



Catalytic dehydrocoupling of thienyl/furyl-substituted carbosilanes – Synthesis and characterization of functional poly(hydrosilane)s $[RMe_2Si(CH_2)_xSiH]_n$, ($R = 2\text{-Th}, 4\text{-Me-2-Th}, 2\text{-Fu}, 5\text{-Me-2-Fu}; x = 2 \text{ and } 3$)

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ABSTRACT

The carbosilanes $RMe_2Si(CH_2)_xSiH_3$, [$R = 2\text{-Th}$ (**1a**, **2a**), 4-Me-2-Th (**3a**, **4a**), 2-Fu (**5a**, **6a**), 5-Me-2-Fu (**7a**, **8a**); $x = 2$ and 3], with primary SiH_3 end groups undergo a facile dehydropolymerization under ambient conditions ($50\text{ }^\circ\text{C}$, 48 h) in presence of $Cp_2TiCl_2/2.2\text{ }n\text{-BuLi}$ catalyst to afford the corresponding poly(hydrosilane)s **1–8** bearing carbosilyl side chains appended with thienyl/furyl groups. These have been characterized by GPC, IR, multinuclear (1H , $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$) NMR, UV and PL spectral studies.

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1. Introduction

Catalytic dehydrocoupling of primary organosilanes, $RSiH_3$ ($R = \text{aryl/alkyl}$) using Group 4 metallocene catalysts is a widely accepted approach for the synthesis of poly(hydrosilane)s, $[RSiH]_n$ [1–8]. Extensive studies have been reported in the past on the role of the metal catalyst, organosilane precursor, reaction conditions etc. to better understand the mechanistic pathways involved in the polymerization process [1–5]. A generally accepted mechanism for group 4 metallocene promoted dehydrocoupling reactions involves σ -bond metathesis which proceed via four-centered transition states with a metallocene hydride and a metal silyl complex acting as the key intermediates [6–9].

Interest in poly(hydrosilane)s is derived from the known reactivity of Si–H groups. A number of chemical transformations of the preformed polysilanes using Si–H functionality have been reported. Notable among these is the hydrosilylation reaction of poly(phenylsilane) with aldehydes, ketones or functional olefins in presence of a free radical initiator such as AIBN [10,16] or a Pt catalyst (Spier's catalyst) [11,12]. The method affords a number of functional polysilanes with pendant alkoxy groups or side chain alkyl substituents appended with hydroxyl, amino or carboxylic acid groups as well as NLO chromophores. A detailed study of dehydrocoupling between $[Ph_2SiH]_2$ and various thiols using $B(C_6F_5)_3$ as the catalyst has been recently studied by Rosenberg

et al. These reactions are found to proceed without the cleavage of Si–Si bond [13].

Although primary silanes with phenyl/substituted phenyl groups are the most studied class of monomers for dehydropolymerization reaction, analogous alkylsilanes are poorly studied due to their volatility and low reactivity towards polymerization [1,14–18]. Recently, we have reported transition metal catalyzed dehydrocoupling of a number of carbosilane monomers $R_3Si(CH_2)_xSiH_3$ with substituents of varying steric attributes such as phenyl/methyl/ethyl groups on the silicon center [16–18]. Due to their non-volatile nature, these carbosilanes undergo polymerization at elevated temperatures to afford poly(hydrosilane)s bearing an appended carbosilyl group on the silicon backbone. These polysilanes offer the possibility to expand the scope of substitution chemistry on the side chain sila-alkyl groups, in addition to the reactivity of the Si–H bond.

Recently, we were intrigued by the lack of literature precedence on the synthetic aspects of polysilanes bearing hetero-aromatic substituents such as 2-thienyl or 2-furyl groups on the silicon backbone. To address this issue, we have undertaken a systematic study to explore viable synthetic protocols for this class of functional polymers. As shown in Chart 1, a number of such polysilanes have been successfully prepared by involving dehalocondensation (Wurtz coupling) of appropriate dichlorosilanes or chemical modification of preformed poly(*n*-hexylsilane) [19,20]. It has also been observed that the thienyl/furyl groups on the appended side chains in these polymers contribute towards stabilization of *in situ* generated silver and palladium nanoparticles. The work presented here-in describes the scope of catalytic dehydrocoupling approach for

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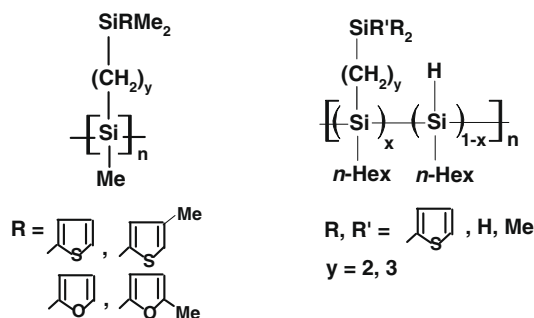


Chart 1.

the polymerization of primary organosilanes bearing 2-thienyl and 2-furyl substituents.

2. Results and discussion

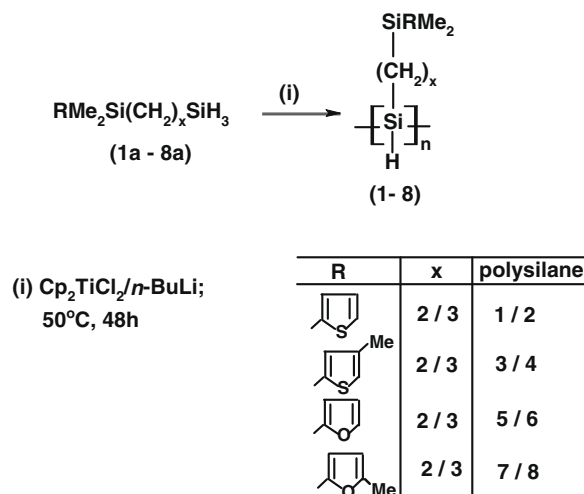
2.1. Synthesis of carbosilanes **1a–8a**

Synthesis of the carbosilanes, $\text{RMe}_2\text{Si}(\text{CH}_2)_x\text{SiH}_3$, [$\text{R} = 2\text{-Th}$ (**1a**, **2a**), 4-Me-2-Th (**3a**, **4a**), 2-Fu (**5a**, **6a**), 5-Me-2-Fu (**7a**, **8a**); $x = 2$ and 3] has been achieved in two steps. Hydrosilylation reaction between equimolar quantities of trichlorovinylsilane/allyltrichlorosilane and the appropriate thienyl/furyl-substituted hydrosilane, RMe_2SiH proceeds regioselectively (90°C , $12\text{--}15\text{ h}$) in presence of Karstedt's catalyst to afford the corresponding β -addition products, $\text{RMe}_2\text{Si}(\text{CH}_2)_x\text{SiCl}_3$. Subsequent treatment of these compounds with LiAlH_4 in diethyl ether yields the desired carbosilanes **1a–8a** as colorless, distillable liquids. The identity of these new compounds has been unequivocally established from the observed molecular ion (M^+) peak in each case in the ESI (product ion) mass spectra. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are quite straight forward and correlate well with the composition. For **3a** and **4a**, two distinct $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ NMR signals due to Me-Th group in the region δ 2.30–2.37/15.04–16.58 suggest the presence of two isomers $\text{RMe}_2\text{Si}(\text{CH}_2)_x\text{SiH}_3$, [$\text{R} = 4\text{-Me-2-Th}$ (85%), 3-Me-2-Th (15%)] which have their origin from the hydrosilane RMe_2SiH . The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of each carbosilane exhibits a distinct resonance at δ -5.56 to -6.42 (Si-Th)/ -8.52 to -10.92 (Si-Fu) due to SiC_4 moiety. The SiH_3 group in each carbosilane exhibits ^{29}Si NMR signal at δ -56.96 to -60.18 . The relevant spectral data are given in the Section 3.

2.2. Synthesis and characterization of poly(hydrosilane)s **1–8**

The feasibility of the carbosilanes **1a–8a** to undergo catalytic dehydrocoupling has been examined in presence of $\text{Cp}_2\text{TiCl}_2/n\text{-BuLi}$ (40:1:2.2) as the catalyst. The reaction mixture in each case turned blue in color suggesting the onset of dehydrocoupling reaction [21]. The mixture was heated at 50°C for 48 h to ensure completion of the reaction. The crude polymer thus obtained was dissolved in *n*-hexane and slow addition of methanol resulted in the separation of the corresponding poly(hydrosilane)s [$\text{RMe}_2\text{Si}(\text{CH}_2)_x\text{SiH}$] $_n$ **1–8** as orange-yellow viscous oils in 47–62% yield (Scheme 1).

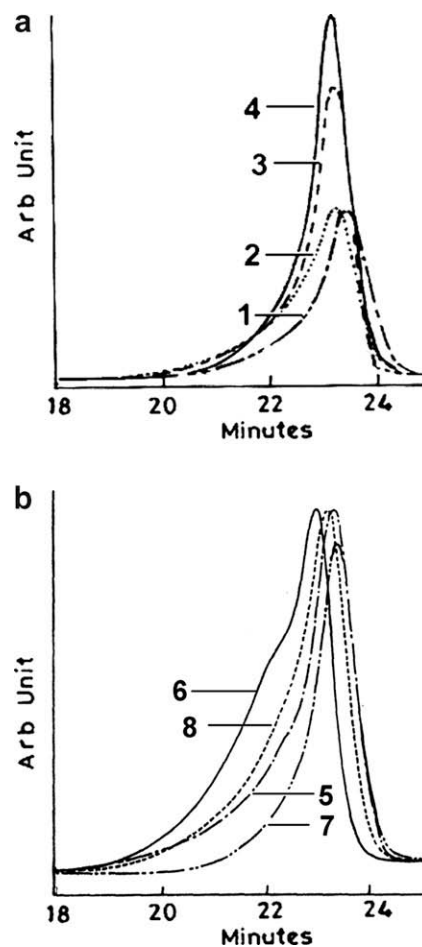
The polysilanes obtained above are soluble in common organic solvents such as dichloromethane, chloroform, tetrahydrofuran, toluene, hexane. However, the solubility of poly(hydrosilane)s **5–8** bearing furyl groups on the side chains tends to decrease significantly upon exposure in air for 5–7 days, in comparison to **1–4**. The IR spectra of the aged, exposed samples reveal new absorptions at 1080 and $2150\text{--}2154\text{ cm}^{-1}$ due to siloxanes containing Si-H groups. Similar phenomenon has been previously reported



Scheme 1.

in a few poly(hydrosilane)s bearing alkyl side chains and attributed to slow autooxidation of the skeletal silicon backbone [22].

All the polysilanes are thermally stable up to $250\text{--}300^\circ\text{C}$ as evident from thermogravimetric analysis (TGA). However, subsequent weight loss is observed in a continuous manner up to 500°C leaving a residual yield of $\sim 25\text{--}40\%$. The GPC analysis (Fig. 1) reveals molecular weight (M_w) in the range of $1625\text{--}2461$ with polydispersity (PDI) as $1.19\text{--}1.53$. For polysilanes **5** and **6**, the appearance of a

Fig. 1. GPC profiles of polysilanes (a) **1–4** and (b) **5–8**.

shoulder in the elution curves may be attributed to the poor resolution of the GPC profiles arising due to the limitation of the instrumental set up which includes columns designated for high molecular weight polymers. The functional groups associated with the appended side chain are identified by characteristic IR absorptions at 3090–3114 (Si–Th/Si–Fu) and 1250–1252 (Si–Me) cm^{-1} , while the Si–H groups are discernible at 2090–2105 (νSiH) and 910–915 (δSiH_2) cm^{-1} . The absence of IR bands in the region 2070–2085 cm^{-1} (νSiH) has been taken as an evidence for the absence of cyclic species in these oligomers [14,15]. The ^1H NMR spectra of **1–8** reveal sharp and distinct resonances due to the hetero-aromatic (δ 5.89–7.62) and Si–Me (δ 0.23–0.42) groups while the signals due to methylene protons associated with the carbosilyl moiety are generally broad and overlapping. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra reveal well resolved signals and allow the detection of side chain substituents in each polysilane. The assignment of the overlapping ^1H NMR resonances of the methylene groups have been made by examining HSQC (^1H – $^{13}\text{C}\{^1\text{H}\}$) NMR spectrum of a representative polysilane **4** (Fig. 2) which shows cross peaks at δ 14.28, 20.81/1.05 (α/γ - CH_2) and 22.90/1.71 (β - CH_2). A detailed spectral assignment of other polysilanes has been made accordingly and the pertinent data are given in the experimental section. For the polysilanes **3** and **4**, ^1H and ^{13}C NMR spectra exhibit two distinct signals due to Me–Th group at δ 2.26–2.53 and 15.02–16.61, respectively, and are corroborated with the presence of two isomers in the precursor carbosilane monomers. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of the polysilanes invariably show a singlet due to the appended carbosilyl moiety at δ –5.56 to –6.42 (for **1–4**) and –9.79 to –11.11 (for **5–8**) and a broad featureless signal at –54.51 to –66.81 associated with the silicon backbone.

The UV and PL (photoluminescence) emission spectra of poly(hydrosilane)s **1–8** have been studied in order to get an insight into the electronic properties associated with the σ -delocalized silicon backbone. The spectral profiles for a representative polysilane **2**

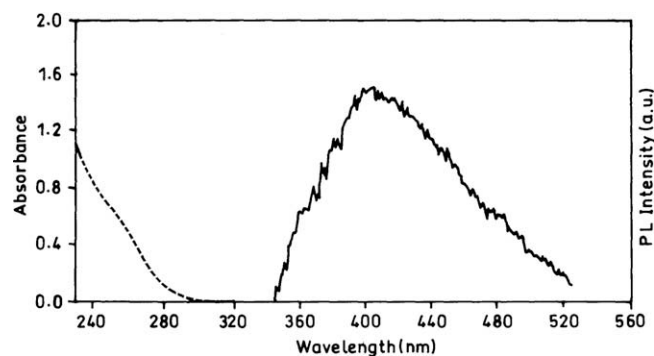


Fig. 3. UV absorption (dashed line) and photoluminescence (solid line) spectra of $[(2\text{-C}_4\text{H}_9\text{S})\text{Me}_2\text{Si}(\text{CH}_2)_3\text{SiH}]_n$ (**2**).

are shown in Fig. 3. As expected, the UV spectral profiles are quite similar and exhibit a shoulder like absorption without any peak at 250–270 nm. A number of previous studies have also reported a similar behavior of short chain poly(hydrosilane)s resulting from predominantly gauche conformation of the silicon backbone due to size difference between hydrogen and the bulky carbosilyl pendant groups [10,16]. Nevertheless, the photoluminescence spectral studies of this class of polymers have not been reported, despite its relevance in understanding the conformational and electronic features of oligo-/polysilanes [23–28]. The PL emission spectra (cyclohexane, RT) of the poly(hydrosilane)s **1–8** reveal a broad (fwhm \sim 85–100 nm) and weak emission profile at 400–415 nm in each case with Stoke's shifts of the order of 140–155 nm. Since the emission is very weak, the recorded spectra are quite noisy. The spectral behavior finds an apparent similarity with those reported for short chain permethyl/perhexyl oligosilanes $[\text{R}_2\text{Si}]_n$ ($n = 4\text{--}7$) [26–28]. For the latter, Michl et al. have attributed the

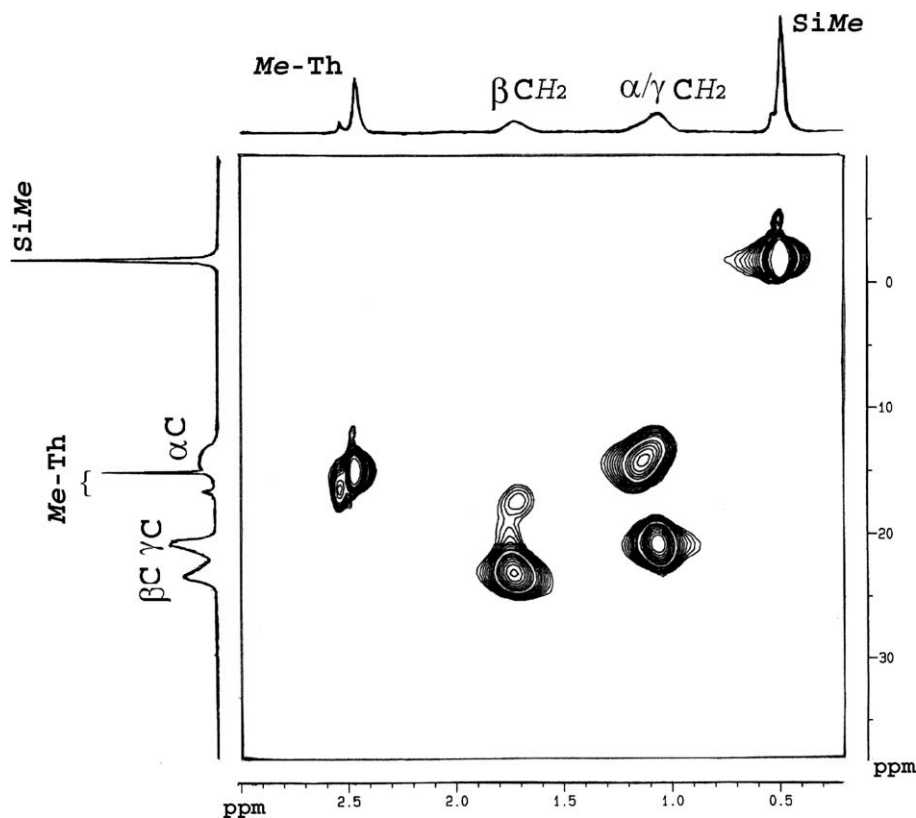


Fig. 2. (^1H – ^{13}C) HSQC NMR spectrum (aliphatic region) of $[(4\text{-Me-2-C}_4\text{H}_9\text{S})\text{Me}_2\text{Si}(\text{CH}_2)_3\text{SiH}]_n$ (**4**).

emission to a non-vertically excited σ - σ^* state of a lower energy arising due to a stretched Si-Si bond ("self trapped exciton"). Consequently, the emission is strongly Stokes-shifted and Frank Condon forbidden. A similar explanation can also be put forth for the emission behavior of **1–8**, assuming that the predominant gauche conformation in these oligosilanes may restrict the σ - σ^* transition in a localized state thereby preventing the "free-exciton" state arising from the entire length of the silicon backbone.

2.3. Catalytic dehydrocoupling of 2-thienylsilane

In order to better understand the scope of catalytic dehydrocoupling for the polymerization of primary silanes bearing 2-thienyl/2-furyl substituents, the reaction of 2-thienylsilane in presence of the titanium-catalyst has been studied under similar conditions as described for **1a–8a**. However, the reaction failed to proceed and did not yield the desired poly(hydrosilane). This observation finds an analogy with that reported earlier by Tanaka et al. for the zirconium-catalyzed dehydropolymerization reaction of 2-thienylsilane [4]. The inert nature of 2-thienylsilane towards dehydrocoupling is quite surprising in view of previous reports which subscribe a higher reactivity of the SiH groups in arylsilanes in comparison to alkylsilanes [2,15]. Although this behavior has not been clearly understood yet, a possible explanation has been put forth by implicating the mechanistic rationale of dehydrocoupling reactions reported earlier. Tilley and others [6–9] have proposed that the reaction proceeds via an intermediate formation of "metal-silyl complex" $Cp_2M(H)(SiH_2R)$ ($M = Ti, Zr, Hf$), which subsequently undergoes a series of σ -bond metathesis steps with the precursor silane to yield the desired poly(hydrosilane)s. By analogy, the formation of a similar intermediate "metal-silyl complex" bearing 2-Th or $ThMe_2Si(CH_2)_x$ substituent on the silicon center may be invoked in the present study (Chart 2). It is believed that the passive nature of 2-thienylsilane towards dehydrocoupling results from intramolecular coordinative association of the sulfur atom with the metal center which impedes the step growth polymerization. On the other hand, the intermediate involved in the dehydrocoupling of the carbosilanes **1a–8a** seems to remain unaffected, since the 2-thienyl substituent is separated from the metal center by the $Si(CH_2)_x$ spacer groups. It must however be mentioned that the complexity involved in tracking the true intermediate species with possible intra/intermolecular coordination of the sulfur (thienyl) atom must be addressed in detail.

In conclusion, the Ti-catalyzed dehydropolymerization of primary silanes, $RMe_2Si(CH_2)_xSiH_3$ ($R = 2$ -thienyl, 4-methyl-2-thienyl, 2-furyl, 5-methyl-2-furyl; $x = 2$ and 3) as well as 2-thienylsilane has been investigated. While the carbosilane monomers readily undergo dehydrocoupling to yield the corresponding poly(hydrosilane)s **1–8**, similar reaction fails to occur for 2-thienylsilane. A plausible explanation for this difference in reactivity has been put forth by considering the known mechanism involving σ -bond metathesis pathway. The photoluminescence emission spectra of these polysilanes are suggestive of emission from "self trapped

exciton" states similar to those observed for short chain permethyl/perhexyl oligosilanes.

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), phosphorus pentoxide (*n*-hexane) and magnesium (alcohols) before use. Trichlorovinylsilane and allyltrichlorosilane, (Aldrich) were distilled over magnesium. 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), 3-methylthiophene, lithium aluminium hydride, furan, 2-methylfuran, chlorodimethylsilane, bis(cyclopentadienyl)titaniumdichloride, triethoxy(2-thienyl)silane (Aldrich) were used as received.

Infrared spectra were obtained as thin films on KBr pellets on a Nicolet FT-IR (protégé) spectrometer. High resolution mass spectra were recorded on a QSTAR XL system mass spectrometer using the electron spray ionization (ESI) in positive product ion mode. UV-Vis and photoluminescence spectra (cyclohexane, room temperature) were recorded on a Perkin-Elmer (Lambda Bio 20) spectrophotometer and a Perkin Elmer LS50B Luminescence spectrofluorometer respectively. For recording the emission spectra, the polysilane solutions have been excited at the wavelength of the corresponding absorption maxima as obtained from the UV spectra and the spectral response from the blank has been subtracted before data analysis. 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 AVANCE II 400 NMR spectrometer at frequency 79.5 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 2s for each of 512 t_1 experiments. Thermo gravimetric analysis of polysilanes was carried out in nitrogen atmosphere between 50 and 900 °C at a rate of 10 °C/min on a Perkin Elmer Thermal analysis system. Elemental analysis (C and H) was performed on a Perkin-Elmer model 2400 CHN elemental analyzer.

3.2. Synthetic methods

The synthesis of 2-thienylsilane [29] and the hydrosilanes, RMe_2SiH [$R = 2$ -Fu, 5-Me-2-Fu, 2-Th, 4-Me-2-Th/3-Me-2-Th (regioisomers)] [20,30–34] was carried out by following the procedure reported earlier.

3.2.1. Synthesis of primary carbosilanes, $RMe_2Si(CH_2)_xSiH_3$, **1a–8a** ($R = 2$ -thienyl /4-methyl-2-thienyl/2-furyl/5-methyl-2-furyl; $x = 2$ and 3)

The carbosilanes **1a–8a** were synthesized by following the hydrosilylation approach. In a typical procedure, dimethyl(2-thienyl)silane (7.0 g, 49.3 mmol) was added drop wise at room temperature to a stirred solution of trichlorovinylsilane (6.3 mL, 8.0 g, 50.0 mmol) containing catalytic amount of Karstedt's catalyst (10^{-7} Pt/mol of silane). Induction period was observed after addition of a few milliliters of the hydrosilane. The reaction mixture was heated at 100 °C for 12 h to ensure the completion of the reaction.

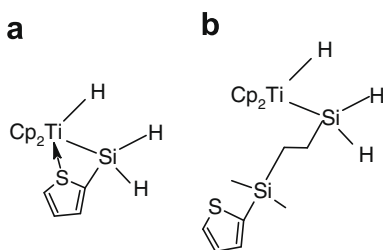


Chart 2. Proposed intermediates in the catalytic dehydrocoupling of (a) 2-thienylsilane and (b) carbosilane.

The crude mixture was fractionally distilled to obtain the chlorocar-bosilane, $\text{ThMe}_2\text{Si}(\text{CH}_2)_2\text{SiCl}_3$. Subsequently, the chlorocar-bosilane (11.5 g, 38.0 mmol) was added drop wise to a dispersion of LiAlH_4 (2.51 g, 66.0 mmol) in ether at 0 °C. The contents were gently re-fluxed for 5–6 h and then hydrolyzed with 1 N HCl. Ether layer was extracted and dried over anhydrous sodium sulfate. Thereafter, the contents were distilled under vacuum to afford the car-bosilane **1a** as colorless liquid. The car-bosilanes **2a–8a** were obtained by following a similar procedure by reacting dimethyl(2-thienyl)silane, dimethyl(4-methyl-2-thienyl)silane/dimethyl(2-furyl)silane/dimethyl(5-methyl-2-furyl)silane with trichlorovinylsilane/allyltrichlorosilane. The relevant spectroscopic data for these car-bosilanes are presented below. For assigning the NMR spectral data, methylene group attached to the SiH_3 moiety is represented with the notation, α - and subsequent groups are designated with β - and γ -notations respectively.

3.2.1.1. (2-C₄H₃S)Me₂Si(CH₂)₂SiH₃ (1a). (B.p. 82–85 °C/5 mm Hg, yield 76%). ¹H NMR (CDCl₃, 300 MHz): δ 7.63 (d, ³J_{HH} = 4.8 Hz, 1H, Th H-3), 7.29 (d, ³J_{HH} = 3.3 Hz, 1H, Th H-5), 7.22 (dd, 1H, ³J_{HH} = 3.3 Hz, ³J_{HH} = 4.9 Hz, Th H-4), 3.55 (t, 3H, ³J_{HH} = 3.6 Hz, SiH₃), 0.81–0.88 (m, 2H, β -CH₂), 0.71–0.78 (m, 2H, α -CH₂), 0.36 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 138.09, 134.36, 130.55, 128.09 (Th), 12.85 (β -CH₂), -0.96 (α -CH₂), -2.34 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -5.83 (SiMe₂), -54.68 (SiH₃). IR (KBr, cm⁻¹): 2147 (ν SiH), 930 (δ SiH₂), 3090 (Si-Th), 1253 (Si-Me). ES-MS: *m/z* Calc. for C₈H₁₆SSi₂: 200.0511; found: 200.1003 [M⁺]. Anal. Calc. for C₈H₁₆SSi₂: C, 47.94; H, 8.05. Found: C, 47.58; H, 8.12%.

3.2.1.2. (2-C₄H₃S)Me₂Si(CH₂)₃SiH₃ (2a). (B.p. 90–92 °C/5 mm Hg, yield 82%). ¹H NMR (CDCl₃, 300 MHz): δ 7.59 (d, ³J_{HH} = 4.5 Hz, 1H, Th H-3), 7.25 (d, ³J_{HH} = 3.9 Hz, 1H, Th H-5), 7.18 (dd, 1H, ³J_{HH} = 3.4 Hz, ³J_{HH} = 4.55 Hz, Th H-4), 3.47 (t, 3H, ³J_{HH} = 3.9 Hz, SiH₃), 1.46–1.57 (m, 2H, β -CH₂), 0.77–0.90 (m, 4H, α -CH₂ + γ -CH₂), 0.32 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 138.32, 135.94, 132.42, 128.51 (Th), 21.46 (β -CH₂), 18.64 (γ -CH₂), 11.21 (α -CH₂), -2.12 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -5.48 (SiMe₂), -59.00 (SiH₃). IR (KBr, cm⁻¹): 2148 (ν SiH), 925 (δ SiH₂), 3090 (Si-Th), 1252 (Si-Me). ES-MS: *m/z* Calc. for C₉H₁₈SSi₂: 214.0668; found: 214.0915 [M⁺]. Anal. Calc. for C₉H₁₈SSi₂: C, 50.40; H, 8.46. Found: C, 50.36; H, 8.39%.

3.2.1.3. (4-Me-2-C₄H₃S)Me₂Si(CH₂)₂SiH₃ (3a). The compound is obtained as isomeric mixture with 4-Me-2-Th (85%) and 3-Me-2-Th (15%) substituents on silicon.

(B.p. 92–95 °C/5 mm Hg, yield 72%). ¹H NMR (CDCl₃, 300 MHz): δ 7.16, 7.04 (s, Th H-3,5), 2.30 (s, Me-Th) (major isomer 85%), 7.45 (d, ³J_{HH} = 4.8 Hz, Me-Th H-5), 7.00 (d, ³J_{HH} = 4.6 Hz, Me-Th H-4), 2.35 (s, Me-Th) (minor isomer 15%), 3.53 (t, 3H, ³J_{HH} = 3.7 Hz, SiH₃), 0.86–0.68 (m, 4H, α -CH₂ + β -CH₂), 0.30 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 138.82, 137.78, 136.45, 130.95, 129.89, 126.67 (Th), 16.58, 15.04 (Me-Th), 12.83 (β -CH₂), -0.98 (α -CH₂), -2.39 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -6.30 (SiMe₂), -59.12 (SiH₃); IR (KBr, cm⁻¹): 2145 (ν SiH), 928 (δ SiH₂), 3078 (Si-Th), 1251 (Si-Me). ES-MS: *m/z* Calc. for C₉H₁₈SSi₂: 214.0668; found: 214.0555 [M⁺]. Anal. Calc. for C₉H₁₈SSi₂: C, 50.40; H, 8.46. Found: C, 50.43; H, 8.43%.

3.2.1.4. (4-Me-2-C₄H₃S)Me₂Si(CH₂)₃SiH₃ (4a). The compound is obtained as isomeric mixture with 4-Me-2-Th (85%) and 3-Me-2-Th (15%) substituents on silicon.

(B.p. 95–97 °C/5 mm Hg, yield 79%). ¹H NMR (CDCl₃, 300 MHz): δ 7.17, 7.05 (s, Th H-3,5), 2.31 (s, Me-Th) (major isomer 85%), 7.45 (d, ³J_{HH} = 4.6 Hz, Me-Th H-5), 7.01 (d, ³J_{HH} = 4.8 Hz, Me-Th H-4), 2.37 (s, Me-Th) (minor isomer 15%), 3.49 (t, ³J_{HH} = 3.9 Hz, SiH₃),

1.48–1.57 (m, β -CH₂), 0.81–0.88 (m, α -CH₂ + γ -CH₂), 0.32 (s, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 138.91, 136.70, 131.84, 131.48, 129.32, 126.15 (Th), 20.97 (β -CH₂), 19.82 (γ -CH₂), 16.56, 15.05 (Me-Th), 10.12 (α -CH₂), -1.90 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -6.22 (SiMe₂), -60.16 (SiH₃); IR (KBr, cm⁻¹): 2146 (ν SiH), 925 (δ SiH₂), 3089 (Si-Th), 1252 (Si-Me). ES-MS: *m/z* Calc. for C₁₀H₂₀SSi₂: 228.0824; found: 228.0881 [M⁺]. Anal. Calc. for C₁₀H₂₀SSi₂: C, 52.56; H, 8.82. Found: C, 52.60; H, 8.79%.

3.2.1.5. (2-C₄H₃O)Me₂Si(CH₂)₂SiH₃ (5a). (B.p. 65–68 °C/5 mm Hg, yield 76%). ¹H NMR (CDCl₃, 300 MHz): δ 7.65 (d, ³J_{HH} = 1.3 Hz, 1H, Fu H-5), 6.63 (d, ³J_{HH} = 3.3 Hz, 1H, Fu H-3), 6.38 (dd, 1H, ³J_{HH} = 1.5 Hz, ³J_{HH} = 3.3 Hz, Fu H-4), 3.51 (t, 3H, ³J_{HH} = 3.6 Hz, SiH₃), 0.70–0.78 (m, 4H, α -CH₂ + β -CH₂), 0.29 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 158.93, 146.68, 120.45, 109.31 (Fu), 11.08 (β -CH₂), -1.11 (α -CH₂), -3.86 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -10.14 (SiMe₂), -60.18 (SiH₃); IR (KBr, cm⁻¹): 2145 (ν SiH), 926 (δ SiH₂), 3112 (Si-Fu), 1252 (Si-Me). ES-MS: *m/z* Calc. for C₈H₁₆OSi₂: 184.0740; found: 184.0671 [M⁺]. Anal. Calc. for C₈H₁₆OSi₂: C, 52.11; H, 8.75. Found: C, 52.19; H, 8.77%.

3.2.1.6. (2-C₄H₃O)Me₂Si(CH₂)₃SiH₃ (6a). (B.p. 69–72 °C/5 mm Hg, yield 76%). ¹H NMR (CDCl₃, 300 MHz): δ 7.65 (d, ³J_{HH} = 1.2 Hz, 1H, Fu H-5), 6.61 (d, ³J_{HH} = 3.3 Hz, 1H, Fu H-3), 6.38 (dd, 1H, ³J_{HH} = 1.52 Hz, ³J_{HH} = 3.3 Hz, Fu H-4), 3.46 (t, 3H, ³J_{HH} = 3.9 Hz, SiH₃), 1.51 (m, 2H, β -CH₂), 0.81–0.85 (m, 4H, α -CH₂ + γ -CH₂), 0.24 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 159.34, 146.60, 119.87, 109.29 (Fu), 20.82 (β -CH₂), 18.63 (γ -CH₂), 10.03 (α -CH₂), -3.41 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -9.76 (SiMe₂), -58.54 (SiH₃). IR (KBr, cm⁻¹): 2147 (ν SiH), 930 (δ SiH₂), 3111 (Si-Fu), 1253 (Si-Me). ES-MS: *m/z* Calc. for C₉H₁₈OSi₂: 198.0896; found: 198.1033 [M⁺]. Anal. Calc. for C₉H₁₈OSi₂: C, 54.48; H, 9.14. Found: C, 54.40; H, 9.12%.

3.2.1.7. (5-Me-2-C₄H₂O)Me₂Si(CH₂)₂SiH₃ (7a). (B.p. 72–75 °C/5 mm Hg, yield 76%). ¹H NMR (CDCl₃, 300 MHz): δ 6.58 (d, ³J_{HH} = 3.1 Hz, 1H, Fu H-3), 6.01 (d, ³J_{HH} = 3.0 Hz, 1H, Me-Fu H-4), 3.58 (t, 3H, ³J_{HH} = 3.6 Hz, SiH₃), 2.37 (s, 3H, Me-Fu), 0.78–0.83 (m, 2H, β -CH₂), 0.36–0.39 (m, 2H, α -CH₂), 0.30 (s, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 156.18, 121.40, 105.70 (Fu), 13.73 (Me-Fu), 11.21 (β -CH₂), -1.13 (α -CH₂), -3.74 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -9.06 (SiMe₂), -56.96 (SiH₃). IR (KBr, cm⁻¹): 2147 (ν SiH), 924 (δ SiH₂), 3112 (Si-Fu), 1254 (Si-Me). ES-MS: *m/z* Calc. for C₉H₁₈OSi₂: 198.0896; found: 198.1438 [M⁺]. Anal. Calc. for C₉H₁₈OSi₂: C, 54.48; H, 9.14. Found: C, 54.42; H, 9.09%.

3.2.1.8. (5-Me-2-C₄H₂O)Me₂Si(CH₂)₃SiH₃ (8a). (B.p. 76–78 °C/5 mm Hg, yield 82%). ¹H NMR (CDCl₃, 300 MHz): δ 6.54 (d, ³J_{HH} = 3.9 Hz, 1H, Fu H-3), 5.99 (d, 1H, ³J_{HH} = 3.3 Hz, Me-Fu H-4), 3.51 (t, 3H, ³J_{HH} = 3.9 Hz, SiH₃), 2.36 (s, 3H, Me-Fu), 1.49–1.59 (m, 2H, β -CH₂), 0.78–0.86 (m, 4H, α -CH₂ + γ -CH₂), 0.27 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 157.40, 156.41, 121.45, 105.67 (Fu), 20.91 (β -CH₂), 18.74 (γ -CH₂), 13.61 (Me-Fu), 10.03 (α -CH₂), -3.30 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -10.92 (SiMe₂), -60.33 (SiH₃). IR (KBr, cm⁻¹): 2148 (ν SiH), 925 (δ SiH₂), 3109 (Si-Fu), 1252 (Si-Me). ES-MS: *m/z* Calc. for C₁₀H₂₀OSi₂: 212.1053; found: 212.0861 [M⁺]. Anal. Calc. for C₁₀H₂₀OSi₂: C, 56.54; H, 9.49. Found: C, 56.50; H, 9.56%.

3.2.2. Synthesis of polysilanes [RMe₂Si(CH₂)_xSiH]_n **1–8 (R = 2-thienyl/4-methyl-2-thienyl/2-furyl/5-methyl-2-furyl; x = 2 or 3)**

The car-bosilanes **1a–8a** (20.0 mmol) prepared above were charged separately with Cp₂TiCl₂ (0.13 g, 0.52 mmol) and *n*-BuLi (0.71 mL, 1.6 M in hexane) under dry N₂ conditions. The solution immediately turned blue in color in each case. The reaction mixture was heated at 50 °C for 48 h and the catalyst was subsequently deactivated by *n*-hexane in air until the intense color

disappeared. The solid residue was filtered and the volatile components of the filtrate were removed in vacuo. The resulting viscous residue obtained in each case was dissolved in minimum amount of *n*-hexane and the corresponding polysilanes **1–8** were obtained as viscous oils by the addition of methanol.

3.2.2.1. [(2-*C*₄*H*₃*S*)Me₂Si(CH₂)₂SiH]_{*n*} (**1**). Yield = 49.5%; ¹H NMR (CDCl₃, 300 MHz): δ 7.59, 7.27, 7.17 (3H, *Th*), 3.56 (br, 1H, SiH), 0.82 (br, 4H, α-CH₂ + β-CH₂), 0.31 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 137.78, 134.41, 130.62, 128.16 (*Th*), 15.44 (β-CH₂), 2.17 (α-CH₂), -2.24 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -54.51 (br, SiH), -5.56 (SiMe₂). IR (KBr, cm⁻¹): 2106 (νSiH), 927 (δSiH₂), 3090 (Si–Th), 1251 (Si–Me). GPC (THF versus polystyrene): *M*_w = 1625, PDI = 1.33. UV–Vis: λ_{max} (nm) = 255. PL (emission): λ_{max}/fwhm (nm) = 400/85.

3.2.2.2. [(2-*C*₄*H*₃*S*)Me₂Si(CH₂)₃SiH]_{*n*} (**2**). Yield = 58.4%; ¹H NMR (CDCl₃, 300 MHz): δ 7.61, 7.29, 7.22 (3H, *Th*), 3.57 (br, 1H, SiH), 1.54 (br, 2H, β-CH₂), 0.91 (br, 4H, α-CH₂ + γ-CH₂), 0.35 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 138.79, 134.19, 130.44, 128.07 (*Th*), 22.44 (β-CH₂), 20.71 (γ-CH₂), 13.47 (α-CH₂), -1.72 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -57.81 (br, SiH), -5.70 (SiMe₂). IR (KBr, cm⁻¹): 2100 (νSiH), 910 (δSiH₂), 3092 (Si–Th), 1252 (Si–Me); GPC (THF versus polystyrene): *M*_w = 2461, PDI = 1.53. UV–Vis: λ_{max} (nm) = 260. PL (emission): λ_{max}/fwhm (nm) = 405/97.

3.2.2.3. [(4-*Me*-2-*C*₄*H*₂*S*)Me₂Si(CH₂)₂SiH]_{*n*} (**3**). Yield = 54.8%; ¹H NMR (CDCl₃, 300 MHz): δ 7.15, 7.03 (2H, *Th*), 3.63 (br, 1H, SiH), 2.31, 2.26 (s, 3H, *Me*-Th), 0.85 (br, 4H, α-CH₂ + β-CH₂), 0.28 (s, 6H, SiMe₂); ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 138.90, 138.38, 137.16, 136.86, 131.87, 126.27 (*Th*), 15.62 (β-CH₂), 16.32, 15.02 (*Me*-Th), 2.98 (α-CH₂), -1.89 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -56.45 (br, SiH), -6.32 (SiMe₂). IR (KBr, cm⁻¹): 2095 (νSiH), 922 (δSiH₂), 3092 (Si–Th), 1252 (Si–Me). GPC (THF versus polystyrene): *M*_w = 2046, PDI = 1.26. UV–Vis: λ_{max} (nm) = 260. PL (emission): λ_{max}/fwhm (nm) = 400/85.

3.2.2.4. [(4-*Me*-2-*C*₄*H*₂*S*)Me₂Si(CH₂)₃SiH]_{*n*} (**4**). Yield = 62.0% ¹H NMR (CDCl₃, 300 MHz): δ 7.36, 7.22 (2H, *Th*), 3.77 (br, 1H, SiH), 2.53, 2.46 (s, *Me*-Th), 1.71 (br, 2H, β-CH₂), 1.05 (br, 4H, α-CH₂ + γ-CH₂), 0.42 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 138.90, 138.69, 136.61, 131.77, 129.27, 126.27 (*Th*), 22.90 (β-CH₂), 20.81 (γ-CH₂), 14.28 (α-CH₂), 16.61, 15.04 (*Me*-Th), -1.77 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -57.56 (br, SiH), -6.41 (SiMe₂). IR (KBr, cm⁻¹): 2096 (νSiH), 915 (δSiH₂), 3094 (Si–Th), 1251 (Si–Me). GPC (THF versus polystyrene): *M*_w = 2081, PDI = 1.19. UV–Vis: λ_{max} (nm) = 265. PL (emission): λ_{max}/fwhm (nm) = 408/89.

3.2.2.5. [(2-*C*₄*H*₃*O*)Me₂Si(CH₂)₂SiH]_{*n*} (**5**). Yield = 47.2%; ¹H NMR (CDCl₃, 300 MHz): δ 7.58, 6.57, 6.32 (3H, *Fu*), 3.62 (br, 1H, SiH), 0.82 (br, 4H, α-CH₂ + β-CH₂), 0.23 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 158.41, 146.39, 120.72, 107.07 (*Fu*), 9.34 (β-CH₂), 2.47 (α-CH₂), -3.03 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -54.20 (br, SiH), -10.83 (SiMe₂). IR (KBr, cm⁻¹): 2101 (νSiH), 908 (δSiH₂), 3112 (Si–Fu), 1252 (Si–Me). GPC (THF versus polystyrene): *M*_w = 2222, PDI = 1.31. UV–Vis: λ_{max} (nm) = 250. PL (emission): λ_{max}/fwhm (nm) = 405/90.

3.2.2.6. [(2-*C*₄*H*₃*O*)Me₂Si(CH₂)₃SiH]_{*n*} (**6**). Yield = 51.9%; ¹H NMR (CDCl₃, 300 MHz): δ 7.62, 6.60, 6.35 (3H, *Fu*), 3.50 (br, 1H, SiH), 1.48 (br, 2H, β-CH₂), 0.82 (br, 4H, α-CH₂ + γ-CH₂), 0.24 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 159.70, 145.93, 119.26, 108.11 (*Fu*), 21.78 (β-CH₂), 18.63 (γ-CH₂), 15.44 (α-CH₂), -3.89 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -56.64 (br, SiH), -9.87 (SiMe₂).

IR (KBr, cm⁻¹): 2104 (νSiH), 910 (δSiH₂), 3108 (Si–Fu), 1252 (Si–Me). GPC (THF versus polystyrene): *M*_w = 2566, PDI = 1.29. UV–Vis: λ_{max} (nm) = 265. PL (emission): λ_{max}/fwhm (nm) = 411/90.

3.2.2.7. [(5-*Me*-2-*C*₄*H*₂*O*)Me₂Si(CH₂)₂SiH]_{*n*} (**7**). Yield = 60.3%; ¹H NMR (CDCl₃, 300 MHz): δ 6.41, 5.85 (2H, *Fu*), 3.57 (br, 1H, SiH), 2.20 (s, 3H, *Me*-Fu), 0.82 (br, 4H, α-CH₂ + β-CH₂), 0.24 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 157.10, 151.96, 121.27, 105.67, (*Fu*), 13.66 (*Me*-Fu), 6.56 (β-CH₂), 3.00 (α-CH₂), -3.76 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -57.02 (br, SiH), -9.43 (SiMe₂). IR (KBr, cm⁻¹): 2098 (νSiH), 911 (δSiH₂), 3111 (Si–Fu), 1253 (Si–Me). GPC (THF versus polystyrene): *M*_w = 1943, PDI = 1.23. UV–Vis: λ_{max} (nm) = 255. PL (emission): λ_{max}/fwhm (nm) = 403/96.

3.2.2.8. [(5-*Me*-2-*C*₄*H*₂*O*)Me₂Si(CH₂)₃SiH]_{*n*} (**8**). Yield = 58.3%; ¹H NMR (CDCl₃, 300 MHz): δ 6.48, 5.92 (2H, *Fu*), 3.53 (br, 1H, SiH), 2.29 (s, 3H, *Me*-Fu), 1.34 (br, 2H, β-CH₂), 0.81 (br, 4H, α-CH₂ + γ-CH₂), 0.24 (s, 6H, SiMe₂). ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 157.01, 156.35, 121.07, 107.07 (*Fu*), 22.87 (β-CH₂), 19.52 (γ-CH₂), 14.82 (α-CH₂), 13.66 (*Me*-Fu), -3.21 (SiMe₂). ²⁹Si{¹H} NMR (CDCl₃, 79.5 MHz): δ -58.31 (br, SiH), -11.31 (SiMe₂); IR (KBr, cm⁻¹): 2094 (νSiH), 915 (δSiH₂), 3104 (Si–Fu), 1252 (Si–Me). GPC (THF versus polystyrene): *M*_w = 2317, PDI = 1.35. UV–Vis: λ_{max} (nm) = 270. PL (emission): λ_{max}/fwhm (nm) = 415/98.

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