

Grignard Metathesis Polymerization and Properties of 1,1-Disubstituted-2,5-dibromo-3,4-diphenylsiloles

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Grignard metathesis polymerizations of 1,1-disubstituted-2,5-dibromo-3,4-diphenylsiloles such as 1,1-dimethyl-2,5-dibromo-3,4-diphenylsilole, 1,1-diethyl-2,5-dibromo-3,4-diphenylsilole, 1,1-diisopropyl-2,5-dibromo-3,4-diphenylsilole, and 1,1-dihexyl-2,5-dibromo-3,4-diphenylsilole were performed to yield poly(1,1-disubstituted-3,4-diphenyl-2,5-silole)s containing fluorescent aromatic chromophore groups such as phenyl and silole in the polymer main chain: poly(1,1-dimethyl-3,4-diphenyl-2,5-silole), poly(1,1-diethyl-3,4-diphenyl-2,5-silole), poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole), and poly(1,1-dihexyl-3,4-diphenyl-2,5-silole), respectively. The obtained materials are highly soluble in common organic solvents such as chloroform and tetrahydrofuran. Fourier-transform infrared spectra of all the polymers have characteristic C=C stretching frequencies at 1620-1628 cm^{-1} . The prepared organosilicon polymers exhibit strong absorption maximum peaks at 273-293 nm in the tetrahydrofuran solution, showing a red-shift of 18-34 nm relative to those of the monomer, strong excitation maximum peaks at 276-303 nm, and strong fluorescence emission maximum bands at 350-440 nm. Thermogravimetric analysis shows that most of the polymers are stable up to 200 °C with a weight loss of 6-16% in nitrogen.

Key Words : Poly(1,1-disubstituted-3,4-diphenyl-2,5-silole)s, 2,5-Dibromo-3,4-diphenylsilole, Grignard metathesis polymerization, Electronic properties, Thermal stability

Introduction

π -Conjugated organosilicon polymeric materials have excited much interest because of their potentially useful applications.^{1,2} Organosilicon polymers bearing fluorescent groups are also of great interest for use in electroluminescence materials.^{3,4}

Silacyclopenta-2,4-dienes, also called siloles, are a series of five-membered silacyclic dienes that contain unique π -electron systems.⁵ Silole derivatives are new π -electronic materials with novel electronic and optical properties.⁶⁻⁸ π -Conjugated polymers containing siloles have also received much attention for potential optoelectronic, photoluminescence,⁹⁻¹¹ and sensor applications.^{12,13} End-capped silole dendrimers on an ethenyl-phenyl-carbosilane skeleton show green to greenish-blue fluorescence and have potential applications as electroluminescent materials.¹⁴ However, few syntheses of poly(1,1-disubstituted-3,4-diphenyl-2,5-silole)s have been reported.^{15,16}

Aryl- and heteroaryl-conjugated polymers are usually synthesized through metal-catalyzed polycondensation reactions, based on Yamamoto, Suzuki, or Stille coupling reactions,^{17,18} including the Grignard metathesis (GRIM) method.¹⁹ In GRIM, Ni(II) complexes are used to polymerize functionalized Grignard monomers at room temperature, which is an advantage over previous procedures. Recently, to expand the use of GRIM, "turbo-Grignard" reagents (LiCl plus a Grignard reagent) have been used for the synthesis of various aryl and heteroaryl conjugated polymers.²⁰ The GRIM method can shorten polymerization times and lower reaction

temperatures, facilitating the preparation of aryl and heteroaryl conjugated polymers.²¹

The melt copolymerizations of 1,3-bis(diethylamino)tetramethyldisiloxane with several fluorescent aryldiols have been reported to yield poly(arylcarbotetramethyl-disiloxane)s containing fluorescent aromatic chromophores in the main chains.²² The melt copolymerizations of several bis(diethylamino)silane derivatives with 2,7-dihydroxyfluoren-9-one were also examined, and were found to produce poly[oxy-(2,7-fluoren-9-onenylene)oxy(diorgnaosilylene)]s containing fluoren-9-one as a fluorescent aromatic chromophore group in the main chains.²³ Recently, the melt copolymerizations of 1,2-bis(diethylamino)tetramethyldisilane with various aryldiols were studied, and these afforded poly[oxy(arylene)oxy(tetramethyldisilylene)]s containing fluorescent aromatic chromophore groups in the polymer main chains.²⁴

With these results in mind, we focused on the preparation of fluorescent poly(carbosilane) materials containing aromatic chromophores from silole derivatives in the polymer main chain, using turbo-Grignard metathesis polymerization to produce poly(1,1-disubstituted-3,4-diphenylsilole)s and evaluated their photoelectronic properties.

Here, we report the syntheses of poly(1,1-disubstituted-3,4-diphenyl-2,5-silole)s, namely poly(1,1-dimethyl-3,4-diphenyl-2,5-silole) (**4a**), poly(1,1-diethyl-3,4-diphenyl-2,5-silole) (**4b**), poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole) (**4c**), and poly(1,1-dihexyl-3,4-diphenyl-2,5-silole) (**4d**) via GRIM polymerizations of 1,1-disubstituted-2,5-dibromo-3,4-diphenylsiloles, namely 1,1-dimethyl-2,5-dibromo-3,4-diphenylsilole (**3a**), 1,1-diethyl-2,5-dibromo-3,4-diphenyl-

silole (**3b**), 1,1-diisopropyl-2,5-dibromo-3,4-diphenylsilole (**3c**), and 1,1-dihexyl-2,5-dibromo-3,4-diphenylsilole (**3d**), respectively, using a “turbo-Grignard” reagent.

The goal of these GRIM polymerizations was to synthesize poly(1,1-disubstituted-3,4-diphenyl-2,5-silole)s with high molecular weights. The materials obtained were characterized using Fourier-transform infrared (FTIR) and ^1H , ^{13}C , and ^{29}Si nuclear magnetic resonance (NMR) spectroscopies in the solution state. We focused on investigating the photoelectronic and thermal properties of the prepared polymers **4a-d** using solution-state absorption, excitation, and fluorescence emission spectroscopies and thermogravimetric analysis (TGA).

Results and Discussion

Monomer Synthesis. 2,5-Dibromo-3,4-diphenylsilole monomers **3a-d** were prepared *via* a two-step reaction, as shown in Scheme 1. For example, in the first step, dichlorodimethylsilane (**1a**) was reacted with phenylethyne, which was prepared *in situ* by a reaction of phenylacetylene with *n*-butyllithium in tetrahydrofuran (THF) at $-70\text{ }^\circ\text{C}$, to yield dimethylbis(phenylethynyl)silane (**2a**) quantitatively. In the second step, intramolecular reductive cyclization of **2a** was performed by treatment with lithium naphthalenide (4 mol), followed by anhydrous ZnCl_2 and *N*-bromosuccinimide (NBS), to afford 2,5-dibromo-1,1-dimethyl-3,4-diphenylsilole (**3a**).

2,5-Dibromosiloles **3b-d** were similarly prepared by cyclization reactions of diethylbis(phenylethynyl)silane (**2b**), diisopropylbis(phenylethynyl)silane (**2c**), and dihexylbis(phenylethynyl)silane (**2d**), respectively, which were pre-

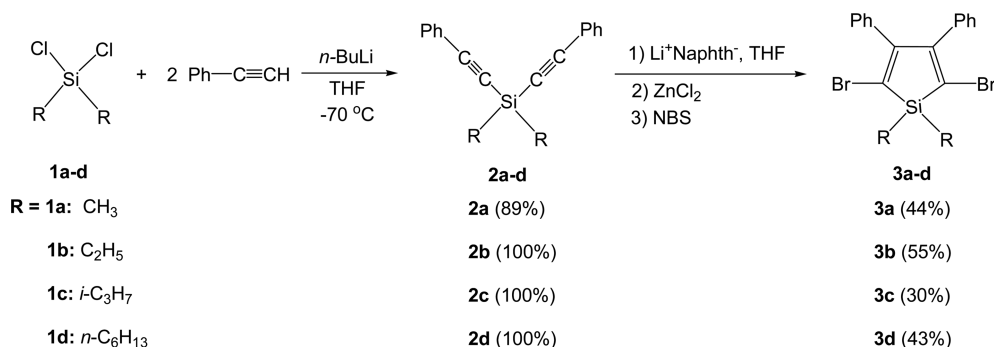
pared from dichlorodiethylsilane (**1b**), dichlorodiisopropylsilane (**1c**), and dichlorodihexylsilane (**1d**), respectively.

The monomers **3a-d** were characterized using various spectroscopic methods, such as ^1H , ^{13}C , and ^{29}Si NMR spectroscopies in the solution state. The ^1H NMR spectrum of **3a** exhibits a clear singlet resonance at 0.47 ppm, ascribed to the methyl group bonded to the silole silicon.^{6,25} In the ^{13}C NMR spectrum of **3a**, one carbon peak from the methyl group bonded to the silicon is observed at -6.05 ppm .^{6,25} In the ^{29}Si NMR spectrum of **3a**, the silicon resonance is observed at 4.96 ppm. The monomers **3a-d** were successfully prepared *via* two-step reactions under the conditions described.

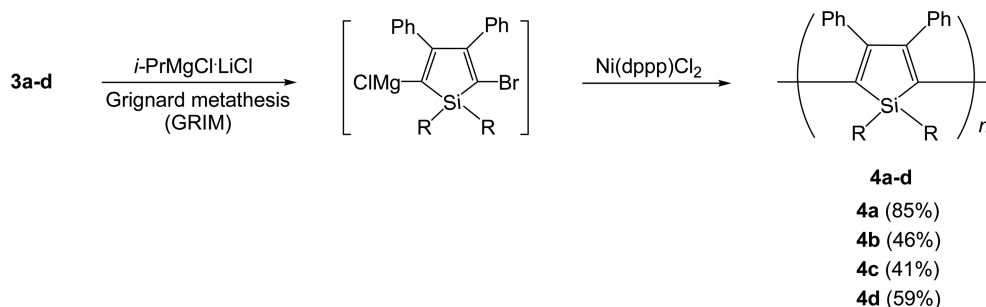
We examined the absorption spectra of the monomers **3a-d** in THF solution. The maximum absorption band for **3a** is observed at 275 nm, with a molar absorptivity of $8.50 \times 10^3\text{ cm}^{-1}\text{ M}^{-1}$. The absorption spectra of **3b-d** also show strong absorption peaks at 260, 253, and 243 nm, respectively. These strong absorption bands in the ultraviolet-visible (UV-vis) spectra of **3a-d** may result from chromophores such as phenyl and diene groups in the 3,4-diphenylsilole monomers.³

Grignard Metathesis Polymerization. Poly(1,1-disubstituted-3,4-diphenyl-2,5-silole)s were synthesized by GRIM polymerizations,²⁰ using a “turbo-Grignard” reagent. Ni(II) complexes such as [1,3-bis(diphenylphosphine)propane]dichloronickel(II) [$\text{Ni}(\text{dppp})\text{Cl}_2$] were used to polymerize the functionalized Grignard monomers at room temperature.²⁶ The addition of LiCl to a Grignard reagent dissociates the polymeric aggregates formed in solution to produce a very reactive complex [$i\text{-PrMgCl}_2\text{Li}^+$].²⁰

A solution of dibromosilole **3a** in THF was added to *i*-PrMgCl-LiCl and stirred for 17 h at room temperature,



Scheme 1



Scheme 2

Table 1. Selected Properties of Poly(1,1-disubstituted-3,4-diphenyl-2,5-silole)s **4a-d**

Polymer	M_w/M_n^a (PDI)	^{29}Si NMR ^b δ (ppm)	IR ^c $\nu_{(\text{C}=\text{C})}$ (cm^{-1})	Absorption ^d $\lambda_{\text{abs, max}}$ (nm) (ϵ) ($\text{nm cm}^{-1}\text{M}^{-1}$)	Excitation ^e $\lambda_{\text{ex, max}}$ (nm)	Fluorescence ^f $\lambda_{\text{em, max}}$ (nm)	Fluorescence FWHM ^g (nm)	TGA ^h
4a	784/573 (1.37)	11.43	1620	293 (5.95×10^3)	300	380	105	54
4b	1,450/1,064 (1.36)	8.58	1628	283 (4.10×10^3)	297	350	104	90
4c	658/610 (1.08)	7.03	1622	273 (3.08×10^3)	276	440	94	41
4d	993/922 (1.09)	6.43	1628	277 (6.44×10^3)	303	393	106	61

^aDetermined by GPC in THF relative to polystyrene standards. M_w/M_n = polydispersity index (PDI). ^bIn CDCl_3 . ^cIn KBr. ^dIn THF solution. ^eDetection wavelengths 380, 350, 440, and 393 nm in THF solution for **4a-d**, respectively. ^fExcitation wavelengths 300, 297, 276, and 303 nm in THF solution for **4a-d**, respectively. ^gFWHM = full width at half maximum. ^h% Percentage weight remaining at 300 °C in nitrogen.

resulting in magnesium-halogen exchange, as shown in Scheme 2.²⁰ Then $\text{Ni}(\text{dppp})\text{Cl}_2$ was added to the reaction mixture, and polymerization was allowed to proceed for 48 h.²⁶ Poly(1,1-dimethyl-3,4-diphenyl-2,5-silole) (**4a**) was obtained as a yellowish viscous liquid. Poly(1,1-disubstituted-3,4-diphenyl-2,5-silole)s **4b-d** were also prepared by GRIM polymerizations of 2,5-dibromo-1,1-diethyl-3,4-diphenylsilole (**3b**), 2,5-dibromo-1,1-diisopropyl-3,4-diphenylsilole (**3c**), and 2,5-dibromo-1,1-dihexyl-3,4-diphenylsilole (**3d**), respectively, as shown in Scheme 2.

The prepared poly(1,1-disubstituted-3,4-diphenyl-2,5-silole)s **4a-d** are brownish or yellowish powders or viscous liquids, and are soluble in common organic solvents such as CHCl_3 and THF. The observed weight-average molecular weights (M_w) of **4a-d** are in the range 658-1450, with polydispersities of 1.08-1.37, as shown in Table 1, indicating that the obtained materials **4a-d** are oligomeric. This phenomenon can be explained by the intrinsic-low reactivities of the functionalities at the 2,5-position of the silole monomers¹⁵ and severe steric congestion.²⁷

We characterized polymers **4a-d** using various spectroscopic methods. Some selected spectral properties of polymers **4a-d** are listed in Table 1. The FTIR spectra of **4a-d** show characteristic C=C stretching frequencies at 1620, 1628, 1622, and 1628 cm^{-1} , respectively, suggesting that conjugated C=C alkene double-bond are formed during copolymerizations.^{28,29} The ^{29}Si NMR spectra of polymers **4a-d** in CDCl_3 solution show major singlet resonance peaks at 11.43, 8.58, 7.03, and 6.43 ppm, respectively, indicating that the silicon atoms in the polymer main chains have the structural environments of silole groups, suggesting structures consistent with the backbone shown in Scheme 2.³⁰

Polymer Properties. We examined the absorption, excitation, and fluorescence emission spectra of polymers **4a-d** in THF solution. A typical absorption spectrum of polymer **4a** in THF is shown in Figure 1 as a dashed line. The maximum absorption band for **4a** is observed at 293 nm, and the band extends from 244 to 460 nm with a molar absorptivity of $5.95 \times 10^3 \text{ cm}^{-1}\text{M}^{-1}$. The absorption spectra of **4b-d** reveal strong absorption peaks at λ_{max} values ranging from 273 to 283 nm. These strong absorption bands in the UV-vis

spectra of **4a-d** are attributed to chromophores such as phenyl and diene groups along the polymer backbone.³ A comparison of maximum the absorption bands of polymers **4a-d** with those of the monomers **3a-d** in THF solution shows a red shift of 18-34 nm, probably because of strong intermolecular interactions through the polymer backbone.

The excitation spectrum for **4a** at a detection wavelength of 380 nm shows a strong excitation peak at $\lambda_{\text{ex, max}} = 300$ nm (Table 1). A typical excitation spectrum of polymer **4a** in THF solution is shown in Figure 1 as a dotted line. The excitation spectra of **4b-d** at the detection wavelengths of 350, 440, and 393 nm, respectively, exhibit strong excitation peaks at $\lambda_{\text{ex, max}}$ values of 297, 276, and 303 nm, respectively (Table 1). These strong excitation bands in the excitation spectra of polymers **4a-d** are attributed to the phenyl and diene groups along the polymer backbone.³

The fluorescence emission spectrum of **4a** at an excitation wavelength of 300 nm in THF solution has a strong emission peak at $\lambda_{\text{em, max}} = 380$ nm (Table 1). A typical fluorescence spectrum of polymer **4a** in THF solution is shown in Figure 1 as a solid line. The fluorescence spectra of **4b-d** at excitation wavelengths of 297, 276, and 303 nm, respectively, show strong emission peaks at $\lambda_{\text{em, max}}$ values of 350, 440,

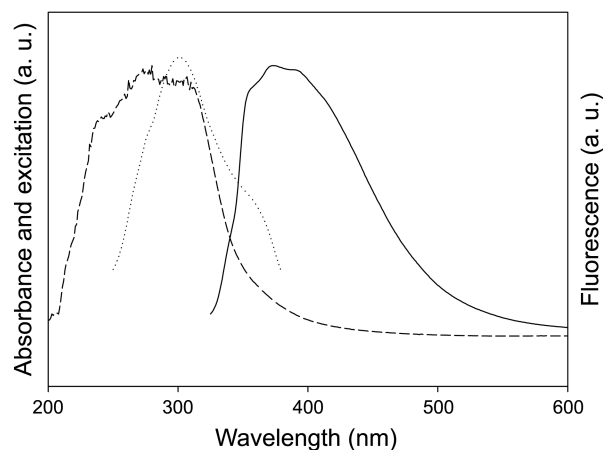


Figure 1. Absorbance (dashed line, $\lambda_{\text{max}} = 293$ nm), excitation (dotted line, $\lambda_{\text{det}} = 380$ nm), and fluorescence emission (solid line, $\lambda_{\text{ex}} = 300$ nm) spectra of polymer **4a** in THF solution.

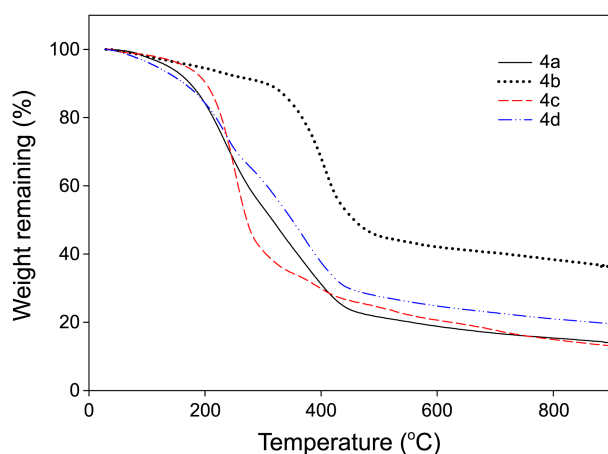


Figure 2. TGA thermograms of polymers **4a-d** in nitrogen.

and 393 nm, respectively (Table 1). These strong emission bands in the fluorescence spectra of the polymers are ascribed to fluorophores such as phenyl and diene groups along the polymer backbone.³ As shown in Table 1, fluorescence emission FWHM (full width at half maximum) values of **4a-d** are observed at 105, 104, 94, and 106 nm, respectively. The excitation and fluorescence emission spectra of the polymers imply that poly(3,4-diphenyl-2,5-silole)s **4a-d** have chromophores containing phenyl and diene groups along the polymer main chains.³ An ultrafast time-resolved kinetic study is needed for further study of the electronic conjugation properties of the prepared polymeric materials as well as the substituent's effects in the 3,4-diphenylsilole derivatives.

The thermal stabilities of poly(1,1-disubstituted-3,4-diphenyl-2,5-silole)s **4a-d** in a nitrogen atmosphere were examined using TGA, with a heating rate of 10 °C/min; the results are shown in Figure 2. Polymers **4a-d** were stable up to 200 °C, with only 6-16% loss of the initial weights in nitrogen. Polymers **4a-d** rapidly lost weight on heating above 200 °C. Rapid weight losses of 53-70% of the initial weights occurred between 200 and 600 °C. Additionally, weight losses of 4-8% of the initial weights occurred between 600 and 900 °C. When **4a-d** were heated to 900 °C, the polymers lost 64-88% of their initial weights, and char yields of about 12-36% were observed.

The prepared polymers **4a-d** were stable up to 200 °C, with weight losses of only 6-16% of the initial weight in nitrogen, and about 19-42% of the initial polymer weights remained at 600 °C in nitrogen, as shown in Figure 2 and Table 1.

Conclusion

We successfully prepared poly(1,1-dimethyl-3,4-diphenyl-2,5-silole) (**4a**), poly(1,1-diethyl-3,4-diphenyl-2,5-silole) (**4b**), poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole) (**4c**), and poly(1,1-dihexyl-3,4-diphenyl-2,5-silole) (**4d**) by GRIM polymerizations of 1,1-dimethyl-2,5-dibromo-3,4-diphenylsilole (**3a**), 1,1-diethyl-2,5-dibromo-3,4-diphenylsilole (**3b**),

1,1-diisopropyl-2,5-dibromo-3,4-diphenylsilole (**3c**), and 1,1-dihexyl-2,5-dibromo-3,4-diphenylsilole (**3d**), respectively. The prepared materials are soluble in common organic solvents such as CHCl_3 and THF. The polymers were characterized in solution, using various spectroscopic methods. The FTIR spectra of all the polymeric materials show characteristic C=C stretching frequencies at 1620-1628 cm^{-1} . In THF solution, the materials have strong maximum absorption bands at 273-293 nm, with red shifts of 18-34 nm relative to those of the monomers, strong maximum excitation peaks at 276-303 nm, and strong maximum fluorescence emission bands at 350-440 nm. All the absorption, excitation, and emission spectra suggest that the obtained poly(1,1-disubstituted-3,4-diphenyl-2,5-silole)s contain chromophores such as phenyl and diene groups in the polymer main chains. TGA shows that most of these polymers are stable up to 200 °C with weight losses of 6-16% in nitrogen.

Experimental Section

General Procedures. All chemicals were purchased from Aldrich Chemicals Inc. All glassware was assembled and then flame-dried while being swept with argon. All solvents were purified prior to use, using the standard literature methods; THF was distilled from sodium benzophenone ketyl before use.³¹ ^1H and ^{13}C NMR spectra were obtained using a Varian Mercury Plus 300 or a Bruker DRX Avance 400 MHz FT-NMR spectrometers, with CDCl_3 as the solvent. ^{29}Si NMR spectroscopy was performed using a Varian Unity INOVA 500 MHz FT-NMR spectrometer at the Daegu Center of the Korea Basic Science Institute using CDCl_3 as the solvent. Chemical shifts were measured using tetramethylsilane as an internal standard or the residual proton signal of the solvent as the standard. IR spectra were recorded using a Shimadzu IR 430 or Bruker IFS-48 FT-IR spectrometer. Gel permeation chromatography (GPC) was performed at 40 °C, using a Waters 1525 pump and Breeze software system, with a Waters Styragel HR 3 column and refractive index detector. The eluent was THF at a flow rate of 1.0 mL/min. Calibration was performed using a series of monodispersed polystyrene standards: M_p 580, 3250, 10100, and 28500 whose M_w/M_n were less than 1.2. UV-vis absorption spectra were obtained using a Hewlett Packard 8453 spectrophotometer. Excitation and fluorescence emission spectra were obtained using a Spex Fluorolog-3-11 fluorescence spectrophotometer. TGA of polymer samples was performed using a TGA-50 Shimadzu thermal analysis system. The temperature was increased at a heating rate of 10 °C/min from room temperature to 900 °C, with a nitrogen flow rate of 20 mL/min.

Dimethylbis(phenylethynyl)silane (2a**)⁶.** A three-necked flask equipped with a thermometer, rubber septa, and magnetic stirring bar was charged with phenylacetylene (25.5 mL, 232 mmol) and THF (180 mL). The solution was cooled to -70 °C in a dry ice/acetone bath. *n*-Butyllithium (2.5 M, 78.6 mL, 197 mmol) was added to the stirred solution,

using a syringe, under a stream of argon. The acetone/dry ice bath was replaced with an ice/water bath. When the reaction temperature reached approximately $-5\text{ }^{\circ}\text{C}$, dichlorodimethylsilane (**1a**; 11.2 mL, 92.8 mmol) was added dropwise using a syringe. The solution was allowed to warm to room temperature, with stirring. The reaction mixture was poured into aqueous ammonium chloride solution (200 mL). The organic phase was separated using a separating funnel and the aqueous layer was extracted with diethyl ether. The combined organic layer was washed with water and brine, dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporation under vacuum. The yellow-white solid was dissolved in boiling hexane, and then cooled in a freezer. White needles of product **2a** (21.4 g, 89%) were obtained by vacuum filtration. ^1H NMR (300 MHz, CDCl_3) δ 0.51 (s, 6H), 7.31-7.35 (m, 6H), 7.52-7.55 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 0.71, 90.85, 106.14, 122.90, 128.43, 129.07, 132.35. ^{29}Si NMR (99.36 MHz, CDCl_3) δ -39.80.

Diethylbis(phenylethynyl)silane (2b) was prepared, using the same procedure as for **2a** from dichlorodiethylsilane (**1b**). The solvent and unreacted materials were removed by rotary evaporation under vacuum. A yellow liquid **2b** was obtained quantitatively. ^1H NMR (300 MHz, CDCl_3) δ 0.91 (q, $J = 8$ Hz, 18 Hz, 4H), 1.21 (t, $J = 8$ Hz, 6H), 7.31-7.36 (m, 6H), 7.53-7.57 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 6.78, 7.52, 89.03, 106.89, 122.95, 128.37, 128.97, 132.33. ^{29}Si NMR (99.36 MHz, CDCl_3) δ -30.70.

Diisopropylbis(phenylethynyl)silane (2c) was prepared, using the same procedure as for **2a** from dichlorodiisopropylsilane (**1c**). A reddish-yellow liquid **2c** was obtained quantitatively. ^1H NMR (300 MHz, CDCl_3) δ 1.22-1.25 (m, 14H), 7.33-7.36 (m, 6H), 7.53-7.57 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 12.75, 17.95, 87.83, 107.35, 123.08, 128.39, 128.95, 132.39. ^{29}Si NMR (99.36 MHz, CDCl_3) δ -23.13.

Dihexylbis(phenylethynyl)silane (2d) was prepared, using the same procedure as for **2a** from dichlorodihexylsilane (**1d**). A scarlet liquid **2d** was obtained quantitatively. ^1H NMR (300 MHz, CDCl_3) δ 0.84-1.62 (m, 26H), 7.28-7.33 (m, 6H), 7.48-7.52 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 14.34, 15.06, 22.81, 23.90, 31.73, 32.92, 89.71, 106.81, 123.10, 128.37, 128.47, 132.33. ^{29}Si NMR (99.36 MHz, CDCl_3) δ -34.69.

2,5-Dibromo-1,1-dimethyl-3,4-diphenylsilole (3a)⁶. A three-necked flask equipped with a thermometer, rubber septa, and magnetic stirring bar was charged with lithium (0.53 g, 75.6 mmol), naphthalene (10.12 g, 79.0 mmol) and THF (50 mL) under a stream of argon. The reaction mixture was stirred at room temperature for 3 h to dissolve the lithium. A solution of **2a** (4.37 g, 16.8 mmol) in THF (120 mL) was added dropwise, through a cannula, to the lithium naphthalenide over 20 min. Once the addition was complete, the solution was cooled to $-10\text{ }^{\circ}\text{C}$ using an acetone bath with a small amount of dry ice. A solution of anhydrous ZnCl_2 (11.45 g, 84.0 mmol) in THF (70 mL) was added to the naphthalenide/silane mixture, through a cannula, over 20 min. The acetone/dry ice bath was removed and the resulting

solution was allowed to warm to room temperature. A three-necked, foil-wrapped, round-bottomed flask equipped with a thermometer, stirring bar, and rubber septa was charged with NBS (7.45 g, 41.9 mmol) and THF under an argon atmosphere. The resulting solution was cooled to $-70\text{ }^{\circ}\text{C}$ using a dry ice/acetone bath. The room-temperature silane solution was added to the cold NBS solution through a cannula, ensuring that the internal temperature did not exceed $-50\text{ }^{\circ}\text{C}$. After the addition was complete, the resulting mixture was stirred for a further 30 min at $-70\text{ }^{\circ}\text{C}$. The reaction mixture was poured into aqueous ammonium chloride solution (200 mL). The organic phase was separated using a separating funnel and the aqueous layer was extracted with diethyl ether. The combined organic layer was washed with aqueous sodium thiosulfate solution, water, and brine, dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporation. The crude naphthalene-silole mixture was sublimed under vacuum at $35\text{ }^{\circ}\text{C}$. The residual material from the sublimation was dissolved in hot hexane, followed by cooling in a freezer. Colorless needles of **3a** (3.2 g, 44%) were obtained by vacuum filtration. ^1H NMR (300 MHz, CDCl_3) δ 0.47 (s, 6H), 6.94-6.99 (m, 4H), 7.14-7.18 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ -6.05, 122.98, 127.66, 127.74, 129.24, 137.17, 156.21. ^{29}Si NMR (99.36 MHz, CDCl_3) δ 4.96. UV-vis (THF) λ_{max} , nm (ϵ , $\text{cm}^{-1}\text{M}^{-1}$): 275 (8.50×10^3).

2,5-Dibromo-1,1-diethyl-3,4-diphenylsilole (3b) was prepared, using the same procedure as for **3a**, from **2b**. A pale yellowish crystalline product **3b** (4.2 g, 55%) was obtained. ^1H NMR (300 MHz, CDCl_3) δ 1.03 (q, $J = 7.5$ Hz, 10.8 Hz, 4H), 1.15 (t, $J = 6.9$ Hz, 6H), 6.94-6.98 (m, 4H), 7.14-7.18 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 1.74, 6.75, 121.06, 127.62, 127.76, 129.22, 137.36, 157.54. ^{29}Si NMR (99.36 MHz, CDCl_3) δ 8.54. UV-vis (THF) λ_{max} , nm (ϵ , $\text{cm}^{-1}\text{M}^{-1}$): 260 (1.19×10^4).

2,5-Dibromo-1,1-diisopropyl-3,4-diphenylsilole (3c) was prepared, using the same procedure as for **3a**, from **2c**. A pale brownish crystalline product **3c** (2.4 g, 30%) was obtained. ^1H NMR (300 MHz, CDCl_3) δ 1.27 (d, $J = 6.9$ Hz, 12H), 1.46-1.58 (m, 2H), 6.92-6.96 (m, 4H), 7.14-7.27 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 10.05, 17.41, 120.03, 127.57, 127.78, 129.19, 137.55, 158.14. ^{29}Si NMR (99.36 MHz, CDCl_3) δ 7.46. UV-vis (THF) λ_{max} , nm (ϵ , $\text{cm}^{-1}\text{M}^{-1}$): 253 (1.21×10^4).

2,5-Dibromo-1,1-dihexyl-3,4-diphenylsilole (3d) was prepared, using the same procedure as for **3a**, from **2d**. A pale brownish powder product **3d** (4.0 g, 43%) was obtained. ^1H NMR (300 MHz, CDCl_3) δ 0.89-1.54 (m, 26H), 6.93-6.97 (m, 4H), 7.14-7.18 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 9.96, 14.36, 22.81, 23.11, 31.66, 32.91, 122.11, 127.59, 127.76, 129.19, 137.46, 157.08. ^{29}Si NMR (99.36 MHz, CDCl_3) δ 6.18. UV-vis (THF) λ_{max} , nm (ϵ , $\text{cm}^{-1}\text{M}^{-1}$): 243 (1.28×10^4).

Poly(1,1-dimethyl-3,4-diphenyl-2,5-silole) (4a) Preparation Using *i*-PrMgCl·LiCl.

Preparation of *i*-PrMgCl·LiCl.²⁰ A three-necked flask was charged with *i*-PrMgCl in THF (2 M, 1.8 mL, 3.6 mmol)

and anhydrous THF (5 mL). LiCl (0.15 g, 3.6 mmol) was added to the flask under nitrogen. The reaction mixture was stirred for 8 h at room temperature.

Poly(1,1-dimethyl-3,4-diphenyl-2,5-silole) (4a). A solution of **3a** (1.50 g, 3.59 mmol) in anhydrous THF (5 mL) was added under nitrogen to the previously prepared solution of *i*-PrMgCl-LiCl (3.59 mmol). The reaction mixture was stirred at room temperature for 17 h. Ni(dppp)Cl₂ (0.020 g, 0.036 mmol) dissolved in anhydrous THF (10 mL) was added to the reaction mixture. The polymerization was allowed to proceed for 48 h at room temperature, followed by quenching of the reaction mixture with methanol. The precipitated polymer was separated and dried under reduced pressure. A viscous yellowish liquid, **4a** (0.79 g, 85%), was obtained. ¹H NMR (300 MHz, CDCl₃) δ 0.11-0.47 (br s, 6 H), 7.08-7.54 (br m, 10 H). ¹³C NMR (75 MHz, CDCl₃) δ -1.49 (br s), 120.87, 126.02-131.20 (br m), 139.04, 151.65. ²⁹Si NMR (99.36 MHz, CDCl₃) δ 11.43. IR (KBr disk) $\tilde{\nu}_{\max}$ 3068, 3025, 2956 (ν_{C-H}), 1755, 1689, 1620 (ν_{C=C}), 1593, 1446, 1256 (ν_{Si-C}), 1072, 1029, 810, 761, 698 cm⁻¹. UV-vis (THF) λ_{max}, nm (ε, cm⁻¹ M⁻¹): 293 (5.95 × 10³). GPC (THF) *M*_w = 784, *M*_n = 573, polydispersity index (PDI) = 1.37.

Poly(1,1-diethyl-3,4-diphenyl-2,5-silole) (4b) was prepared, using the same procedure as for **4a**, from **3b** (2.00 g, 4.20 mmol) and Ni(dppp)Cl₂ (0.018 g, 0.034 mmol) for 4 d. A reddish-yellow powder **4b** (0.59 g, 46%) was obtained. ¹H NMR (300 MHz, CDCl₃) δ 0.74-1.06 (br m, 10 H), 6.92-7.24 (br m, 10 H). ¹³C NMR (75 MHz, CDCl₃) δ 0.80, 5.63, 120.88, 124.38-129.75 (br m), 143.75, 158.50. ²⁹Si NMR (99.36 MHz, CDCl₃) δ 8.58. IR (KBr disk) $\tilde{\nu}_{\max}$: 3054, 2956, 2927, 2870 (ν_{C-H}), 1628 (ν_{C=C}), 1459, 1439, 1072, 1022, 768, 698, 549 cm⁻¹. UV-vis (THF) λ_{max}, nm (ε, cm⁻¹ M⁻¹): 283 (4.10 × 10³). GPC (THF) *M*_w = 1450, *M*_n = 1064, PDI = 1.36.

Poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole) (4c) was prepared, using the same procedure as for **4a**, from **3c** (2.00 g, 4.20 mmol) and Ni(dppp)Cl₂ (0.018 g, 0.034 mmol) for 5 d. A pale yellow powder **4c** (0.54 g, 41%) was obtained. ¹H NMR (300 MHz, CDCl₃) δ 1.12-1.53 (m, 14 H), 6.07 (s, 0.6H), 6.92-7.27 (m, 10H). ¹³C NMR (75 MHz, CDCl₃) δ 10.07, 10.56, 17.41, 18.01, 18.30, 120.04, 124.63-129.36 (m), 137.56-140.98 (m), 156.87-163.11 (m). ²⁹Si NMR (99.36 MHz, CDCl₃) δ 7.03. IR (KBr disk) $\tilde{\nu}_{\max}$: 3068, 2941, 2863 (ν_{C-H}), 1622 (ν_{C=C}), 1459, 1079, 698, 578 cm⁻¹. UV-vis (THF) λ_{max}, nm (ε, cm⁻¹ M⁻¹): 273 (3.08 × 10³). GPC (THF) *M*_w = 658, *M*_n = 610, PDI = 1.08.

Poly(1,1-dihexyl-3,4-diphenyl-2,5-silole) (4d) was prepared, using the same procedure as for **4a**, from **3d** (2.00 g, 4.46 mmol) and Ni(dppp)Cl₂ (0.020 g, 0.036 mmol) for 5 d. A viscous brownish liquid **4d** (0.84 g, 59%) was obtained. ¹H NMR (300 MHz, CDCl₃) δ 0.72-1.54 (br m, 26 H), 6.83-7.51 (br m, 10H). ¹³C NMR (75 MHz, CDCl₃) δ 9.96, 14.36, 15.59, 22.91-23.59 (m), 31.59-31.75 (m), 32.92-33.44 (m), 122.10, 127.25-129.21 (m), 137.48, 157.08. ²⁹Si NMR (99.36 MHz, CDCl₃) δ 6.43. IR (KBr disk) $\tilde{\nu}_{\max}$: 3062, 2956, 2927, 2856 (ν_{C-H}), 1628 (ν_{C=C}), 1446, 1199, 1092, 768, 691 cm⁻¹. UV-vis (THF) λ_{max}, nm (ε, cm⁻¹ M⁻¹): 277 (6.44 × 10³). GPC

(THF) *M*_w = 993, *M*_n = 922, PDI = 1.09.

The excitation and fluorescence emission spectra in THF solution and TGA thermograms for polymers **4a-d** are described in the Results and Discussion.

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Supporting Information. The NMR, IR, and electronic spectroscopic data for compounds **2a-d**, **3a-d**, and **4a-d** are available on request from the corresponding author.

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