



*Citation for published version:*

Shankar, R, Chaudhary, M, Molloy, KC & Kociok-Kohn, G 2013, 'New cyclotetrasiloxanes bearing sila-alkyl substituted side chains and their applications as templates for gold nanowires', *Dalton Transactions*, vol. 42, no. 21, pp. 7768-7774. <https://doi.org/10.1039/c3dt50284h>

*DOI:*

[10.1039/c3dt50284h](https://doi.org/10.1039/c3dt50284h)

*Publication date:*

2013

*Document Version*

Peer reviewed version

[Link to publication](#)

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

# New cyclotetrasiloxanes bearing sila-alkyl substituted side chains and their applications as templates for gold nanowires

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

New sila-alkyl substituted cyclotetrasiloxanes, [RMe<sub>2</sub>SiCH<sub>2</sub>CH<sub>2</sub>(Me)SiO]<sub>4</sub> [R = Ph(**1**), 2-thienyl(**2**), 2-furyl(**3**)] have been synthesized by a hydrosilylation reaction between 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, (D<sub>4</sub><sup>VI</sup>) and dimethylphenylsilane/ dimethyl-2-thienylsilane/ dimethyl-2-furylsilane in the presence of Karstedt's catalyst. X-ray crystallographic studies of **1** and **2** reveal *all-trans* conformation of the methyl groups bonded to puckered siloxane core and formation of 3D supramolecular assemblies by virtue of intermolecular C—H---π interactions. These siloxanes act as potential templates for expeditious one pot synthesis of gold nanowires of varying aspect ratios which are obtained by reduction of HAuCl<sub>4</sub>·3H<sub>2</sub>O with triethylsilane (CHCl<sub>3</sub>, RT). On the other hand, the use of linear polysiloxane, [2-ThMe<sub>2</sub>SiCH<sub>2</sub>CH<sub>2</sub>(Me)SiO]<sub>n</sub> (**4**) in lieu of the cyclosiloxane **2** affords predominant formation of polydispersed AuNPs along with a few extended structures. These results suggest that conformational confinement of the appended groups on the cyclosiloxanes, **1-3** plays an important role to impart morphological control of the gold nanorod assemblies.

## Introduction

Polysiloxanes with silicon-oxygen bonded skeletal frameworks constitute an important family of inorganic polymers with wide ranging applications.<sup>1-4</sup> In recent years, a great deal of attention has been focused on the development of synthetic methods to incorporate appended functional substituents on these hydrophobic, flexible polymeric supports. A widely accepted approach to functionalize preformed polysiloxane frameworks involves chemical modification of Si-H/ Si-Vinyl groups using a hydrosilylation reaction,<sup>5-10</sup> while thiol-ene click chemistry has been studied extensively to introduce appended thioether functionalities.<sup>11</sup> Brook et al. have reported a systematic study on the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyzed synthesis of three-dimensional siloxane frameworks with precise control over molecular weight by appropriate choice of alkoxy silane and hydrosilane precursors.<sup>12</sup> An important offshoot in this area relates to the chemical modification of molecular cyclosiloxanes, [RMeSiO]<sub>n</sub> (n = 3-5) bearing Si-H/Si-vinyl reactive groups.<sup>13-19</sup> The incorporation of appended functionalities such as ferrocenyl, oligoethers and naphthalenediimide, etc. has been achieved by following the classical synthetic methods. Synthesis and structural aspects of a series of hydroxy substituted cyclosiloxanes, [R(OH)SiO]<sub>n</sub> (n = 3,4) have been reported by Unno et al.<sup>20</sup> The studies have shown different conformational attributes of the appended Si-OH groups on the planar/puckered siloxane core and formation of supramolecular assemblies as a result of O-H---O type hydrogen bonding interactions.

Studies related to potential applications of functional

cyclo/polysiloxanes as scaffolds to metal nanoparticles remain an active area of research. For example, stabilization of preformed Pd nanoparticles of 2-5 nm size domains has been achieved by a new family of polysiloxanes modified by fluorescent cinchonidine pendant groups.<sup>21</sup> The catalytic activity of the thus formed polymer-palladium nanoassembly towards enantioselective hydrogenation reactions has been demonstrated. Brook et al.<sup>22</sup> have utilized reducing and structure directing properties of water soluble, redox active polysiloxanes bearing citric acid groups as the pendant side chains to synthesize gold nanoplatelets and hyperbranched nanocrystals. Chauhan et al.<sup>23</sup> have reported the synthesis of silver nanoparticles of necklace-like morphology by exploiting the reducing, as well as the stabilizing, properties of poly(methylhydrosiloxane), [Me(H)SiO]<sub>n</sub> in presence of trioctylamine.

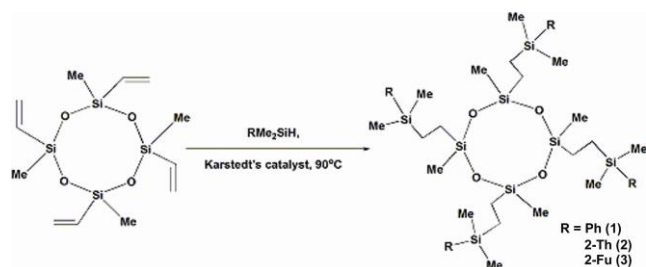
As part of our systematic study on functional silicon-based polymers,<sup>24</sup> we have utilized the intrinsically variable reducing property of linear [R<sub>2</sub>Si]<sub>n</sub>, branched [(R<sub>2</sub>Si)<sub>x</sub>(R<sup>1</sup>Si)<sub>1-x</sub>]<sub>n</sub> and network [RSi]<sub>n</sub> (R, R<sup>1</sup> = Me, Ph or sila-alkyl) polysilanes to achieve synthesis of nearly spherical Ag and Pd nanoparticles with control over their size domains. The inclusion of appended thioether groups on linear polysilane support has paved the way to construct self-assemblies of spherical AuNPs. These results have prompted us to explore the synthetic utility of functional cyclo-/polysiloxanes in the synthetic domain of noble metal nanoparticle assemblies. Herein, we report the synthesis and structural characterization of sila-alkyl substituted cyclotetrasiloxanes, [RMe<sub>2</sub>SiCH<sub>2</sub>CH<sub>2</sub>(Me)SiO]<sub>4</sub> [R = Ph(**1**), 2-thienyl(**2**), 2-furyl(**3**)] as the first examples among the siloxane family with *all-trans*

conformational attributes and their potential application as templates for the synthesis of gold nanowire assemblies.

## Results and discussion

### 5 Synthesis and characterization of functional cyclotetrasiloxanes, 1-3

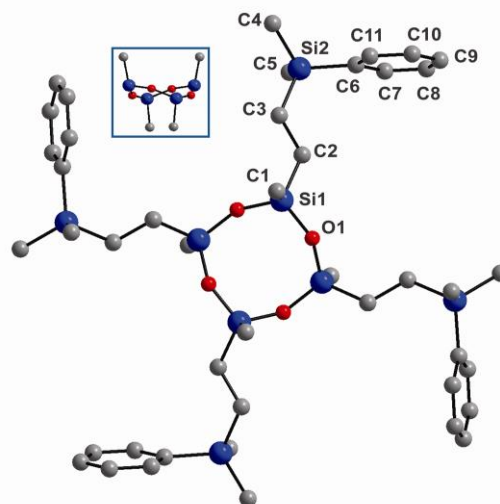
The synthesis of **1-3** (scheme 1) has been achieved by following a hydrosilylation reaction between 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, ( $D_4^{VI}$ ) and dimethylphenylsilane/  
10 dimethyl-2-thienylsilane/ dimethyl-2-furylsilane in presence of Karstedt's catalyst (90°C, 15-18h). After a brief induction period, the extent of each reaction was monitored at different time intervals by  $^1\text{H}$  NMR spectroscopy. The complete disappearance  
15 of diagnostic signals at  $\delta$  5.5-6.5 due to Si-vinyl groups provides evidence for the completion of the reaction. The isolation of **1-3** as colorless, low melting solids is effected by repeated washing of the crude mixture with methanol and subsequent cooling at 5  
°C for several days.



20 **Scheme 1** Synthesis of cyclotetrasiloxanes, 1-3.

The identity of each compound has been established by IR, multinuclear NMR and ESI-MS spectral studies as well as X-ray crystal structure analysis of **1** and **2**. The spectral data are  
25 summarized in the experimental section. In the ESI-MS spectra, the observed peaks associated with  $[\text{M}+\text{Na}]^+$  ions are identified and are in conformity with the suggested composition of each compound. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data are quite similar in the aliphatic region and reveals diagnostic signals due to  
30 peripheral methyl and sila-alkyl groups. The presence of a single  $^1\text{H}$  NMR resonance due to Si-Me groups is suggestive of only one stereoisomer in solution. The results are further supported by  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra which exhibit a distinct signal in the chemical shift region of  $\delta$  -19.8 to -19.6 due to the silicon atoms  
35 associated with siloxane core. In addition, the resonance at -7.2 to -1.05 is assigned to the appended sila-alkyl groups. The formation of a single conformer in **1** and **2** from  $D_4^{VI}$  as the starting precursor which exists as a mixture of geometrical isomers<sup>25</sup> is quite noteworthy.

40 Single crystals suitable for X-ray crystal structure analysis for **1** and **2** are obtained by slow evaporation of the solution of each compound separately in chloroform-methanol mixture. The molecular structure of **1** along with atomic labels is shown in figure 1 while crystal data as well as selected bond lengths and  
45 angles are given in Tables 1 and 2 respectively. The structure reveals a puckered cyclosiloxane core (figure 1, inset) with dihedral angles of the four silicon atoms as 45.8(5) and 7.0(5)°. The Si1-O-Si1 and O-Si1-O angles are observed as 150.92(17)° and 110.12(13)° respectively. The metrical parameters are in



50 **Fig. 1** Molecular structure of **1**. The inset shows puckered siloxane ring with *all-trans* methyl groups. Hydrogen atoms omitted for clarity.

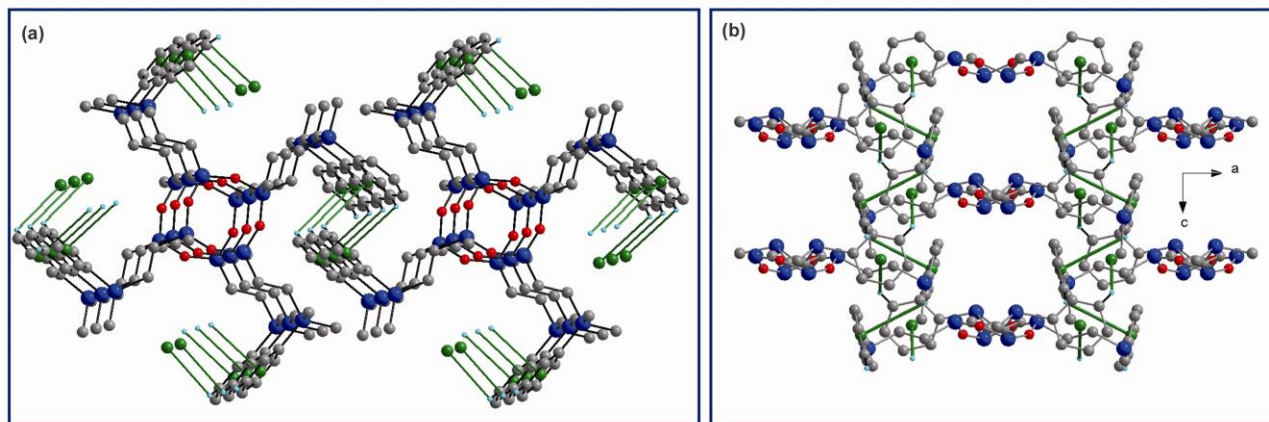
55 conformity with those reported earlier for 1,3,5,7-tetrahydroxy-1,3,5,7-tetraorganocyclotetrasiloxanes.<sup>20</sup> As evident from figure 1, each methyl group occupies a quasi-axial position with respect to the plane of the cyclic ring while the sila-alkyl chain exhibits a quasi-equatorial disposition. In this respect, the structure  
60 represents a unique example of *all-trans* conformation which is rarely observed<sup>25</sup> in the family of heterosubstituted cyclosiloxanes. The molecular structure of **1** is extended to a novel three-dimensional motif by virtue of intermolecular C—H--- $\pi$  interactions [H8—centroid = 3.628 Å, C8—centroid = 4.129 Å,  
65 C8—H8—centroid = 115.63°]. The perspective view along the crystallographic *b*-axis (Figure 2) reveals the formation of helical chain-like motif (Flack parameter = 0.5), while stacking of the cyclosiloxane core in the three-dimensional self-assembly is distinct along the *c*-axis. The crystal structure analysis of **2**  
70 reveals that the final *R* value is high (20%) and reflects poor sample quality (weak diffraction). Nevertheless, a chemically reasonable structure solution could be refined which unequivocally establishes the atom connectivity, and again reveals an *all-trans* conformation of the methyl groups with  
75 respect to the siloxane core (figure S1). The metrical parameters associated with the cyclic (Si-O)<sub>4</sub> structure resembles those described above for **1** but due to the low quality of the data will not be discussed further.

### Synthesis and characterization of gold nanoparticles

80 As a case study, we have explored the reduction of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  with triethylsilane as a mild reducing agent<sup>26</sup> in presence of the cyclosiloxanes, **1-3**. Thus, addition of triethylsilane into a sonicated solution containing the gold salt and the cyclosiloxane (1:2 molar ratio) in chloroform (HPLC, 25 mL) results in instant  
85 colour change of each solution from yellow to pink (for **1**) and blue (for **2,3**) suggesting the formation of AuNPs. The cyclosiloxane-gold assemblies thus formed are stable in solution

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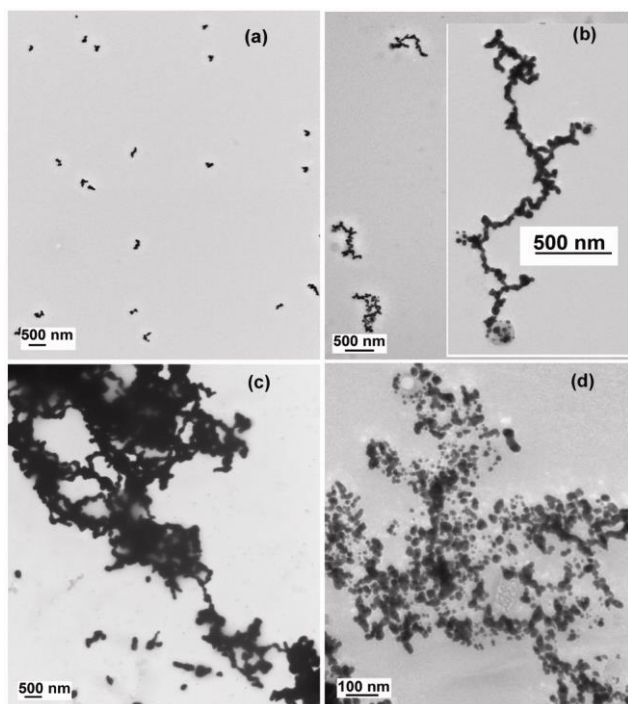


**Fig. 2** 3D structure of **1** (a) view along *c* axis (b) view along *b* axis. C-H... $\pi$  interactions shown with green solid lines. Color codes: Si, blue; C, grey; H, cyan; O, Red; centroid, dark green.

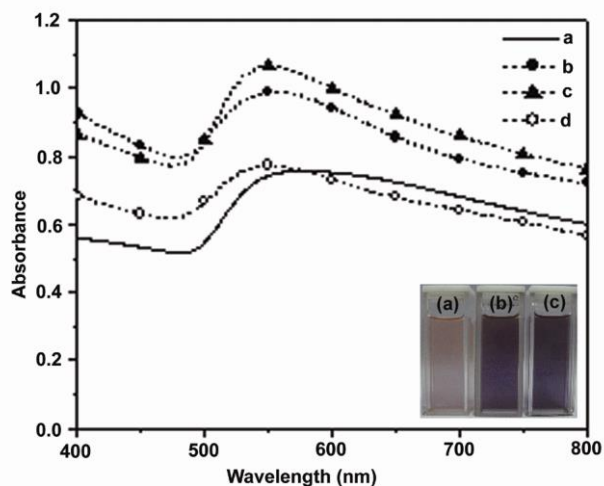
5 for several weeks. Transmission electron microscopic (TEM) studies of gold nanoassemblies were performed by depositing one drop of the solution on a carbon-coated copper grid. The TEM images shown in figure 3 are typical of those found over the entire grid and reveal the formation of worm-like growth of Au nanoparticles in **1**, the nanowires of varying chain lengths in **2**, and a network of nanowire assemblies in **3**. In the later case, the high resolution TEM (HRTEM) image (figure S2) shows that AuNWs have morphological features of polycrystalline structure and identifies the (111) plane with a 0.229 nm spacing between two adjacent lattice planes. In addition, the truncated branching sites are also evident along with the growing chains, in addition to individual nanoparticles at the terminal ends. The UV-Vis spectral profiles of the as-prepared solutions of the gold assemblies are shown in figure 4. A common feature of the spectra is a broad plasmonic resonance centered at 540-550 nm which tails in the near IR region. These results have been corroborated with a few earlier reports,<sup>27</sup> which relate the plasmonic features with the shape/morphology of the gold nanoparticles/nanoassemblies. Accordingly, the former value is attributed to transverse surface plasmons, while the tailing in the longer wavelength region is believed to originate from superposition of the longitudinal surface plasmon resonance of the Au nanowires with various aspect ratios. A close similarity between the spectral profiles (figure 4a-c) of the extended gold nanostructures in the near IR region may in part be attributed to weak plasmonic couplings in the presence of cyclosiloxane scaffolds.<sup>27a</sup> To better understand the role of cyclosiloxanes as the scaffolds and structure-directing templates to attain gold nanowire morphology, we performed the synthesis of AuNPs using linear polysiloxane, [ThMe<sub>2</sub>Si(CH<sub>2</sub>)<sub>2</sub>Si(Me)O]<sub>n</sub> (**4**) (M<sub>w</sub> = 6255/PDI = 1.15 with respect to polystyrene standards) which represents a linear analog of the cyclosiloxane **2**. The synthesis of

the polymer **4** is effected by hydrosilylation reaction between poly(methylvinylsiloxane) and ThMe<sub>2</sub>SiH in presence of Karstedt's catalyst and the details are described in the experimental section. The reduction of HAuCl<sub>4</sub>·3H<sub>2</sub>O with triethylsilane in presence of two equivalents of the polymer **4** in chloroform results in a blue colored solution similar to that observed in the gold nanoassemblies derived from **2**. Interestingly, TEM study of thus-formed AuNPs reveals only a few regions of elongated structures with predominant formation of polydispersed AuNPs. Because of the structural inhomogeneity, a plausible analysis of the plasmonic properties showing a close resemblance (figure 4d) with those observed for gold nanowires is not warranted. These results provide a basis to put forth a plausible rationale for the formation of gold-nanowires in the cyclosiloxanes, **1-3**. It is likely that complexation of Au(III) ions with phenyl, 2-thienyl or 2-furyl functionalities associated with spatially confined sila-alkyl side chains in **1-3** (figure 2) allows an orderly arrangement of Au ions prior to reduction by triethylsilane. This nucleation process results in initial formation of nearly spherical gold nanoparticles as evident from figure 3b (inset) thereby assisting extended one-dimensional growth. The driving force for 1D assembly formation of AuNPs is not yet clearly understood. We believe that the transverse confinement provided by the lattice framework of the siloxane may favour the





**Fig. 3** TEM images of gold nanowire assemblies (**a-c**) and nanoparticles (**d**) with compounds **1-3** and **4**, respectively.



**Fig. 4** UV-vis spectra (chloroform, RT) showing surface plasmon resonance of gold nanowires **a-c** in **1-3** respectively and that of nanoparticles **d** in **4**. (The inset showing the color of the nanowires **a-c** in **1-3**)

growth of nanowires from the nanoparticles, presumably due to inherent anisotropy of NP-NP interactions. Such unconventional chain growth mode of colloidal AuNPs has been recently documented.<sup>28</sup> In this context, the role of **1-3** to act as molecular templates is quite revealing in view of the well-documented literature which subscribe the use of already directional organic templates such as polyelectrolytes and biomolecules, among others to produce 1D nanoassemblies with diverse applications.

**Table 1** Crystal data and structure refinement for **1**<sup>a</sup>

Formula	C <sub>44</sub> H <sub>72</sub> O <sub>4</sub> Si <sub>8</sub>
Fw	889.74
T, K	150 (2)
λ (Å)	0.71073
Crystal system	Tetragonal
Space group	I $\bar{4}$
a (Å)	19.8932(7)
b (Å)	19.8932(7)
c (Å)	6.6091(2)
α (deg)	90
β (deg)	90
γ (deg)	90
V, (Å <sup>3</sup> )	2615.48(15)
Z	2
ρ <sub>calcd</sub> (Mg/m <sup>3</sup> )	1.130
μ (mm <sup>-1</sup> )	0.242
F(000)	960
Crystal size	0.20 x 0.10 x 0.10 mm
θ range (deg)	4.10 - 25.01
Reflections collected	27924
Unique data	2300
R <sub>int</sub>	0.0633
Reflections observed (>2σ)	2052
Data completeness	0.993
Max. and min. Transmission	0.9762 and 0.9532
Data / restraints / parameters	2300 / 0 / 130
GOF	1.065
Final R indices (I>2σI)	R~1 = 0.0575 wR~2 = 0.1435
R indices (all data)	R~1 = 0.0657 wR~2 = 0.1505
Largest diff. peak and hole	0.800 and -0.253 e.Å <sup>-3</sup>
Flack parameter	0.500

<sup>20</sup> <sup>a</sup> CCDC 921374 contain the crystallographic data in the CIF format for compound **1**

## Conclusions

In summary, the study describes synthesis and structural characterization of functional cyclosiloxanes **1-3** with an exclusive *all-trans* conformation of the appended groups. Potential applications of these molecular compounds in the construction of Au nanowires have opened up avenues for the development of new silicon-based templates that may prove to be useful in the construction of Au nanoassemblies with interesting morphological features.

## Experimental

### General comments

All operations were carried out using standard Schlenk line techniques under dry nitrogen atmosphere unless otherwise stated. Solvents were freshly distilled under inert atmosphere over phosphorus pentoxide (chloroform, dichloromethane) and magnesium (alcohols) before use. 2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, dimethylphenylsilane, hydrogen tetrachloroaurate(III) trihydrate and Karstedt's catalyst (Aldrich) were used as received. The synthesis of hydrosilanes, RMe<sub>2</sub>SiH

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**Table 2** Selected bond lengths (Å) and angles (°) for **1**

Si(1)—O	1.610(3)	O—Si(1) <sup>ii</sup>	1.620(2)
Si(1)—O <sup>i</sup>	1.620(2)	C(6)—C(7)	1.363(6)
Si(1)—C(2)	1.836(4)	C(6)—C(11)	1.379(6)
Si(1)—C(1)	1.844(6)	C(7)—C(8)	1.389(7)
Si(2)—C(5)	1.868(4)	C(8)—C(9)	1.389(9)
Si(2)—C(3)	1.869(3)	C(9)—C(10)	1.335(9)
Si(2)—C(4)	1.878(5)	C(10)—C(11)	1.409(7)
Si(2)—C(6)	1.880(4)		
O—Si(1)—O <sup>i</sup>	110.14(18)	C(4)—Si(2)—C(6)	109.4(2)
O—Si(1)—C(2)	108.22(17)	Si(1)—O—Si(1) <sup>ii</sup>	150.9(2)
O <sup>i</sup> —Si(1)—C(2)	109.93(16)	Si(1)—C(1)—H(1A)	109.5
O—Si(1)—C(1)	109.1(2)	C(3)—C(2)—Si(1)	113.4(2)
O <sup>i</sup> —Si(1)—C(1)	108.6(2)	Si(1)—C(2)—H(2A)	108.9
C(2)—Si(1)—C(1)	110.9(2)	C(2)—C(3)—Si(2)	114.7(2)
C(5)—Si(2)—C(3)	108.80(18)	Si(2)—C(3)—H(3A)	108.6
C(5)—Si(2)—C(4)	111.4(2)	Si(2)—C(5)—H(5A)	109.5
C(3)—Si(2)—C(4)	108.12(19)	C(7)—C(6)—Si(2)	122.8(3)
C(5)—Si(2)—C(6)	110.4(2)	C(11)—C(6)—Si(2)	120.0(3)
C(3)—Si(2)—C(6)	108.67(16)		
Si(1)—C(2)—C(3)—Si(2)	179.6(2)	Si(1)—O—Si(1) <sup>ii</sup> —O <sup>ii</sup>	-7.0(5)
C(1)—Si(1)—O—Si(1) <sup>ii</sup>	-73.2(5)	C(1)—Si(1)—O <sup>i</sup> —Si(1) <sup>i</sup>	126.3(4)
O—Si(1)—O <sup>i</sup> —Si(1) <sup>i</sup>	7.0(5)	Si(1) <sup>ii</sup> —O—Si(1)—O <sup>i</sup>	45.8(5)

<sup>a</sup> Symmetry codes : (i) y, -x+1, -z (ii) -y+1, x, -z

(R = 2-Fu, 2-Th) was carried out by following the procedure reported earlier.<sup>24c</sup> Electrospray ionization (ESI) mass spectra (positive ion mode) of the cyclotetrasiloxanes, **1-3** were recorded on Bruker micrOTOF-Q II Spectrometer. UV-Vis spectra were recorded on a Perkin-Elmer (Lambda Bio 20) spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on Bruker Spectrospin DPX 300 MHz instrument at frequency 300 and 75.5 MHz respectively while <sup>29</sup>Si spectra were recorded on Bruker AVANCE II 400 NMR spectrometer at frequency 79.5 MHz and chemical shifts are quoted relative to Me<sub>4</sub>Si. Infrared spectra were obtained on a Nicolet FT-IR (protege) spectrometer using KBr optics. Transmission electron microscopic (TEM) studies were carried out on a Philips CM 20 electron microscope operated at 100 kV. Molecular weights (Mw) and polydispersity index (PDI) of the polysilanes were estimated using Hitachi ELITE LaChrom chromatograph equipped with L-2490 refractive index detector and Waters styragel HR3 and HR4 columns in series (gel permeation chromatography [GPC]).

### X-ray Crystallography

The intensity data of **1** were collected on a Nonius Kappa CCD diffractometer equipped with a molybdenum-sealed tube and a highly oriented graphite monochromator at 150(2) K. Cell

parameters, data reduction, and absorption corrections were performed with Nonius software (DENZO and SCALEPACK).<sup>29</sup> The structure was solved by direct methods using SIR-97<sup>30</sup> and refined by a full-matrix least-squares method on *F*<sup>2</sup> using SHELXL-97.<sup>31</sup> All calculations and graphics were performed using WinGx.<sup>32</sup> Partial atoms were refined isotropically. For **2**, intensity data were collected on a BRUKER AXS SMARTAPEX diffractometer with a CCD area detector (KR) (0.71073 Å, monochromator: graphite).<sup>33</sup> Frames were collected at *T* = 273(2) K by  $\omega$ ,  $\phi$ , and  $2\theta$  – rotation at 10 s per frame with SAINT.<sup>33</sup> The measured intensities were reduced to *F*<sup>2</sup> and corrected for absorption with SADABAS.<sup>34</sup> Structure solution, refinement and data output were carried out with the SHELXTL program.<sup>35</sup> Images were created with the Diamond program.<sup>36</sup> All of the non-H atoms were refined anisotropically. H-atoms were placed in geometrically calculated positions by using a riding model unless stated otherwise.

Satisfactory data refinement for **2** was hampered by a weak data set (intensity of data decreased dramatically above 35 degrees in  $2\theta$ ), the fact that the crystal was twinned and the presence of disorder in the thienyl group. This led to high residual electron density with the largest difference peak at 3.65eÅ<sup>-3</sup>. The atom connectivity was, however, established.

## Synthetic Methods

### Synthesis of functional cyclotetrasiloxanes, 1-3

In a typical procedure, the reactions between 2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (2.0 g, 2.0 mL, 6.0 mmol) and dimethylphenylsilane/ dimethyl(2-thienyl)silane/ 2-furyldimethylsilane (25.0 mmol) were performed separately in presence of Karstedt's catalyst. An induction period was observed upon addition of a few mL of the silane into the reaction mixture. The contents of reaction were heated at 80-90°C for 15-18 h. The viscous liquid thus obtained was dissolved in dichloromethane and treated with activated charcoal to remove the catalyst. The clear colorless solution was filtered on Celite and the solvent was removed under vacuum. The viscous residue obtained in each case was washed with methanol and kept in the freezer to afford **1-3** as crystalline solids. (Yield: 75-80%)

**[PhMe<sub>2</sub>SiCH<sub>2</sub>CH<sub>2</sub>SiOMe]<sub>4</sub>**: (m.pt 34-36 °C), <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.10, 7.25 (br, *Ph*), 0.20 (s, 6H, PhMe<sub>2</sub>Si), 0.00 (s, Si-CH<sub>3</sub>), 0.40, 0.68 (m, CH<sub>2</sub>-CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 140.8, 135.1, 130.2, 129.2 (SiPh), 10.7, 8.4 (SiCH<sub>2</sub>CH<sub>2</sub>), 0.0 (SiCH<sub>3</sub>), -2.0 (SiMe<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR: δ -1.0 (s, PhMe<sub>2</sub>Si), -19.6 (s, Si-O). IR (KBr, cm<sup>-1</sup>): 3064 (ν C-H, aromatic), 2957, 2908 (ν C-H, aliphatic), 1421 (δ C-H), 1076 (ν Si-O-Si), 1255 (ν Si-Me), 1138 (ν Si-Ph). ESI-MS (+ve mode, m/z): 911.3475 [M+Na]<sup>+</sup>. Anal. Calcd for C<sub>44</sub>H<sub>72</sub>O<sub>4</sub>Si<sub>8</sub>: C, 59.40; H, 8.16. Found: C, 58.8; H, 8.01.

**[(2-Th)Me<sub>2</sub>SiCH<sub>2</sub>CH<sub>2</sub>SiOMe]<sub>4</sub>**: (m.pt 32-35°C), <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.14, 7.20, 7.54 (s, *Th*), 0.25 (s, 6H, ThMe<sub>2</sub>Si), 0.00 (s, Si-CH<sub>3</sub>), 0.42, 0.69 (m, CH<sub>2</sub>-CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 138.6, 134.2, 130.4, 128.0 (SiTh), 9.1, 7.9 (SiCH<sub>2</sub>CH<sub>2</sub>), -1.5 (SiCH<sub>3</sub>), -2.3 (SiMe<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR: δ -3.5 (ThMe<sub>2</sub>Si), -19.8 (Si-O). IR (KBr, cm<sup>-1</sup>): 3066 (ν C-H, aromatic), 2957, 2908 (ν C-H, aliphatic), 1407 (δ C-H), 1081 (ν Si-O-Si), 1255 (ν Si-Me), 1135 (ν Si-Th). ESI-MS (+ve mode, m/z): 935.1719 [M+Na]<sup>+</sup>. Anal. Calcd for C<sub>36</sub>H<sub>64</sub>O<sub>4</sub>Si<sub>8</sub>S<sub>4</sub>: C, 47.32; H, 7.06. Found: C, 46.76; H, 6.89.

**[(2-Fu)Me<sub>2</sub>SiCH<sub>2</sub>CH<sub>2</sub>SiOMe]<sub>4</sub>**: <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.66, 6.68, 6.40 (br, *Fu*), 0.32 (s, 6H, FuMe<sub>2</sub>Si), 0.18 (s, Si-CH<sub>3</sub>), 0.58, 0.77 (m, CH<sub>2</sub>-CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 158.9, 146.1, 119.5, 108.5 (SiFu), 8.6, 6.1 (SiCH<sub>2</sub>CH<sub>2</sub>), -1.9 (SiCH<sub>3</sub>), -4.3 (SiMe<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR: -7.6 (FuMe<sub>2</sub>Si), -19.8 (Si-O). IR (KBr, cm<sup>-1</sup>): 3112 (ν C-H, aromatic), 2959, 2910 (ν C-H, aliphatic), 1408 (δ C-H), 1078 (ν Si-O-Si), 1255 (ν Si-Me), 1139 (ν Si-Fu). ESI-MS (+ve mode, m/z): 871.2645 [M+Na]<sup>+</sup>.

### Synthesis of polysiloxane [ThMe<sub>2</sub>Si(CH<sub>2</sub>)<sub>2</sub>Si(Me)O]<sub>n</sub> 4

(2-Thienyl)dimethylsilane (5.0 g, 5.0 mL, 36.0 mmol) was added dropwise at room temperature to a stirred solution of poly(methylvinylsiloxane) (3.1 g, 3.0 mL, 36.0 mmol) in toluene containing catalytic amount of Karstedt's catalyst (10<sup>-5</sup> Pt/mol of silane). After the complete addition of 2-ThMe<sub>2</sub>SiH, the reaction mixture was heated at 90-93 °C for 15-18 h and the product obtained was centrifuged to separate the catalyst. Subsequent removal of the solvent under reduced pressure yields the crude polymer which was subjected to careful fractionation using a toluene/methanol mixture. The high molecular weight polymer fraction was obtained as light yellow colored viscous

liquid. (yield = 60-70%)

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.29, 7.60 (br, *Th*), 0.34 (s, 6H, ThMe<sub>2</sub>Si), 0.09 (br, CH<sub>3</sub> of backbone), 0.51, 0.73 (br, CH<sub>2</sub>-CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: δ 141.1, 136.6, 132.8, 130.4 (SiTh), 11.5, 10.3 (SiCH<sub>2</sub>CH<sub>2</sub>), 0.88 (SiCH<sub>3</sub>), -0.35 (SiMe<sub>2</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR: δ -3.58 (ThMe<sub>2</sub>Si), -23.21 (linear Si-O backbone). IR (KBr, cm<sup>-1</sup>): 3066 (ν C-H, aromatic), 2957, 2907 (ν C-H, aliphatic), 1407 (δ C-H), 1079 (ν Si-O-Si), 1255 (ν Si-Me), 1135 (ν Si-Th).

### Synthesis of gold nanoassemblies

To a sonicated suspension of hydrogen tetrachloroaurate(III) trihydrate (4 mg, 0.01 mmol) [20 mL, HPLC (high performance liquid chromatography) grade], a solution of cyclotetrasiloxane, **1-3** (0.02 mmol) in the same solvent (10 mL, dry CHCl<sub>3</sub>) was added separately and then sonicated. Upon addition of triethylsilane, the solution in each case turned yellow to pink (for **1**) and blue (for **2,3**) within a few seconds. The resulting solutions containing Au nanoassemblies were kept overnight to attain equilibrium and used for TEM and UV-vis spectroscopic studies.

## Acknowledgments

This research was supported by financial grant (Project No. 01(2561)/12/EMR-II) from CSIR (India). We thank CSIR (India) for a fellowship to Manchal and Department of Physics, IIT Delhi for TEM studies.

## Notes

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† Electronic Supplementary Information (ESI) available: [Crystal data and structural view of **2**. HRTEM image of gold nanowires.]. See DOI: 10.1039/b000000x/

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