

Chemical modification of poly(*n*-hexylsilane) – Synthesis of functional polysilanes bearing thienyl groups on the appended sila-alkyl side chains and their application in the generation and stabilization of silver nanoparticles

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Abstract

The linear polysilanes $[\{RR'_2Si(CH_2)_ySi(n\text{-hex})\}_x\{HSi(n\text{-hex})\}_{1-x}]_n$ (**1–4**; R = 2-thienyl, R' = H; R = Me, R' = 2-thienyl; y = 2, 3) have been synthesized by hydrosilylation reaction between preformed poly(*n*-hexylsilane) and (2-thienyl)vinyldichlorosilane/allyl(2-thienyl)dichlorosilane/bis(2-thienyl)methylvinylsilane/allyl-bis(2-thienyl)methylsilane using AIBN as the free radical initiator. GPC analysis reveals a monomodal molecular weight distribution in each case with $M_w = 2492\text{--}3280$ and PDI = 1.18–1.44. The polysilane **1** (R = 2-thienyl, R' = H, y = 2) acts as reducing agent towards silver tetrafluoroborate under mild conditions (cyclohexane, rt, 5 h) to afford spherical silver nanoparticles of size 8.4 ± 0.7 nm, as evident from the TEM and dynamic light scattering (DLS) studies. The silver nanoparticles in the polymer matrix exhibit surface plasmon absorption at 420 nm suggesting the donor–acceptor interaction between the thienyl group and the metal nanocluster surface. This stabilization effect provides long shelf life stability to the nanoparticles in solution with no sign of agglomeration even after three months.

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1. Introduction

Linear oligo/polysilanes with alkyl and/or aryl side chain substituents are an extensively studied class of silicon catenates due to their intrinsic electronic and optical properties associated with a σ -delocalized silicon backbone [1]. The occurrence of $\sigma\text{--}\sigma^*$ electronic transition in the UV region in these polymers has allowed to establish the role of side chain substituents in affecting the HOMO–LUMO band gap energy as a consequence of conformational changes in the silicon backbone [1,2]. Due to these properties, polysilanes have been extensively studied for their potential applications in photoresists, lithography, NLO materials [3] and as precursors to silicon carbide [4]. By vir-

tue of σ -delocalized electrons, oligo/polysilane films such as those of poly(methylphenylsilane), poly(di-*n*-hexylsilane) or poly(phenylsilane) are also known to act as reducing agent for noble metal ions [5]. Such polysilane supported metal nanoparticles/colloids are being explored for their application as catalysts in various organic transformations as well as electroless deposition of copper on polysilane films.

Poly(dialkyl/arylsilane)s are generally accessible by dehalocondensation of the dichloroorganosilanes [1]. However, the harsh reaction conditions employed in this approach generally impede the use of functional organosilicon monomers. Consequently, a great deal of attention has been focused on the development of synthetic methods which can afford oligo/polysilanes with functionally appended/heteroatom-substituted side chain groups. Among these, catalytic dehydrocoupling of primary silanes

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[6], anionic ring opening polymerization of cyclic monomers/masked disilanes [7] and chemical modification of preformed polysilanes bearing Si–H or Si–Ph groups are widely used. These synthetic protocols provide access to polysilanes with pendant alkoxy, amino and mercapto groups [8] as well as with alkyl side chain substituents appended with hydroxyl, amino or carboxylic acid functionalities [9] or crown ether/aza crown ether moieties [10]. In addition, the incorporation of chloromethyl-substituted phenyl groups on the silicon backbone and subsequent chemical modification of the –CH₂Cl moiety has been utilized to anchor a variety of π -conjugated and other non-linear optical (NLO) chromophores [11].

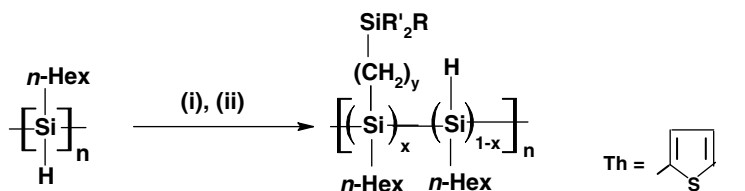
A perusal of the literature however reveals that there are only a few attempts to synthesize polysilanes bearing donor heteroaromatic functionalities such as thienyl, furyl or pyridyl groups [12]. A previous study on the polymerization of 2-thienylsilane by zirconium catalyzed dehydrocoupling approach [12a] has shown that the reaction is extremely sluggish and only yields a mixture of disilane and trisilane even under prolonged reaction conditions. It has been suggested that the sulfur atom in 2-thienylsilane coordinates with the transition metal and deactivates the catalyst in the mechanistic steps involving the σ -bond metathesis pathway. Thus, it is desired to develop alternate synthetic protocols to related functional polysilanes bearing donor heteroaromatic groups on the side chains. We envision that chemical modification of a preformed polysilane with appropriately functionalized precursor may offer a viable approach to these class of functional polymers. In our earlier communications [13], we have reported on the synthesis of oligo/polysilanes bearing sila-alkyl side chain groups of varying steric and electronic attributes. As a part of ongoing studies, we report herein the synthesis and characterization of polysilanes of the general formula $[\{RR'_2Si(CH_2)_ySi(n\text{-hex})\}_x\{HSi(n\text{-hex})\}_{1-x}]_n$ (**1–4**; R = 2-thienyl, R' = H; R = Me, R' = 2-thienyl; y = 2, 3). The chemical reactivity of polysilane **1** towards silver tetrafluoroborate has been explored to comprehend the reducing property

of the catenated silicon backbone as well as the role of donor thienyl substituents in the stabilization of *in situ* generated silver nanoparticles. The results obtained are reported herein.

2. Results and discussion

2.1. Chemical modification of poly(*n*-hexylsilane) – synthesis and characterization of polysilanes, **1–4**

Synthesis of poly(*n*-hexylsilane) has been achieved by following the known procedure involving dehydrocoupling of *n*-hexylsilane in presence of Cp₂TiCl₂/2.2*n*-BuLi as the catalyst [6a]. GPC analysis of the polysilane prepared under different runs shows monomodal molecular weight distribution with $M_w = 1729$ –1809 and PDI = 1.24–1.37 while IR and multinuclear (¹H, ¹³C{¹H} and ²⁹Si{¹H}) NMR data are in conformity with those reported earlier. The chemical modification of the Si–H groups in the polysilane has been performed by hydrosilylation with (2-thienyl)vinyldichlorosilane/allyl(2-thienyl)dichlorosilane/bis(2-thienyl)methylvinylsilane/allyl-bis(2-thienyl)methylsilane using AIBN as the free radical catalyst. The extent of hydrosilylation was monitored at different time intervals by IR and ¹H NMR spectroscopy. The concentration of Si–H content in the reaction mixture was found to decrease with time and finally remain practically unchanged after 48 h. The isolation of the corresponding linear polysilanes **1–4** (Scheme 1) from the crude mixture was effected by repeated treatment with THF/methanol mixture. These polymers are orange-yellow viscous gums and are soluble in common organic solvents like hexane, dichloromethane, chloroform, toluene, THF, etc. The results obtained from thermo gravimetric analysis (TGA) reveal that these are stable up to 250–300 °C. However, a continuous weight loss is observed up to 500–550 °C leaving a residual yield of 35–45%. An examination of the gel permeation chromatography (GPC) data (Table 1) reveals a monomodal molecular weight distribution in each case with $M_w = 2492$ –3280



R, R'	y	polysilane
Th, H	2	1
Th, H	3	2
Me, Th	2	3
Me, Th	3	4

(i) CH₂=CHSiThCl₂/ CH₂=CHCH₂SiThCl₂/ CH₂=CHSiTh₂Me/ CH₂=CHCH₂SiTh₂Me ; (ii) AIBN

Scheme 1.

Table 1
 ^1H , ^{13}C $\{^1\text{H}\}$, ^{29}Si $\{^1\text{H}\}$ NMR, UV and GPC data of polysilanes **1–5**

Polysilane	δ ^1H NMR (ppm)	δ $^{13}\text{C}\{^1\text{H}\}$ NMR (ppm)	δ $^{29}\text{Si}\{^1\text{H}\}$ NMR (ppm)	UV ^a $\lambda_{\text{max}}/\epsilon$	M_w^b	PDI ^c
1	7.67, 7.39, 7.18 (SiTh), 4.41 (SiThH ₂), 3.53 (SiH, residual backbone), 1.26 (br, H2–H5 + α -H) 0.88 (br, H1/H6 + β -H)	136.97, 131.87, 128.98 (SiTh), 33.83, 31.55, 29.72, 22.63, 19.41, 14.14 (SiHex), 7.83(α -CH ₂), 3.02 (β -CH ₂)	– 24.04 to – 27.40 (br, Si backbone) –37.00 (SiThH ₂) –56.70 (br, SiH residual backbone)	284/ 809	2492 (1809) ^d	1.32 (1.37) ^d
2	7.55, 7.28, 7.16 (SiTh), 4.35 (SiThH ₂), 3.49 (SiH, residual backbone), 1.21 (br, H2–H5 + α - β -H) 0.79 (br, H1/H6 + γ -H)	135.76, 131.34, 128.87 (SiTh), 33.21, 31.09, 29.62, 22.91, 19.11, 14.54 (SiHex), 12.83 (α - γ -CH ₂), 20.62 (β -CH ₂)	–26.00 to –28.48 (br, Si backbone) –36.03 (SiThH ₂) –54.76 (br, SiH residual backbone)	292/ 954	2605 (1809) ^d	1.44 (1.37) ^d
3	7.65, 7.34, 7.21 (Si-Th) 3.48 (SiH, residual backbone), 1.27 (br, H2–H5 + α - β -H), 0.88 (br, H1/H6), 0.63 (SiMe)	135.75, 131.33, 128.15 (Si-Th), 33.21, 31.61, 29.37, 22.69, 19.82, 14.14 (SiHex), 25.86 (β -CH ₂), 10.48 (α -CH ₂), –2.56 (SiMe)	–14.97 (SiMeTh ₂) –24.06 to –28.44 (br, Si backbone) –50.07 (br, SiH residual backbone)	287/ 789	2833 (1729) ^d	1.18 (1.24) ^d
4	7.49, 7.21, 7.08 (SiTh), 3.54 (SiH, residual backbone), 1.18 (br, H2–H5 + α - β - γ -H), 0.81 (br, H1/H6) 0.54 (SiMe)	135.61, 131.28, 128.16 (Si-Th), 33.98, 31.66, 29.69, 22.74, 19.77, 14.17 (SiHex), 21.88(α - γ -CH ₂), 27.15 (β -CH ₂), –1.82 (SiMe)	–15.12 (SiMeTh ₂) –23.80 to –27.48 (br, Si backbone) –54.21 (br, SiH residual backbone)	294/ 944	3280 (1729) ^d	1.25 (1.24) ^d
5	4.28 (SiMeH ₂), 3.62 (SiH, residual), 1.28 (br, H2–H5 + α - β -H), 0.86 (br, H1/H6), 0.24 (SiMe)	33.70, 31.56, 29.32, 22.63, 19.81, 14.09 (SiHex), 10.22 (α -CH ₂), 6.94 (β -CH ₂), –6.77 (SiMe)	–29.47 (SiMeH ₂) –24.43 to –27.54 (br, Si backbone) –52.91 (br, SiH residual backbone)	279/ 722	2169 (1692) ^d	1.19 (1.17) ^d

^a ϵ units: (Si repeat unit)^{–1} dm³ cm^{–1}; λ_{max} units: nm.

^b Molecular weights determined by GPC relative to polystyrene standards; eluent: THF; 30 °C.

^c PDI = polydispersity index (M_w/M_n).

^d Molecular weight and PDI of poly(*n*-hexylsilane) prepared under different runs.

and PDI = 1.18–1.44 suggesting no apparent cleavage of the silicon backbone in the parent poly(*n*-hexylsilane) during the free radical hydrosilylation reaction. The GPC profile of a representative polysilane **1** along with the parent poly(*n*-hexylsilane) is shown in Fig. 1. The thienyl groups associated with the carbosilyl chain in these polysilanes have been identified by a characteristic IR absorption at 1496–1498 cm^{–1} (Si–Th) while the bands due to Si–H (for **1** and **2**) and Si–Me (for **3** and **4**) appear at 2140–2145 (νSiH₂); 925–927 (δSiH₂) and 1252–1254 cm^{–1}, respectively. The residual Si–H groups of the backbone are discernable at 2090–2105 cm^{–1} in the IR spectra of all the polysilanes. This is further supported by the presence of a broad ^1H NMR signal at δ 3.48–3.54, in addition to the

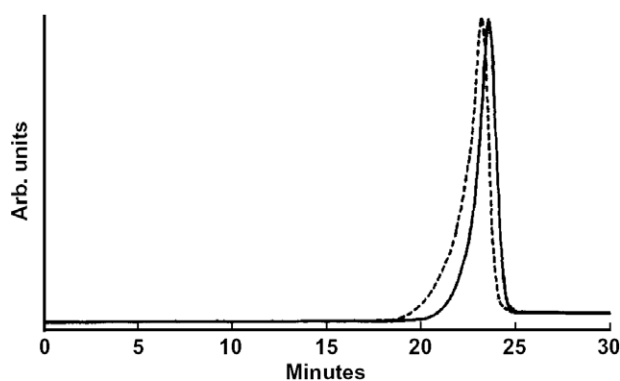


Fig. 1. GPC profiles of (a) **1** (dashed line) and (b) poly(*n*-hexylsilane) (solid line).

observed resonances due to the thienyl (δ 7.08–7.67) as well as SiH₂ (δ 4.35–4.41) (for **1** and **2**) and Si–Me (δ 0.54–0.63) (for **3** and **4**) groups associated with the appended carbosilyl moiety. A close scrutiny of these data suggests 70–75% inclusion of the carbosilyl moiety in the polysilanes **1–4** and is in accord with the results obtained from GPC. The ^1H NMR spectrum of each polysilane in the alkyl region reveals two broad signals at δ 0.79–0.88 and 1.18–1.27 due to the overlapping methylene protons of the appended carbosilyl and the *n*-hexyl groups. On the other hand, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of each polymer is well resolved and the spectral assignments have been made by comparison with those of poly(di-*n*-hexylsilane) reported earlier [14]. The assignments of various overlapping ^1H and $^{13}\text{C}\{^1\text{H}\}$ resonances in the alkyl region are confirmed by examining HSQC (^1H – $^{13}\text{C}\{^1\text{H}\}$) NMR spectrum of a representative polysilane **4** (Fig. 2) which shows distinct cross peaks at 22.74/1.18 (C5-hexyl), 27.15/1.18 (β -CH₂), 29.69/1.18 (C2), 31.65/1.18 (C4), 33.98/1.18 (C3), 21.88/1.40 (α - γ -CH₂), 19.76/0.80 (C1) and 14.17/0.80 (C6). The pertinent data are given in Table 1. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra reveal a sharp resonance at δ –37.00 (SiThH₂)/–15.12 (SiMeTh₂) due to the appended carbosilyl moiety. A broad featureless signal at δ –23.80 to –28.44 is attributed to the silicon atoms associated with the SiC₂ backbone while a weak signal at –50.07 to –54.21 reveals the presence of the backbone silicon atoms with residual Si–H groups. The UV spectra of **1–4** exhibit a broad absorption at $\lambda_{\text{max}} = 284$ –294 nm with molar absorptivity (ϵ) as 789–944 (Si repeat unit)^{–1} dm³ cm^{–1}. The spectral profile in

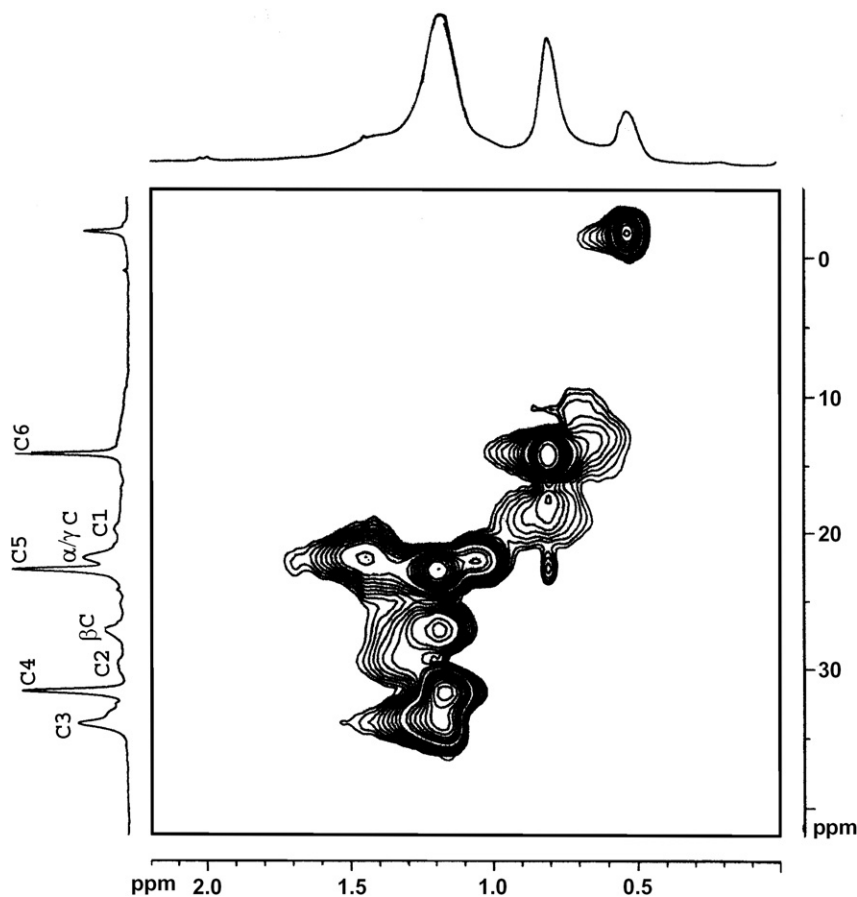


Fig. 2. (^1H - ^{13}C) HSQC NMR spectrum (aliphatic region) of **4**.

each case is quite typical of short chain silicon catenates bearing alkyl/H side chain groups and is suggestive of random coil conformation of the silicon backbone [13b].

2.2. Reaction of polysilane **1** with silver tetrafluoroborate – synthesis and characterization of silver nanoparticles

In accord with the earlier reports on the reducing behavior of poly(dialkyl/phenylsilane)s towards noble metal ions [5], a suspension of silver tetrafluoroborate (7.8 mg, 0.04 mmol) in cyclohexane (HPLC grade, 20 mL) upon treatment with two monomer equivalents of **1** in the same solvent immediately results in a change of color (colorless to yellow) of the resultant solution. The intensity of the yellow color increases with the slow dissolution of the silver salt and the reaction is complete within 5 h. The appearance of yellow color in solution suggests the formation of silver nanoparticles and is further supported by the characteristic surface plasmon band at ~ 420 nm in the UV–Vis spectrum (Fig. 3). An examination of the spectra at different time intervals reveals that the intensity of this band increases with time and finally remains constant after 5 h. Transmission electron microscopic (TEM) studies of the silver nanoparticles were performed by the deposition of one drop of the solu-

tion on a carbon coated copper grid without any additional staining and the particle size distribution obtained from dynamic light scattering studies. The results are shown in Figs. 4 and 5, respectively and reveal the formation of spherical silver nanoparticles in a quasi-monodispersed phase with an average particle size of 8.4 ± 0.7 nm. It has been reported that unprotected silver

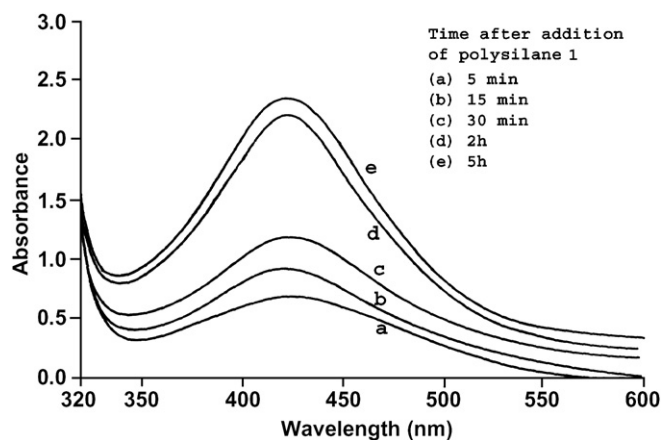


Fig. 3. Monitoring of plasmon resonance band of silver nanoparticles in polysilane **1** matrix (in cyclohexane).

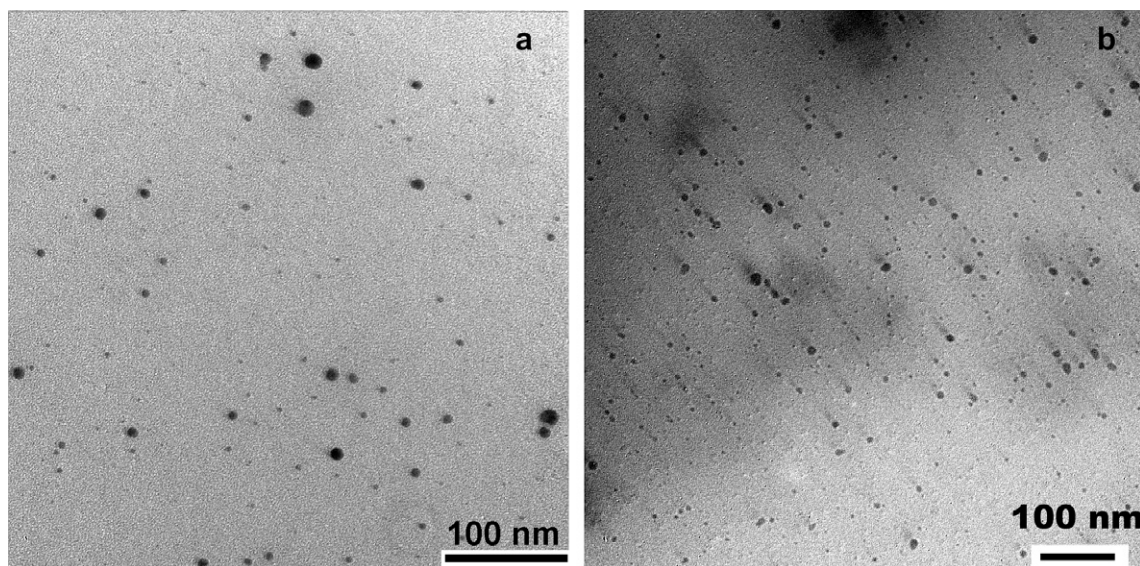


Fig. 4. TEM images of polysilane **1**-silver nanoparticle assembly (a) fresh sample and (b) aged sample (3 months).

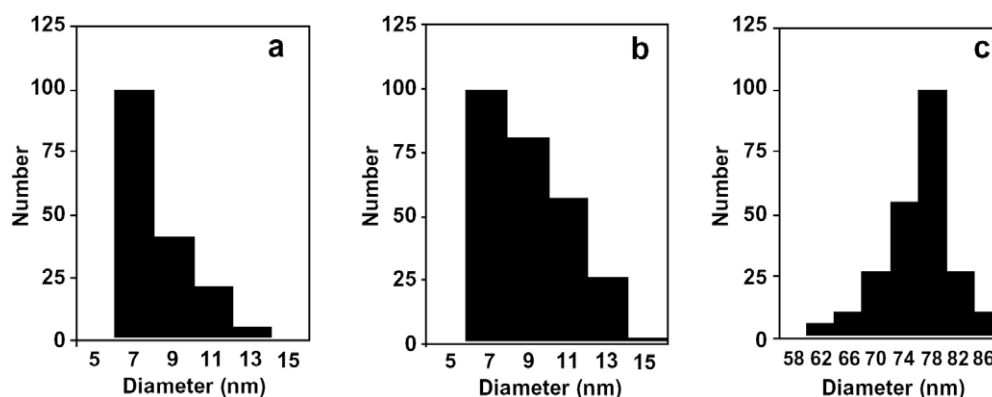


Fig. 5. Particle size distribution of silver nanoparticles in polysilane **1** matrix (a) fresh sample (b) aged sample (3 months) and (c) in polysilane **5** matrix.

nanoparticles in the size domain of <15 nm display the surface plasmon absorption band with the maxima at *ca.* 390 nm [15] whereas a red shift of this band occurs for silver nanoassemblies in which the stabilization is effected by capping agents involving neutral or anionic ligands [16]. By analogy, the observed plasmon absorption at 420 nm in the present case may be attributed to strong donor–acceptor interactions between the thienyl ligands and the silver nanoparticles. Furthermore, a consequence of this stabilization can be observed in the shelf life stability of the hybrid assembly in solution. The TEM images and the dynamic light scattering studies of the aged solution (Figs. 4 and 5) reveal that the silver nanoparticles exhibit no sign of agglomeration even after three months, although small variation in the particle size distribution within the nano regime (8.9 ± 1.2 nm) has been observed. In addition, the hybrid assembly obtained after evaporation of the solvent can be redissolved in cyclohexane and this procedure can be repeated without the loss of stability of the nanoparticles.

In order to further validate the role of the appended thienyl groups in the polysilane **1** in the stabilization of silver nanoparticles, it was appropriate to examine the reducing behavior of an analogous polysilane which is devoid of donor functionality on the appended side chain. In this context the polysilane $[\{\text{MeH}_2\text{Si}(\text{CH}_2)_2\text{Si}(n\text{-Hex})\}_{0.6}\{\text{H-Si}(n\text{-Hex})\}_{0.4}]_n$, **5** was synthesized by chemical modification of poly(*n*-hexylsilane). The spectral data (Table 1) are in accord with the suggested composition while the GPC profile reveals $M_w = 2169$ and $\text{PDI} = 1.19$. This polymer was reacted with silver tetrafluoroborate under similar reaction conditions as described for polysilane **1**-silver nanoparticle assembly. Interestingly, the silver nanoparticles ($\lambda_{\text{max}} = 406$ nm) formed in this case are much larger in size (75.5 ± 4.9 nm) even in the fresh samples (Fig. 5) in comparison to those formed in the polysilane **1** and undergo precipitation within 5–7 days. This implies that the silver nanoparticles tend to agglomerate in the polysilane **5** matrix which is devoid of a capping functionality for the metal nanoparticle surface.

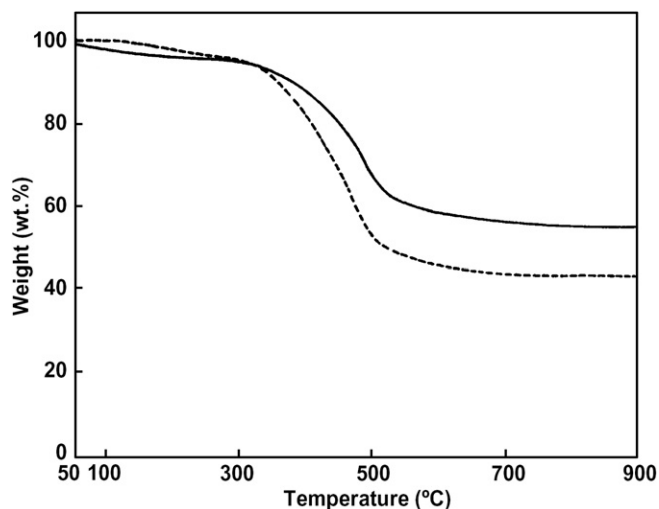


Fig. 6. TGA curves of (a) polysilane **1** (dashed line) and (b) polysilane **1**-silver nanoparticle assembly (solid line).

An intriguing aspect concerns the fate of the polysilane **1** in the nanometal hybrid assembly. Preliminary studies reveal a few interesting features which deserve special mention. The TGA analysis of the hybrid assembly reveals the onset temperature of thermal decomposition at ~ 300 °C with continuous weight loss being observed

up to 500 °C. Although these results are quite similar to those observed for the parent polysilane (Fig. 6), the residual yield (56%) is much higher and tentatively corresponds to the material composition, $4\text{SiO}_2 + \text{AgO}$ (theoretical yield = 52%). Furthermore, the polymer residue obtained after precipitation of the silver nanoparticles by centrifugation in THF solution has been subjected to GPC and UV spectral studies. The polymer thus obtained is found to possess M_w/PDI as 1864/1.64 and suggests some degree of chain scission in the catenated silicon backbone of the parent polysilane without the apparent loss of polydispersity. The UV spectrum identifies a weak absorption at 284 nm due to the $\sigma\text{-}\sigma^*$ transition of the catenated silicon backbone. These results suggest the presence of short chain oligosilanes as integral part of the polymer matrix in the hybrid assembly.

It has been reported earlier [5a] that the reduction of Ag(I) ions by poly(methylphenylsilane) thin films is accompanied by the formation of Si–O–Si linkages as the oxidized species (IR: $\nu\text{Si-O-Si} \sim 1080\text{ cm}^{-1}$). However, the detection of the siloxane units in the IR spectra of the hybrid assemblies obtained from polysilane **1** or **5** as the matrix was obscured by the presence of other absorptions due to alkyl groups (Fig. 7) and thus no definitive evidence in favor of the Si–O–Si linkages could be discernible. Interestingly, the SiH_2 group has been identified by characteristic IR absorption at 2140–

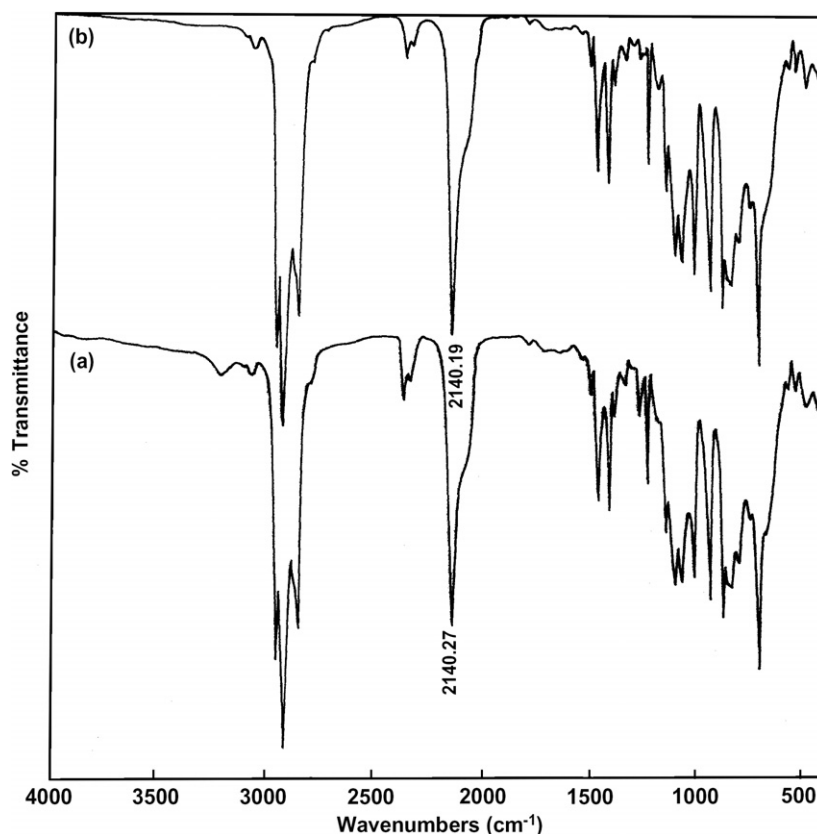


Fig. 7. IR spectra of (a) polysilane **1** and (b) polysilane **1**-silver nanoparticle assembly.

2145 cm^{-1} and implies the inert character of this group towards reduction of silver ion under the reaction conditions employed. This observation is consistent with the literature precedence wherein the Si–H groups, in general are found to act as weak reducing agents unless catalyzed by a base or a transition metal Lewis acid such as PdCl_2 [17]. This concept has been further validated by examining the reducing behavior of poly(*n*-hexylphenylsilane), prepared via the Wurtz coupling approach ($M_w = 3076$, PDI = 1.32) towards silver tetrafluoroborate. The formation of silver nanoparticles of size 149.5 ± 22.05 nm was observed in this case too thereby suggesting the involvement of σ -delocalized electrons of the silicon backbone in the reduction of silver ions, as reported earlier for other polysilanes [5].

In summary, new functional polysilanes 1–4 have been synthesized by chemical modification of poly(*n*-hexylsilane) involving AIBN catalyzed hydrosilylation of Si–H groups with thienyl-substituted allyl/vinylsilanes. The reaction of 1 with silver tetrafluoroborate allows the synthesis of silver nanoparticles with particle size of <10 nm and their long term stability in solution underlines the role of the well established concept of donor–acceptor interaction between the thienyl group of the polysilane matrix and the metal nanocluster surface.

3. Experimental

3.1. General comments

All operations were carried out using standard Schlenk line techniques under dry nitrogen atmosphere. Solvents were freshly distilled under inert atmosphere over sodium benzophenone (ether, tetrahydrofuran, and toluene), phosphorus pentoxide (*n*-hexane) and magnesium (alcohols) before use. Trichlorovinylsilane, allyltrichlorosilane, dichloromethylvinylsilane, allyldichloromethylsilane, phenyltrichlorosilane and hexyltrichlorosilane (Aldrich) were distilled over magnesium. *n*-Hexylbromide, Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex), 2-thienyllithium (1.0 M in THF), *n*-butyllithium (1.6 M in hexane), lithium aluminium hydride, bis(cyclopentadienyl)titaniumdichloride, silver tetrafluoroborate (Aldrich) were used as received. AIBN [2,2'-azo(bisobutyronitrile)] (Merck) was recrystallized from methanol before use. Literature procedures were followed for the preparation of poly(*n*-hexylsilane) [6a] and poly(*n*-hexylphenylsilane) [18].

Infrared spectra were obtained as thin films on KBr disc on a Nicolet FT-IR (protégé) spectrometer. UV–Vis spectra were recorded on a Perkin–Elmer (Lambda Bio 20) spectrophotometer. Molecular weights 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. The chromatograph was calibrated with polystyrene standards and THF was used as eluent. ^1H and ^{13}C spectra were

recorded in CDCl_3 on Bruker Spectrospin DPX 300 MHz instrument at frequency 300 and 75.5 MHz respectively while ^{29}Si spectra were recorded on Bruker Advance II 400 NMR spectrometer at a frequency 79.49 MHz and chemical shifts are quoted relative to Me_4Si . HSQC (^1H – ^{13}C) spectra were recorded using standard pulse sequence with a relaxation delay of 2 s for each of 512t₁ experiments. For assigning the ^{13}C NMR spectral data, the carbon atoms of hexyl group are designated by C1–C6 while the methylene carbons of the carbosilyl side chain are designated by C- α , C- β and C- γ . Thermogravimetric analysis of polysilanes was carried out in nitrogen atmosphere between 50 and 900 °C at a heating rate of 10 °C/min on a Perkin–Elmer Thermal analysis system. Particle size measurements were carried out using a laser light scattering particle size analyzer (Brookhaven, 90 PLUS). Transmission electron microscopic (TEM) studies were done on a Philips CM 20 electron microscope operated at 100 kV. Elemental analysis (C and H) was performed on a Perkin–Elmer model 2400 CHN elemental analyzer.

3.2. Synthesis of vinylallylsilane precursors

3.2.1. (2-Thienyl)vinylchlorosilane

2-Thienyllithium (1.0 M solution in THF; 56 mL, 56.0 mmol) was slowly added to a stirred solution of trichlorovinylsilane (10.5 mL, 82.5 mmol) in THF (150 mL) at -78 °C. After complete addition, the reaction mixture was gradually brought to room temperature and stirred overnight. The volatiles were removed under reduced pressure and *n*-hexane was added to precipitate the salt which was removed by filtration. The filtrate thus obtained was fractionally distilled to obtain (2-thienyl)vinylchlorosilane (b.p. 78–80 °C/5 mm Hg, yield = 58%). ^1H NMR: δ 7.77 (d, $^3J_{\text{HH}} = 4.45$ Hz, 1H, *Th* H-3), 7.57 (d, $^3J_{\text{HH}} = 3.15$ Hz, 1H, *Th* H-5), 7.24 (dd, 1H, $^3J_{\text{HH}} = 3.49$ Hz, $^3J_{\text{HH}} = 4.52$ Hz, *Th* H-4), 6.07–6.57 (m, 3H, $\text{CH}=\text{CH}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 138.12, 135.32, 132.41, 128.54 (*SiTh*), 135.61 ($\text{CH}=\text{CH}_2$), 126.52 ($\text{CH}=\text{CH}_2$). $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ 7.61. Anal. Calc. for $\text{C}_6\text{H}_6\text{Cl}_2\text{SSi}$: C, 34.45; H, 2.89. Found: C, 34.37; H, 2.81%.

3.2.2. Allyl(2-thienyl)dichlorosilane

The title compound was synthesized by following a similar procedure as above using allyltrichlorosilane (9.0 mL, 62.1 mmol) and 2-thienyllithium (1.0 M solution in THF; 55 mL, 55.0 mmol) as the reagents (b.p. 90–92 °C/5 mm Hg, yield = 63%). ^1H NMR: δ 7.80 (d, $^3J_{\text{HH}} = 4.81$ Hz, 1H, *Th* H-3), 7.61 (d, $^3J_{\text{HH}} = 3.60$ Hz, 1H, *Th* H-5), 7.28 (dd, 1H, $^3J_{\text{HH}} = 3.31$ Hz, $^3J_{\text{HH}} = 3.69$ Hz, *Th* H-4), 5.82 (m, 1H, $\text{CH}=\text{CH}_2$), 5.13 (m, 2H, $\text{CH}=\text{CH}_2$), 2.37 (d, 2H, $^3J_{\text{HH}} = 8.1$ Hz, SiCH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 138.12, 135.32, 132.41, 128.54 (*SiTh*), 132.61 ($\text{CH}=\text{CH}_2$), 116.52 ($\text{CH}=\text{CH}_2$), 19.21 (SiCH_2). $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ 7.73. Anal. Calc. for $\text{C}_7\text{H}_8\text{Cl}_2\text{SSi}$: C, 37.67; H, 3.61. Found: C, 37.58; H, 3.54%.

3.2.3. Bis(2-thienyl)methylvinylsilane

Dichloromethylvinylsilane (8.0 mL, 61.3 mmol) in THF (10 mL) was slowly added to a stirred solution of 2-thienyllithium (1.0 M solution in THF; 130 mL, 130.0 mmol) in the same solvent at -78°C . The reaction mixture was gradually brought to room temperature and stirred overnight. The volatiles were removed under reduced pressure and *n*-hexane was added to precipitate the salt which was removed by filtration. The filtrate thus obtained was fractionally distilled under reduced pressure to obtain bis(2-thienyl)methylvinylsilane (b.p. $134\text{--}136^{\circ}\text{C}/5\text{ mm Hg}$, yield = 54%). ^1H NMR: δ 7.70 (d, $^3J_{\text{HH}} = 4.53\text{ Hz}$, 1H, *Th* H-3), 7.40 (d, $^3J_{\text{HH}} = 3.36\text{ Hz}$, 1H, *Th* H-5), 7.26 (dd, 1H, $^3J_{\text{HH}} = 3.36\text{ Hz}$, $^3J_{\text{HH}} = 4.50\text{ Hz}$, *Th* H-4), 6.51 (m, 1H, $\text{CH}=\text{CH}_2$), 6.04 (m, 2H, $\text{CH}=\text{CH}_2$), 0.77 (s, 3H, *SiMe*). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 136.51, 135.96, 132.01, 128.64 (*SiTh*), 135.36 ($\text{CH}=\text{CH}_2$), 128.53 ($\text{CH}=\text{CH}_2$), -1.6 (*SiMe*). $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ -22.52 . Anal. Calc. for $\text{C}_{11}\text{H}_{12}\text{S}_2\text{Si}$: C, 55.88; H, 5.12. Found: C, 55.79; H, 5.16%.

3.2.4. Allyl-bis(2-thienyl)methylsilane

The reaction between allylmethyldichlorosilane (8.5 mL, 58.0 mmol) and 2-thienyllithium (1.0 M solution in THF; 120 mL, 120.0 mmol) was carried out by following the procedure similar to that described above for bis(2-thienyl)methylvinylsilane. The title compound was obtained by fractional distillation of the crude product (b.p. $140\text{--}142^{\circ}\text{C}/5\text{ mm Hg}$, yield = 62%). ^1H NMR: δ 7.69 (d, $^3J_{\text{HH}} = 4.53\text{ Hz}$, 1H, *Th* H-3), 7.42 (d, $^3J_{\text{HH}} = 3.60\text{ Hz}$, 1H, *Th* H-5), 7.25 (dd, 1H, $^3J_{\text{HH}} = 3.38\text{ Hz}$, $^3J_{\text{HH}} = 3.60\text{ Hz}$, *Th* H-4), 5.87 (m, 1H, $\text{CH}=\text{CH}_2$), 4.99 (m, 2H, $\text{CH}=\text{CH}_2$), 2.14 (d, 2H, $^3J_{\text{HH}} = 8.1\text{ Hz}$, SiCH_2), 0.69 (s, 3H, *SiMe*). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 138.12, 135.32, 132.41, 128.54 (*SiTh*), 134.60 ($\text{CH}=\text{CH}_2$), 115.93 ($\text{CH}=\text{CH}_2$), 18.10 (SiCH_2), -1.72 (*SiMe*). $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ -21.80 . Anal. Calc. for $\text{C}_{12}\text{H}_{14}\text{S}_2\text{Si}$: C, 57.55; H, 5.63. Found: C, 57.58; H, 5.69%.

3.3. Reaction of poly(*n*-hexylsilane) with (2-thienyl)vinyl-dichlorosilane/allyl(2-thienyl)dichlorosilane – synthesis of polysilanes 1, 2

A solution containing poly(*n*-hexylsilane) (1.63 g, 14.3 mmol), (2-thienyl)vinyl-dichlorosilane/allyl(2-thienyl)dichlorosilane (14.8 mmol) and catalytic amount of AIBN (1.2 mmol) in toluene (20 mL) was heated at 90°C for 48 h. Thereafter, the solvent was removed under vacuum. The resulting viscous mass obtained in each case was dissolved in diethyl ether and added separately to a dispersion of LiAlH_4 (15.5 mmol) in the same solvent at 0°C . The contents were gently refluxed for 4–5 h. The reaction mixture was hydrolyzed using 1 N HCl. The ether layer was separated and dried over anhydrous sodium sulfate. The crude polymer thus obtained in each case was dissolved in THF and methanol was added dropwise into it until a viscous gum separates out. This procedure was

repeated 2–3 times in order to get the polysilanes **1** and **2** in 28–32% isolable yield.

3.4. Reaction of poly(*n*-hexylsilane) with bis(2-thienyl)methylvinylsilane/allyl-bis(2-thienyl)methylsilane – synthesis of polysilanes 3, 4

To a stirred solution of poly(*n*-hexylsilane) (1.46 g, 12.8 mmol) and AIBN (1.1 mmol) in toluene (20 mL) was added bis(2-thienyl)methylvinylsilane/allyl-bis(2-thienyl)methylsilane (13.4 mmol). The contents were heated at 90°C for 48 h. Thereafter, the solvent was removed under vacuum leaving behind a viscous mass. The linear polysilanes **3/4** were separated from the corresponding crude product by repeated treatment with THF/methanol mixture (yield = 36–41%).

3.5. Reaction of poly(*n*-hexylsilane) with dichloromethylvinylsilane – synthesis of polysilane 5

Polysilane **5** was prepared by following a similar procedure as described above for **1** using poly(*n*-hexylsilane) (1.17 g, 10.3 mmol) and dichloromethylvinylsilane (1.5 mL, 11.5 mmol) as the starting precursors and subsequent reduction of the Si–Cl groups with LiAlH_4 (11.5 mmol). The polymer was obtained as a viscous gum in 34% isolable yield.

3.6. Reduction of silver tetrafluoroborate using polysilanes 1, 5

To a stirred suspension of silver tetrafluoroborate (7.8 mg, 0.04 mmol) in cyclohexane (20 mL, HPLC grade) was added a solution of polysilane **1** (17.0 mg, 0.08 mmol) in the same solvent. Slow dissolution of silver tetrafluoroborate was observed and a clear yellow solution was obtained after 5 hours which was centrifuged at 2000 rpm in order to remove any traces of unreacted silver tetrafluoroborate. The resulting solution containing silver nanoparticles was used for TEM and dynamic light scattering studies. The sample was stored at room temperature in the dark. The reduction of silver tetrafluoroborate with polysilane **5** or poly(*n*-hexylphenylsilane) was carried out by following a similar procedure as described for **1**.

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