiv. of $n\text{BuLi}$ or freshly prepared $(\text{Me}_3\text{Si})_2\text{NLi}$ (as a base) in THF followed by 0.5 equiv. of Ph_2SiCl_2 at -78°C , a mixture of $\text{HC}\equiv\text{CRC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CH}$ and $\text{HC}\equiv\text{CRC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CH}$ ($\text{R} = 1,4\text{-phenylene}$, $5,5'\text{-bithienylene}$ or $9,10\text{-anthrylene}$) was formed along with small amounts of their higher oligomers and the recovered starting diethynyl compounds. Purification of **4–6** was effected by preparative TLC on silica, leading to the isolation of the products as white (**4a** and **4b**), pale yellow (**5a** and **5b**) and orange-yellow (**6a** and **6b**) solids in moderate to good yields. Compounds **4–6** are generally stable as solids in air at room temperature and dissolve readily in common organic solvents such as CH_2Cl_2 and CHCl_3 . However, **5** and **6** decompose slightly when kept in solution for a prolonged period of time or under light and do not melt below their decomposition temperatures. All the new compounds in this



Scheme 2 (i) $n\text{BuLi}$, -20°C , Ph_2SiCl_2 , THF.

study were satisfactorily characterised by common spectroscopic methods (IR, MS, ^1H and ^{13}C NMR).

Spectroscopic properties

All the spectroscopic data of compounds **1–6** are consistent with their structures (Experimental section). The IR spectra of these oligoacetylenic species display strong $\nu_{\text{C}\equiv\text{C}}$ absorption bands in the range 2040–2159 cm^{-1} .^{28,38,43} The terminal acetylenic C–H signal also appears around 3275–3305 cm^{-1} for **2**, **4**, **5** and **6**. In all cases, ^1H NMR resonances arising from the protons of the organic fragments were observed, and all the phenyl, phenylene, bithienylene and anthrylene carbon atoms were clearly identified in the aromatic region of the ^{13}C - $\{^1\text{H}\}$ NMR spectra. Notably, there are four and six distinct ^{13}C NMR signals for all the individual sp carbons in **4a–6a** and **4b–6b**, respectively, in accordance with their formulations. Assignment of these ^{13}C resonances was made on the basis of peak intensities and by analogy with results of other similar acetylide compounds.^{28,38,43,44} For **4–6**, the ^{13}C chemical shifts remain relatively unshifted for the outermost acetylene carbons as compared to the free ligand $\text{HC}\equiv\text{C}\text{RC}\equiv\text{CH}$ whereas the innermost acetylene carbons in close proximity to Si appear at more downfield positions. For comparison, while the sp carbons of 5,5'-diethynyl-2,2'-bithiophene resonate at δ 76.66 ($\text{C}\equiv\text{CH}$) and 82.68 ($\text{C}\equiv\text{CH}$),⁴³ those for **5a** appear at δ 76.58 and 82.77 for the outermost carbons and at δ 93.46 and 101.03 for the innermost $\text{C}\equiv\text{C}$ units close to the SiPh_2 group. The ^{13}C NMR spectrum of **5b** shows six resonances of sp carbon atoms. The nearly unaltered chemical shift values at δ 76.58 and 82.76 in **5b** correspond to the two outer carbons, while the lower field signals at δ 93.46, 93.62, 101.00 and 101.05 are ascribed to the middle and innermost acetylene carbons. The ^{29}Si NMR chemical shifts of **4** and **6** do not differ significantly from those for the longer chain homologues,⁴⁵ in line with the UV/VIS spectral data (*vide infra*). These results indicate that there is a diminishing effect on the degree of electronic conjugation with increasing number of Si residues in the backbone. The formulae of these oligoacetylenic silanes were successfully confirmed by EI and positive FAB mass spectrometry and the respective molecular ion peaks were detected in each case.

The optical properties of our new compounds have been investigated in CH_2Cl_2 solutions. The electronic absorption and emission data are given in the Experimental section. Trimethylsilyl-capped Si-containing tetrayne **3** shows *ca.* 50 nm red-shifted absorption bands in comparison with **1**, probably due to the extended conjugation through Si as the chain length is doubled. The absorption spectra of **4a** and **4b** are dominated by π – π^* transitions of the bridging units in the near-UV region, and a notable bathochromic shift in λ_{max} with increased extinction coefficients is observed upon going from 1,4-diethynylbenzene (260, 273 nm) to **4a** (274, 290 nm) and **4b** (274, 289, 303 nm). Both **5a** and **5b** exhibit strong π – π^* transitions in the near-UV range with a similar absorption pattern, attributable to the bithienyl moiety.⁴³ The lowest energy band red-shifts from 353 (5,5'-diethynyl-2,2'-bithiophene)⁴³ to 365 (**5a**) and 370 nm (**5b**). The polymeric analogue of **5** with a single thiophene group $[-\text{C}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{C}(2,5\text{-C}_4\text{H}_2\text{S})\text{C}\equiv\text{C}-]_n$ shows its lowest energy absorption at 304 nm in the same solvent.⁴⁵ The UV/VIS spectra of **6a** and **6b** are characterised by intense absorption bands with fine structure most likely arising from transitions similar to those for anthracene.⁴⁶ With reference to the bands in anthracene (326, 342, 359, 378 nm), those for **6a** and **6b** are red-shifted by *ca.* 50–80 nm, the bathochromic shift being greater than for 9,10-diethynylanthracene (λ_{max} 361, 380, 402, 426 nm).²⁸ The corresponding absorption peaks in **6b** with a longer chain length are further red-shifted with respect to those in **6a**. These properties are suggestive of the presence of through-Si conjugation along the backbone in these oligomeric organosilicon systems. However,

the extent of bathochromic shifts induced by the increased chain length is less pronounced with increasing number of repeat units. The fact that the polymeric homologues of **4** and **6**, $[-\text{C}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{C}\text{RC}\equiv\text{C}-]_n$, display very similar lowest energy peaks at 303 ($\text{R} = 1,4\text{-phenylene}$) and 450 ($\text{R} = 1,10\text{-anthrylene}$) nm as those of **4b** and **6b**, respectively, suggest that there would probably be little benefit in increasing the number of repeating units above three in the control of spectral properties of these diphenylsilylene materials.^{36,45}

In the solution state, compounds **4–6** are luminescent at room temperature and the emission peaks range from 339 to 484 nm. There is a slight bathochromic shift in the emission wavelength upon going from compounds **a** to **b** within each series incorporating a particular R group. We also note that the position of the absorption maximum depends on the nature of the aromatic unit R. For the series **4a–6a**, the λ_{max} of the low-energy band increases from 290 nm for **4a** to 365 nm for **5a** and a significant red-shift of the absorption maximum is observed for **6a** (438 nm) when a more electron-rich unit such as anthracene is introduced. A similar trend was also encountered for the group **4b–6b**. It has been suggested for some conjugated aromatic copolymers that the position of the absorption maximum is related to the degree of destabilisation of the HOMO and stabilisation of the LUMO.⁴⁷ The presence of the electron-rich anthracene residue in **6a** and **6b** tends to reduce the energy gap between these frontier levels, and gives rise to a bathochromic shift of the absorption and emission compared to the other two groups of molecules having phenylene and bithienylene moieties.

Crystal structure analysis

The crystallographically determined structure of **4b** by an X-ray diffraction experiment serves to identify the oligomeric nature of the product unequivocally. A perspective drawing of compound **4b** is shown in Fig. 1, which includes the atom numbering scheme. The principal bond lengths and angles are listed in Table 1. There is a crystallographic centrosymmetry at the central phenylene ring such that two halves of the molecule are related by an inversion centre at the centroid of the C(25)–C(26)–C(27A)–C(25A)–C(26A)–C(27) plane. In the solid state, **4b** possesses three $-\text{C}\equiv\text{C}(p\text{-C}_6\text{H}_4)\text{C}\equiv\text{C}-$ moieties alternately connected by two SiPh_2 units in a linear fashion. There are a total of six $\text{C}\equiv\text{C}$ units in the entire molecule. The $\text{C}\equiv\text{C}$ bond lengths lie within the narrow range of 1.197(2)–1.206(3) Å and the $\text{C}\equiv\text{CH}$ bond shows a slight shortening of bond length [1.164(4) Å] due to the libration effect.⁴⁸ The Si–C(sp) single bond lengths are 1.810(2)–1.822(2) Å [ave. 1.816(2) Å], which are slightly shorter than those observed in related silylacetylene compounds such as the two silapericyclopentynes conformers [1.83(2)–1.836(3) Å],⁴⁹ the *cis-trans* and all-*trans* isomers of 1,2,5,6-tetramethyl-1,2,5,6-tetraphenyl-1,2,5,6-tetrasilacycloocta-3,7-diyne [1.841(5)–1.843(5), 1.828(6)–1.836(6) Å, respectively]³⁵ and the 1G-dendrimer with 10 silicon atoms and 9 acetylene units [1.827(5)–1.851(5) Å].⁵ These data, together with the slightly shorter $\equiv\text{C}-\text{C}(\text{ring})$ bond [*ca.* 1.427(3)–1.436(2) Å], are consistent with a partial conjugation effect along the molecular backbone. The linearity of the acetylene units is evident from the bond angles of Si–C(sp)–C(sp) and C(sp)–C(sp)–C(sp²), and the unusually small Si(1)–C(10)–C(9) bond angle [172.7(2)°] is presumably caused by the solid-state packing effect in the crystal lattice. All the aromatic rings are nearly planar with normal bond parameters.

Concluding remarks

The present work provides a convenient entry to a new series of oligoacetylenic silanes. The results here indicate through-Si conjugation along the backbone of these molecules and

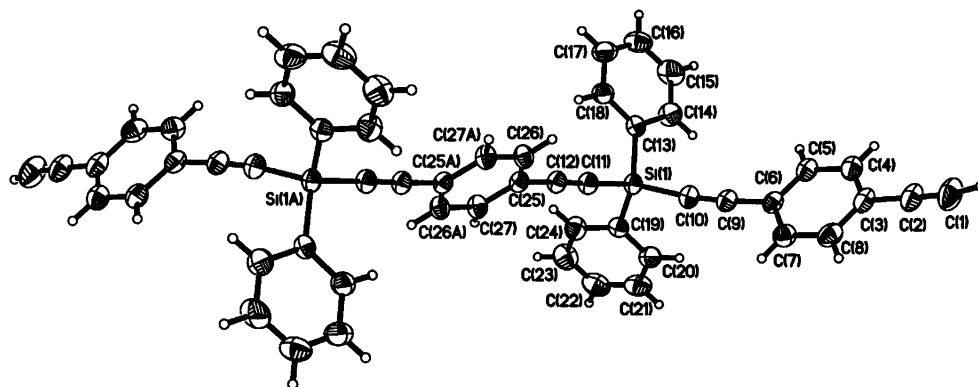


Fig. 1 A perspective drawing of **4b** with the atom numbering scheme.

Table 1 Selected bond lengths (Å) and angles (°) for compound **4b**

C(1)–C(2)	1.164(4)	C(2)–C(3)	1.433(3)
C(6)–C(9)	1.427(3)	C(9)–C(10)	1.206(3)
Si(1)–C(10)	1.810(2)	Si(1)–C(11)	1.822(2)
Si(1)–C(13)	1.855(2)	Si(1)–C(19)	1.855(2)
C(11)–C(12)	1.197(2)	C(12)–C(25)	1.436(2)
C(1)–C(2)–C(3)	177.3(3)	C(6)–C(9)–C(10)	176.7(2)
Si(1)–C(10)–C(9)	172.7(2)	Si(1)–C(11)–C(12)	178.0(2)
C(10)–Si(1)–C(11)	109.44(9)	C(11)–C(12)–C(25)	178.1(2)

attempts have been made to evaluate how the nature of the linking unit R and the chain length of this type of oligomers would influence their optical and spectroscopic properties. We are currently extending these studies to higher generations and further investigations of other properties (such as conducting properties) of these π -electronic systems are now in progress.

Experimental

General

All reactions were conducted under an atmosphere of dry nitrogen with the use of standard Schlenk techniques. Solvents for preparative work were dried and distilled before use. IR spectra were recorded on a Nicolet FTIR-550 spectrometer. NMR spectra were recorded in CDCl_3 on a JEOL JNM-EX 270, Varian Inova 400 MHz or Bruker 600 MHz FT-NMR spectrometer. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded on a Finnigan-SSQ 710 spectrometer. Electronic absorption and luminescence spectra were measured in appropriate solvents with a Varian Cary 100 UV/VIS spectrophotometer and a Perkin-Elmer LS50B luminescence spectrometer, respectively. Unless otherwise stated, all reagents were from commercial sources and used as received. The starting diethynyl compounds $\text{HC}=\text{C}(\text{R})\text{C}\equiv\text{CH}$ (R = 1,4-phenylene, 5,5'-bithienylene or 9,10-anthrylene) were prepared according to the reported procedures.^{41,43,44,50} Separation of products was accomplished by column chromatography on silica or preparative silica TLC plates (Merck, Kieselgel 60).

Synthetic procedures

$\text{Me}_3\text{SiC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CSiMe}_3$, 1. $n\text{-BuLi}$ (13 cm^3 , 20.8 mmol, 1.6 M solution in hexane) was added dropwise to a solution of trimethylsilylacetylene (1.96 g, 20.0 mmol) in dry diethyl ether (40 cm^3) at -78°C under a nitrogen atmosphere. After the mixture was stirred at -78°C for 1 h, Ph_2SiCl_2 (2.53 g, 10.0

mmol) was added in one portion and the reaction mixture was stirred for 2 h at this temperature. The solution was then allowed to warm up to room temperature and stirred for an additional 3 h. The crude material was partitioned between NH_4Cl solution and diethyl ether. The aqueous layer was extracted with ether and the organic phase was dried over Na_2SO_4 , filtered and concentrated. The title product was purified by column chromatography on silica, eluting with petroleum ether– CH_2Cl_2 (4 : 1, v/v). The product was obtained as a white solid in 72% yield (3.76 g). m.p.: $65\text{--}67^\circ\text{C}$. IR (KBr): 2109 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 0.22 (s, 18H, Me), 7.36–7.39 (m, 6H, Ph) and 7.70–7.73 (m, 4H, Ph). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ -0.16 (Me), 106.10, 118.90 ($\text{C}\equiv\text{C}$), 127.86, 129.99, 134.69 (aromatic CH) and 132.73 (aromatic quaternary C). ^{29}Si NMR (CDCl_3): δ -17.58 and 0.00. EI MS: m/z 376 (M^+). UV/VIS (cyclohexane): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon \times 10^4\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) 211 (3.0) and 224 (2.8). Calcd for $\text{C}_{22}\text{H}_{28}\text{Si}_3$: C, 70.14; H, 7.49. Found: C, 69.89; H, 7.20%.

$\text{Me}_3\text{SiC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CH}$, 2. To a solution of **1** (132 mg, 0.35 mmol) in MeOH (10 cm^3) was added CaCO_3 (35 mg). The reaction mixture was stirred at room temperature for 5 h and the course of the reaction was monitored closely by spot TLC. When $\text{HC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CH}$ started to appear, the reaction was subsequently quenched by water and the mixture extracted with CH_2Cl_2 . The resulting organic extract was dried over Na_2SO_4 , filtered and concentrated. The concentrate was then subjected to flash column chromatography on silica using petroleum ether– CH_2Cl_2 (6 : 1, v/v) as eluent to give **2** as a colourless liquid (45 mg, 42%). This compound can be used for the following preparation without further purification. IR (CH_2Cl_2): 3283 (ν_{CH}) and 2040 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 0.22 (s, 9H, Me), 2.70 (s, 1H, $\text{C}\equiv\text{CH}$), 7.38–7.41 (m, 6H, Ph) and 7.72–7.74 (m, 4H, Ph). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ -0.33 (Me), 83.91, 105.24 and 119.52 ($\text{C}\equiv\text{C}$), 96.96 ($\text{C}\equiv\text{CH}$), 128.07, 130.36, 134.76 (aromatic CH) and 131.99 (aromatic quaternary C). ^{29}Si NMR (CDCl_3): δ -49.77 and -17.27 . EI MS: m/z 304 (M^+). A satisfactory elemental analysis was not obtained, probably due to contamination by a trace amount of $\text{HC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CH}$.

$\text{Me}_3\text{SiC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CSiMe}_3$, 3. Compound **2** (48 mg, 0.16 mmol) was dissolved in dry THF (10 cm^3) in a Schlenk flask. After cooling the flask to -78°C , $n\text{-BuLi}$ was added dropwise to the stirred solution. After stirring for 1 h at -78°C , Ph_2SiCl_2 (20 mg, 0.08 mmol) was added dropwise. The resulting mixture was stirred at -78°C for 2 h and then warmed at room temperature for another 0.5 h. The crude material was extracted between NH_4Cl solution and CH_2Cl_2 . The organic layer was dried over Na_2SO_4 and filtered. Concentration of the filtrate followed by silica column chromatography using petroleum ether– CH_2Cl_2 (6 : 1, v/v) as eluent

afforded **3** as a colourless oil in 65% yield (41 mg). IR (KBr): 2040 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 0.22 (s, 18H, Me), 7.34–7.43 (m, 18H, Ph) and 7.75–7.79 (m, 12H, Ph). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ -0.33 (Me), 105.31, 110.39, 111.97, 119.69 ($\text{C}\equiv\text{C}$), 128.06, 128.07, 130.29, 130.44, 134.87, 134.98 (aromatic CH), 132.08 and 134.76 (aromatic quaternary C). ^{29}Si NMR (CDCl_3): δ -50.48, -27.31 and -17.28. EI MS: m/z 788 (M^+). UV/VIS (cyclohexane): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 256 (1.9), 262 (2.4), 266 (2.5) and 273 (2.0). A satisfactory analytical analysis was not obtained due to contamination by a trace amount of $\text{HC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CH}$ that was present in the previous step.

$\text{HC}\equiv\text{CRC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CH}$, **4a, and $\text{HC}\equiv\text{CRC}\equiv\text{C-Si}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CH}$, **4b** (**R** = 1,4-phenylene).** To a chilled solution of 1,4-diethynylbenzene (200 mg, 1.59 mmol) in dried THF (20 cm^3) at -20°C , $(\text{Me}_3\text{Si})_2\text{NLi}$ (266 mg, 1.59 mmol) freshly prepared from $(\text{Me}_3\text{Si})_2\text{NH}$ and $^n\text{BuLi}$ in THF (20 cm^3) or $^n\text{BuLi}$ (1.0 cm^3 , 1.60 mmol, 1.6 M in hexane) was added dropwise under a nitrogen purge. The mixture was stirred for 30 min at this temperature and then 2 h at room temperature. The resulting solution was again cooled to -20°C and a solution of Ph_2SiCl_2 (201 mg, 0.80 mmol) in THF (10 cm^3) was added dropwise over 30 min. The reaction mixture was stirred for a further 30 min at -20°C prior to stirring at room temperature for 3 h. The volatile components were evaporated and the residue was extracted with CH_2Cl_2 . The organic extract was dried over Na_2SO_4 and filtered. The filtrate was concentrated and subjected to preparative TLC isolation using silica plates and hexane- CH_2Cl_2 (3 : 1, v/v) as eluent. From the second ($R_f=0.55$) and third ($R_f=0.45$) bands, compounds **4a** and **4b** were obtained as white solids with yields of 52 (179 mg) and 17% (67 mg), respectively, based on 1,4-diethynylbenzene. The starting 1,4-diethynylbenzene was also recovered in a pure form from the top band (40 mg, 20%), which can be employed as a precursor for the synthesis of more **4a** and **4b**. **4a**: m.p.: 96–98 $^\circ\text{C}$. IR (KBr): 3276 (ν_{CH}) and 2157 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 3.24 (s, 2H, $\text{C}\equiv\text{CH}$), 7.47–7.52 (m, 10H, Ph), 7.58–7.60 (m, 4H, C_6H_4) and 7.89–7.94 (m, 4H, C_6H_4). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ 79.43 ($\text{C}\equiv\text{CH}$), 83.02, 89.62, 107.98 ($\text{C}\equiv\text{C}$), 128.17, 130.42, 131.97, 132.00, 134.89 (aromatic CH), 122.69, 122.95 and 132.44 (aromatic quaternary C). ^{29}Si NMR (CDCl_3): δ -47.88. FAB MS: m/z 432 (M^+). UV/VIS (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 228 (3.1), 274 (9.0) and 290 (1.1). Emission (CH_2Cl_2 , $\lambda_{\text{excitation}}=290 \text{ nm}$): 339 nm. Calcd for $\text{C}_{32}\text{H}_{20}\text{Si}_2$: C, 88.85; H, 4.66. Found: C, 88.59; H, 4.40%. **4b**: m.p.: 180–182 $^\circ\text{C}$. IR (KBr): 3287 (ν_{CH}) and 2159 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 3.19 (s, 2H, $\text{C}\equiv\text{CH}$), 7.43–7.47 (m, 16H, aromatic), 7.52–7.54 (m, 8H, aromatic) and 7.83–7.85 (m, 8H, aromatic). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ 79.44 ($\text{C}\equiv\text{CH}$), 83.01, 89.56, 90.00, 107.95, 108.00 ($\text{C}\equiv\text{C}$), 128.17, 130.43, 131.96, 132.17, 132.20, 134.89 (aromatic CH), 122.67, 122.93, 123.08 and 132.38 (aromatic quaternary C). ^{29}Si NMR (CDCl_3): δ -47.89. FAB MS: m/z 738 (M^+). UV/VIS (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 228 (4.7), 274 (14.1), 289 (14.8) and 303 (11.3). Emission (CH_2Cl_2 , $\lambda_{\text{excitation}}=289 \text{ nm}$): 329, 399sh nm. Calcd for $\text{C}_{54}\text{H}_{34}\text{Si}_2$: C, 87.76; H, 4.64. Found: C, 87.52; H, 4.31%.

$\text{HC}\equiv\text{CRC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CH}$, **5a, and $\text{HC}\equiv\text{CRC}\equiv\text{C-Si}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CH}$, **5b** (**R** = 5,5'-bithienylene).** These compounds were prepared using the conditions described above for **4a** and **4b** but used instead of 1,4-diethynylbenzene (118 mg, 0.55 mmol) was used instead of 1,4-diethynylbenzene. Elution using a 2 : 1 hexane- CH_2Cl_2 mixture gave three yellow bands, from which three compounds were separated. In order of elution, these compounds were 5,5'-diethynyl-2,2'-bithiophene ($R_f=0.68$, 20 mg, 17%), **5a** ($R_f=0.50$, 42

mg, 25%) and **5b** ($R_f=0.27$, 18 mg, 10%), all as pale yellow solids. **5a**: m.p.: 90–92 $^\circ\text{C}$ (dec.). IR (KBr): 3284 (ν_{CH}), 2139 and 2098 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 3.42 (s, 2H, $\text{C}\equiv\text{CH}$), 7.04 (d, $^3J_{\text{H-H}}=1.6 \text{ Hz}$, 2H, thienyl), 7.05 (d, $^3J_{\text{H-H}}=1.6 \text{ Hz}$, 2H, thienyl), 7.17 (d, $^3J_{\text{H-H}}=4.0 \text{ Hz}$, 2H, thienyl), 7.27 (d, $^3J_{\text{H-H}}=4.0 \text{ Hz}$, 2H, thienyl), 7.43–7.48 (m, 6H, Ph) and 7.81–7.84 (m, 4H, Ph). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ 82.77 ($\text{C}\equiv\text{CH}$), 76.58, 93.46, 101.03 ($\text{C}\equiv\text{C}$), 123.97, 124.04, 128.21, 130.52, 133.99, 134.88, 134.94 (aromatic CH), 121.53, 121.56, 132.01, 137.97 and 138.92 (aromatic quaternary C). ^{29}Si NMR (CDCl_3): δ -47.78. FAB MS: m/z 608 (M^+). UV/VIS (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 229 (2.5), 259 (1.4) and 365 (5.3). Emission (CH_2Cl_2 , $\lambda_{\text{excitation}}=365 \text{ nm}$): 409 nm. Calcd for $\text{C}_{36}\text{H}_{20}\text{Si}_4$: C, 71.01; H, 3.31. Found: C, 70.81; H, 3.42%. **5b**: m.p.: 53–54 $^\circ\text{C}$ (dec.). IR (KBr): 3285 (ν_{CH}), 2142 and 2100 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 3.42 (s, 2H, $\text{C}\equiv\text{CH}$), 7.04 (d, $^3J_{\text{H-H}}=1.6 \text{ Hz}$, 2H, thienyl), 7.05 (d, $^3J_{\text{H-H}}=1.6 \text{ Hz}$, 2H, thienyl), 7.06 (d, $^3J_{\text{H-H}}=3.6 \text{ Hz}$, 2H, thienyl), 7.17 (d, $^3J_{\text{H-H}}=3.6 \text{ Hz}$, 2H, thienyl), 7.26 (t, $^3J_{\text{H-H}}=4.0 \text{ Hz}$, 4H, thienyl), 7.42–7.48 (m, 12H, Ph) and 7.81–7.83 (m, 8H, Ph). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ 82.76 ($\text{C}\equiv\text{CH}$), 76.58, 93.46, 93.62, 101.00, 101.05 ($\text{C}\equiv\text{C}$), 123.98, 124.05, 124.14, 128.21, 130.52, 133.99, 134.89, 134.91, 134.95 (aromatic CH), 121.55, 121.56, 121.74, 132.00, 137.98, 138.85 and 138.93 (aromatic quaternary C). ^{29}Si NMR (CDCl_3): δ -47.79. FAB MS: m/z 1002 (M^+). UV/VIS (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 230 (2.9), 260 (1.5) and 370 (7.2). Emission (CH_2Cl_2 , $\lambda_{\text{excitation}}=370 \text{ nm}$): 412 nm. Calcd for $\text{C}_{60}\text{H}_{34}\text{Si}_2\text{S}_6$: C, 71.82; H, 3.42. Found: C, 71.45; H, 3.21%.

$\text{HC}\equiv\text{CRC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CH}$, **6a, and $\text{HC}\equiv\text{CRC}\equiv\text{C-Si}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CSi}(\text{Ph})_2\text{C}\equiv\text{CRC}\equiv\text{CH}$, **6b** (**R** = 9,10-anthrylene).** These anthryl-substituted oligoalkynes were similarly synthesised as described for **4a** and **4b** from 9,10-diethynylanthracene (288 mg, 1.27 mmol). The resulting brown-yellow suspension was then purified by silica TLC separation, eluting with hexane- CH_2Cl_2 (3 : 1, v/v) to give three major yellow bands identified as 9,10-diethynylanthracene ($R_f=0.73$, 72 mg, 25%), **6a** ($R_f=0.54$) and **6b** ($R_f=0.44$). Further purification of the desired products **6a** and **6b** was accomplished by another TLC separation using the same solvent mixture, followed by recrystallisation to afford orange-yellow solids of **6a** and **6b** in 27 (109 mg) and 10% (44 mg) yield, respectively. **6a**: m.p.: 155–156 $^\circ\text{C}$ (dec.). IR (KBr): 3303 (ν_{CH}) and 2131 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 4.10 (s, 2H, $\text{C}\equiv\text{CH}$), 7.50–7.56 (m, 4H, anthryl), 7.57–7.67 (m, 10H, Ph), 8.09–8.20 (m, 4H, anthryl), 8.57–8.67 (m, 4H, anthryl) and 8.69–8.79 (m, 4H, anthryl). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ 90.24 ($\text{C}\equiv\text{CH}$), 80.18, 101.26, 105.60 ($\text{C}\equiv\text{C}$), 126.98, 127.02, 127.08, 127.30, 128.32, 130.50, 135.01 (aromatic CH), 117.74, 118.34, 127.66, 132.35 and 132.62 (aromatic quaternary C). ^{29}Si NMR (CDCl_3): δ -47.40. FAB MS: m/z 632 (M^+). UV/VIS (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 228 (3.1), 270 (11.7), 390 (1.3), 412 (2.6) and 438 (3.4). Emission (CH_2Cl_2 , $\lambda_{\text{excitation}}=390 \text{ nm}$): 436 and 480 nm. Calcd for $\text{C}_{48}\text{H}_{28}\text{Si}_2$: C, 91.10; H, 4.46. Found: C, 90.84; H, 4.28%. **6b**: m.p.: 96–98 $^\circ\text{C}$ (dec.). IR (KBr): 3290 (ν_{CH}) and 2130 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3): δ 4.09 (s, 2H, $\text{C}\equiv\text{CH}$), 7.47–7.55 (m, 4H, anthryl), 7.56–7.72 (m, 20H, Ph), 8.06–8.23 (m, 8H, anthryl), 8.57–8.65 (m, 4H, anthryl) and 8.69–8.83 (m, 8H, anthryl). ^{13}C - $\{^1\text{H}\}$ NMR (CDCl_3): δ 90.24 ($\text{C}\equiv\text{CH}$), 80.17, 101.20, 101.74, 105.55, 105.65 ($\text{C}\equiv\text{C}$), 126.98, 127.02, 127.07, 127.30, 127.38, 128.32, 130.52, 135.01, 135.16 (aromatic CH), 117.70, 118.34, 127.16, 130.78, 132.34, 132.63 and 132.65 (aromatic quaternary C). ^{29}Si NMR (CDCl_3): δ -47.41. FAB MS: m/z 1040 (M^+). UV/VIS (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 228 (6.4), 270 (16.7), 391 (1.6), 413 (3.1), 423 (2.9), 438 (3.6) and 450 (3.6). Emission (CH_2Cl_2 , $\lambda_{\text{excitation}}=413 \text{ nm}$): 454 and 484 nm. Calcd for $\text{C}_{78}\text{H}_{46}\text{Si}_2$: C, 90.14; H, 4.46. Found: C, 89.85; H, 4.14%.

Table 2 Summary of crystal structure data for compound **4b**

Empirical formula	C ₅₄ H ₃₄ Si ₂
<i>M</i>	738.99
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> /Å	8.0001(7)
<i>b</i> /Å	9.4959(9)
<i>c</i> /Å	14.769(1)
α /°	80.960(2)
β /°	74.773(2)
γ /°	82.454(2)
<i>U</i> /Å ³	1064.4(2)
<i>Z</i>	1
μ (Mo-K α)/mm ⁻¹	0.119
No. reflections collected	6216
Unique reflections	4519
<i>R</i> _{int}	0.0188
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	4519
<i>R</i> ₁	0.0583
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1741
<i>R</i> ₁	0.0695
<i>wR</i> ₂ (all data)	0.1890

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}.$$

Crystallography

Colourless crystals of **4b** suitable for X-ray diffraction analysis were grown by evaporation of its solution in a hexane–CH₂Cl₂ mixture. Geometric and intensity data were collected using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) on a Bruker AXS SMART CCD area detector. The collected frames were processed with the software SAINT⁵¹ and an absorption correction was applied (SADABS⁵²) to the collected reflections. The structure was solved by direct methods (SHELXTL⁵³) in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses. All non-hydrogen atoms were assigned with anisotropic displacement parameters. Hydrogen atoms were generated in their idealised positions and allowed to ride on the respective carbon atoms. Crystallographic and other experimental details are collected in Table 2.

CCDC reference number 177961. See <http://www.rsc.org/suppdata/nj/b1/b108510g> for crystallographic data in CIF or other electronic format.

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