Articles

Highly Efficient Hydrosilylation of Diyne and Triyne π-Electron Bridges: Its Application to Fluorescent Dyes and Silylene-Spaced Vinylarene Compounds

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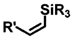
A variety of diyne and triyne π-electron bridges were hydrosilylated to afford the bis- and tris(silylvinyl) π-electron bridges. The hydrosilylation products underwent substitution reactions with a variety of compounds containing chromophore units to give fluorescent dye substituted products. The easy access of the silyl hydrides may be applied to construct a large number of copolymers.

Introduction

The introduction of a flexible bridge such as $SiMe_2$ between well-defined chromophores in a mononuclear compound[1] or in a polymer chain[2] has received much attention because it facilitates the intramolecular photoinduced charge transfer process.[3] Moreover, conjugated polymers containing silylene and π-electron moieties are attractive because such polymers afford processable electroluminescent materials and the silicon-based spacers interrupt the π-conjugated chains, resulting in unusual optical properties.[4] Color-tunable luminescence can be achieved by varying the HOMO−LUMO gap of the polymer. The HOMO−LUMO gap can be adjusted by modification of the conjugation length in the polymer or by the proper choice of chromophores.[5] For the control of the conjugation length, it is desirable to isolate conjugated π-electron moieties in the polymer. The incorporation of silicon units into polymer backbones meets this requirement.

Recently, Luh et al.[6] reported silylene-spaced divinylarene copolymers synthesized by hydrosilylation of bisalkynes with bisvinylsilanes. However, the bisvinylsilane was prepared via a four-step process. For easy access to a variety of bisvinylsilanes, the general synthetic development for bis- or trisvinylsilyl chromophores such as **4** and **5** would be highly desirable.



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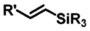

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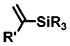

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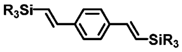

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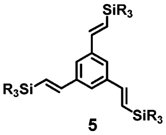

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Hydrosilylation provides a useful entry to the synthesis of σ,π-conjugated silicon compounds.[7] Although there has been significant progress using a variety of metal-catalyzed reactions to provide 1,2- or 1,1-substituted vinylsilanes of the type **1**, **2**, or **3**,[8] there has been reported only a limited general access to the bis(silylvinyl) π-electron bridge (**4**)[6] and very little is known about tris(silylvinyl)benzene (**5**). In this paper, we report the first hydrosilylation of diyne and triyne π-electron bridges, which is catalyzed by the Karstedt catalyst.[9]

Results and Discussion

Many metal complexes were found to be efficient catalysts for the hydrosilylation of diyne and triyne π-electron bridges (Table 1). Among the platinum catalysts tested, the Karstedt catalyst exhibited the

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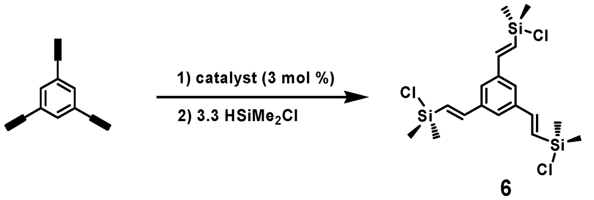
Table 1. Catalyzed Hydrosilylation of 1,3,5-Triethynylbenzene and Catalyst Screening[a]



6

catalyst	solvent	temperature	yield (%)[b]
Pt/C	toluene	reflux	88
	THF	reflux	0
H_2PtCl_6	toluene	rt	90
	ether	rt	88
	THF	rt	82
Karstedt	THF	rt	35
	ether	rt	96
	toluene	rt	76
$Rh(PPh_3)_3Cl$	THF	reflux	46
	toluene	reflux	37
	ether	reflux	0
$[Rh(cod)(PPh_3)_2]PF_6$	THF	reflux	38

[a] To a solution of catalyst (3 mol %) and 1,3,5-triethynylbenzene (0.8 mmol) was added $HSiMe_2Cl$ (2.64 mmol). The mixture was then stirred at rt or reflux for 12 h. [b] Isolated yields.

highest activity, completing the hydrosilylation under mild condition. Other platinum catalysts also gave **6** in good yield. The selection of solvent is crucial for achieving a high yield of product **6**. For example, no hydrosilylation was observed with the Pt/C catalyst in THF. For the Karstedt catalyst, diethyl ether appears to be the best among the solvents tried, giving product **6** in quantitative yield. Rhodium-based catalysts also were effective, but led to lower yields. The hydrosilylation product was readily isolable by extraction with hexane, but the hydrolytic lability of the Si−Cl bond hampered its isolation using chromatography on silica gel.

A variety of diyne π-electron bridges proved amenable to the hydrosilylation (Table 2). Considering the ease of handling, good yields, and good reactivities, the Karstedt catalyst became our catalyst of choice. The data for the hydrosilylation in Table 2 were obtained using the Karstedt catalyst under the optimum reaction conditions. The Pt-catalyzed hydrosilylation of 1,4-diethynylbenzene afforded the bis(silylvinyl)benzene **7** in high yield. Although it has been well documented that the hydrosilylation of terminal alkynes affords dramatic differences in product distribution depending on the nature of the catalyst and substrates,[10] interestingly enough, the diyne was completely converted to the *trans* product with no detectable formation of any isomers. However, the *trans* addition product has been observed for some metal catalysts[11] or strong Lewis acids[12] with terminal alkynes to afford a 1,2-disubstituted vinylsilane (**2**). The complete selectivity exhibited under our reaction conditions is significant. The *trans* configuration was readily assigned by the characteristic large coupling constant of the concomitant vinyl group (J_{ab} = 18.6−19.2 Hz). Hydrosilylation of the 2,2′-diethoxy-6,6′-diethynyl-1,1′-binaphthalene proceeded at a rate similar to that of the bis(silylvinyl)benzene, affording bis(silylvinyl)binaphthalene (entry 7).

The stereoselective hydrosilylation protocol has many potential applications in the synthesis of bichromophoric molecules. Addition of bis(silylvinyl)benzene **7** to 1-pyrenyllithium in 1:2 ratio provides the dipyrenyl-substituted silyl compound **13**. Under similar conditions, treatment of **7** with 1-lithio-3,5-di(*N*-7-azaindolyl)benzene (which is prepared from the reaction of *n*-BuLi and 1-bromo-3,5-di(*N*-7-azaindolyl)benzene) in 1:2 ratio afforded bis[3,5-di(*N*-7-azaindolyl)phenyl]-substituted silyl compound **14** (Scheme 1). Even though the synthetic scheme is completely different, bis(silylvinyl)benzene has been prepared by the reaction of a styryllithium intermediate and chlorotrimethylsilane by Son et al.[13] The ^{1}H NMR spectrum of **13** showed a low-field resonance at 7.43 ppm due to the core aromatic proton. Characteristic signals at 7.08 and 6.90 ppm (doublet) with a large coupling constant (J = 19.2 Hz) of **13** clearly show the formation of *E*-alkenylsilane. The ^{29}Si NMR spectrum of **13** showed one resonance at −16.3 ppm arising from the equivalent silicon atoms. The structures of **13** and **14** (Figures 1 and 2, respectively) were unequivocally determined by their X-ray crystallographic analyses. Crystallographic data and processing parameters are given in Table 3. The compounds **13** and **14** have an inversion center of symmetry, and the two pyrene groups and bis[3,5-di(*N*-7-azaindolyl)phenyl] groups are oriented opposite each other. Two silicon atoms are coplanar with the 1,4-divinylbenzene unit. The vinylic C═C bond length (1.3279(19) Å) in **13** is comparable to the typical value for the carbon−carbon double bond (1.317 Å).[14] The Si(1)−C(19) bond length (1.8619(14) Å) is slightly shorter than the Si(1)−C(1) bond length (1.8847(14) Å), indicative of a slight delocalization of π-electrons through the organosilicon units by σ−π conjugation. The bond angles and distances for **13** and **14** are comparable to those found in 1,3-di(1-pyrenyl)hexamethyltrisilane[15] and 1,3-di(*N*-7-azaindolyl)benzene.[16]

Other synthetic utilities of the hydrosilylation products were demonstrated by transformations of the representative product **6** (Scheme 2). Treatment of **6** with 9-lithio-10-(dimesitylboryl)anthracene afforded the trianthryl-substituted silyl compound **15**, which was stable enough to be isolated by silica gel chromatography. Two anthryl chromophores[15] bridged by a silane have already been reported. The amorphous 5-lithio-2-{4-[bis(9,9-dimethylfluoren-2-yl)amino]phenyl}-thiophene underwent a substitution reaction with **6** to give **16** possessing a highly steric bulk. Two new fluorophores have been fully characterized by NMR and elemental analysis data. The photophysical data of the new series of fluorophores are shown in Table 4. Figure

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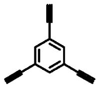
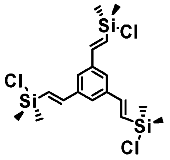
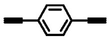
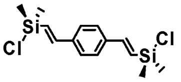
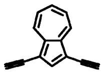
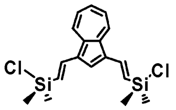
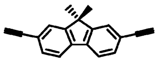
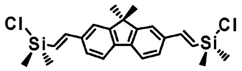
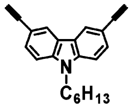
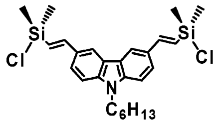
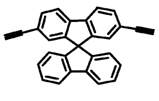
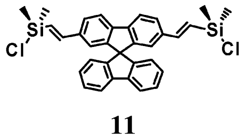
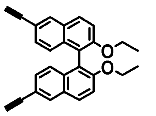
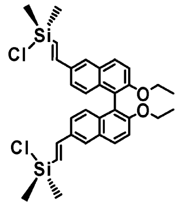
Table 2. Hydrosilylation of Diynes and Triyne Catalyzed by Karstedt Catalyst

entry	alkyne	product	solvent (°C, hr, yield)[a]
1		 **6**	ether (rt, 6 h, 96%)
2		 **7**	THF (reflux, 8 h, 95%)
3		 **8**	ether (rt, 12 h, 88%)
4		 **9**	ether (rt, 12 h, 92%)
5		 **10**	ether (rt, 12 h, 90%)
6		 **11**	ether (rt, 12 h, 84%)
7		 **12**	ether (rt, 12 h, 86%)

[a] °C = reaction temperature; hr = reaction time; yield = isolated yield.

3 shows the UV–visible absorption and photoluminescence spectra of **15** and **16**. We observe that all fluorophores display intense absorptions in the near UV–visible violet region. The trianthryl-substituted silyl compound **15** has absorption bands at 344 and 420 nm attributed to the π–π* transitions of the anthryl moiety and, in addition, an intense band at 254 nm attributed to the 1,3,5-trivinylbenzene moiety (**17**).[17] The UV–visible absorption spectrum of **17** was known to have an absorption maximum at 248 nm.[17] The wavelength of the maximum absorption (λ_{max}) of **16** has a strong absorption band at 373 nm, which is attributed to the π–π* transition of the 2-{4-[bis(9,9-dimethylfluoren-2-yl)amino]phenyl}thiophene segment. Upon an excitation wavelength of 362 nm, both spectra give a peak in the PL spectra at 464 and 457 nm, respectively. The PL spectrum of 1,3,5-trivinylbenzene differs significantly from that of **15**. The maxima of the fluorescence of **15** and **16** with respect to **17** suggest that the fluorescence of both compounds is not due to the isolated 1,3,5-trivinylbenzene unit, but to substituted chromophores. These results also indicate that the π-conjugated system

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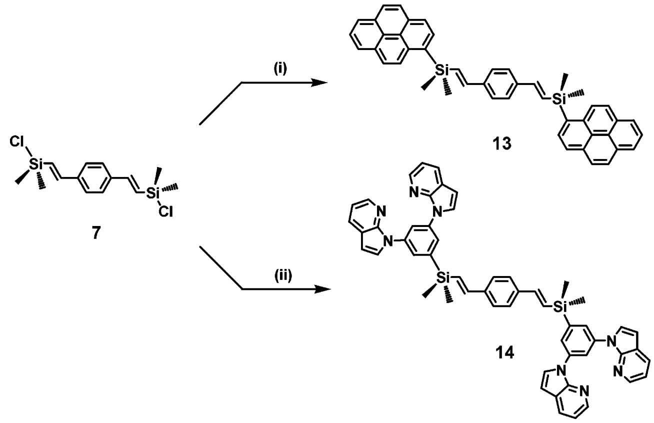
Scheme 1[a]



[a] Reaction conditions: (i) 2 equiv of 1-pyrenyllithium in THF, rt, 8 h, 55%; (ii) 2 equiv of 1-lithio-3,5-di(*N*-7-azaindolyl)-benzene in THF, rt, 8 h, 50%.

was effectively interrupted by the silicon moieties. The PL quantum yield for the compounds is relatively low. This is probably because their relatively small band gap between the ground state and the lowest excited state allows more routes of nonirradiative decay.

Preliminary results with bis(silylvinyl)benzene in silylene-spaced divinylarene copolymers[6] encouraged us to explore such bis- or trissilyl hydrides in a variety of polymer syntheses. Indeed, trissilyl hydride **18** was readily prepared by the reduction of **6** with $LiAlH_4$ in good yield. Interestingly, the rhodium-catalyzed hydrosilylation of **18** with 4-ethynylbenzonitrile afforded the conjugated vinyl product **19** linked by $SiMe_2$ (Scheme 3).

We extended this methodology to the reaction of 2,2′-diethoxy-6,6′-bis(silylvinyl)-1,1′-binaphthalene to obtain polymer precursor. As expected, the reaction of **12** with $LiAlH_4$ proceeded smoothly to afford bissilyl compound **20** via simple two-step reactions (Scheme 4). Recently, Luh et al.[6] prepared bis(silylvinyl)aromatic compounds by the reaction of dithioacetals with Grignard reagents via a four-step procedure. The rhodium-catalyzed hydrosilylation of **20** with 2,2′-diethoxy-6,6′-diethynyl-1,1′-binaphthalene yielded polymer **21** in 80% yield. The molecular weight (M_w) and the polydispersity of the polymer, determined by gel-permeation chromatography

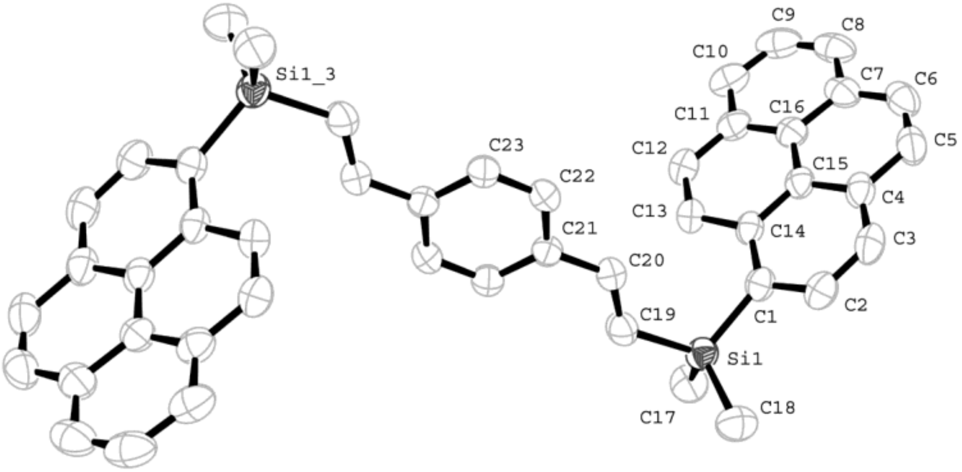


Figure 1. X-ray crystal structure of **13** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): C(20)−C(21) = 1.4754(18), Si(1)−C(1) = 1.8847(14), C(19)−C(20) = 1.3279(19), Si(1)−C(17) = 1.8676(16), Si(1)−C(19) = 1.8619(14), Si(1)−C(18) = 1.8703(17), C(19)−Si(1)−C(1) = 110.43(6), Si(1)−C(19)−C(20) = 125.14(11), C(19)−C(20)−C(21) = 127.27(13), C(20)−C(21)−C(22) = 119.86(12).

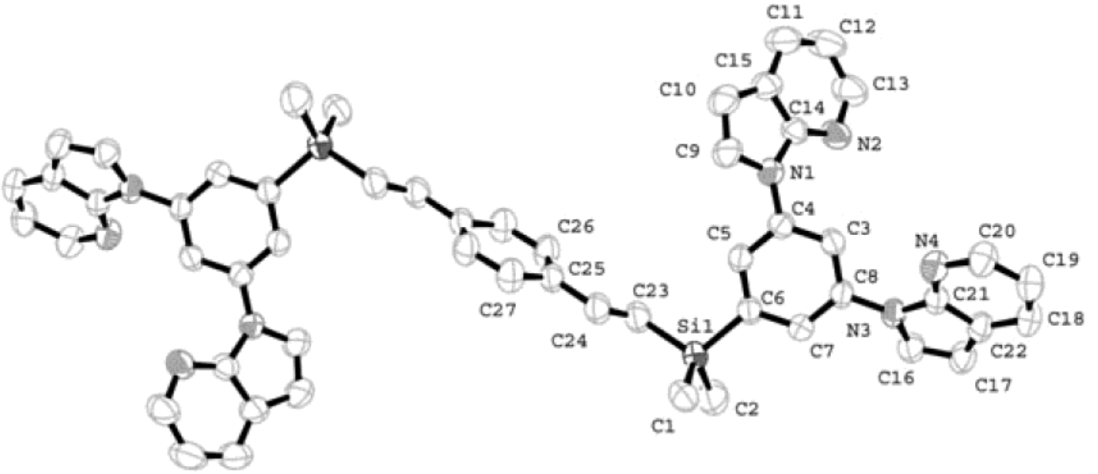
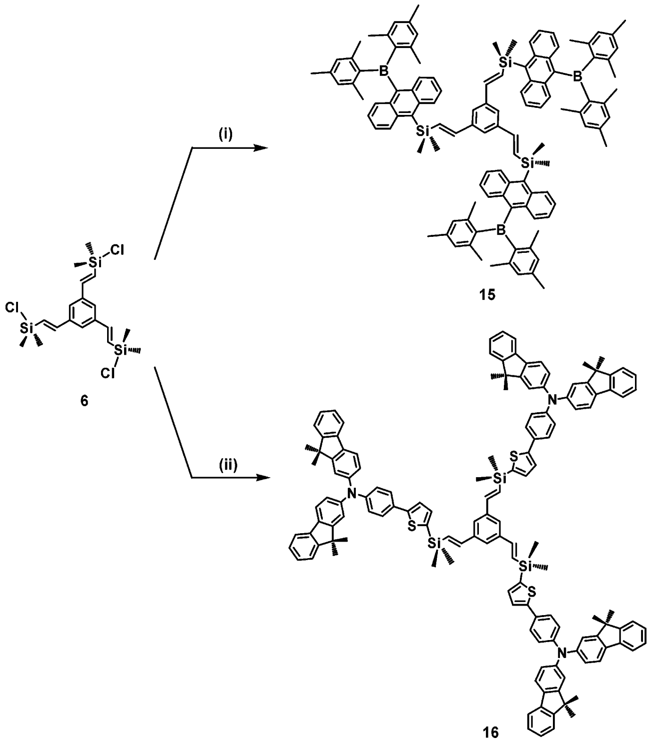


Figure 2. X-ray crystal structure of **14** with 50% probability thermal ellipsoids depicted. Selected bond lengths (Å) and angles (deg): C(24)−C(25) = 1.483(3), C(23)−C(24) = 1.329(3), Si(1)−C(23) = 1.868(2), Si(1)−C(6) = 1.887(19), Si(1)−C(1) = 1.872(2), C(4)−N(1) = 1.426(2), C(23)−C(24)−C(25) = 128.2(2), C(24)−C(23)−Si(1) = 125.50(18), C(6)−Si(1)−C(23) = 107.66(9), C(5)−C(4)−N(1) = 119.39(16).

Table 3. Crystal Data and Structure Refinement for 13 and 14

	13	**14**
empirical formula	$C_{46}H_{38}Si_2$	$C_{54}H_{46}N_8Si_2$
fw	646.94	863.17
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	8.9340(9)	9.0316(11)
b (Å)	18.4841(18)	11.7209(15)
c (Å)	10.5116(10)	12.7278(16)
α (deg)		92.261(2)
β (deg)	92.124(2)	109.800(2)
γ (deg)		109.826(2)
V, Å^3	1734.7(3)	1174.3(3)
Z	2	1
D_{calcd} (g cm^{-3})	1.239	1.221
F(000)	684	454
μ (mm^{-1})	0.135	0.121
no. of reflns collected	10 776	7076
no. of unique reflns	4148	5108
R (int)	0.0167	0.0153
no. of params	293	381
R1, wR2 ($I > 2.0\sigma(I)$)	0.0404, 0.1045	0.0498, 0.1232
R1, wR2 (all data)	0.0519, 0.1144	0.0696, 0.1336
goodness of fit	1.024	1.039
largest diff peak and hole, e Å^{-3}	0.356 and −0.176	0.485 and −0.173

Scheme 2[a]



[a] Reaction conditions: (i) 3 equiv of 9-lithio-10-(dimesitylboryl)anthracene in THF; (ii) 3 equiv of 5-lithio-2-{4-[bis(9,9-dimethylfluoren-2-yl)amino]phenyl}thiophene in THF.

using polystyrene standard, was in the range 14 500−14 600 and 3.15, respectively. The polymer was soluble in common solvents such as THF, $CHCl_3$, and benzene. The ^1H NMR spectrum of **21** reveals a characteristic resonance at 6.50 ppm with a large coupling constant (J = 19.2 Hz) due to an equivalent vinylic hydrogen, while the polymer **21** shows no resonance attributed to the Si−H. The ^{29}Si NMR spectrum of the polymer reveals a single resonance at −18.8 ppm, in accord with the upfield shift for the silylenevinylene-bridged system which appears in the region from −12 to −30 ppm.[18]

Table 4. Photophysical Data for 13−16 in CH_2Cl_2 at Room Temperature[a]

	UV−vis		emission	
compound	λ_{max} (nm)	ϵ (dm^3 mol^{-1} cm^{-1})	λ_{max} (nm)	Φ_{em}[b]
13	348	6430	395	0.14
14	292	5260	367	0.08
15	254, 344, 420	18 340, 3055, 3715	464	0.18
16	262, 373	11 853, 16 640	457	0.24

[a] Concentration of compounds is in the range 10^{-4}−10^{-5} mol dm^{-3}. [b] Quinine sulfate in 1 M H_2SO_4 (Φ_{f1} = 0.55) was used as quantum yield standard.

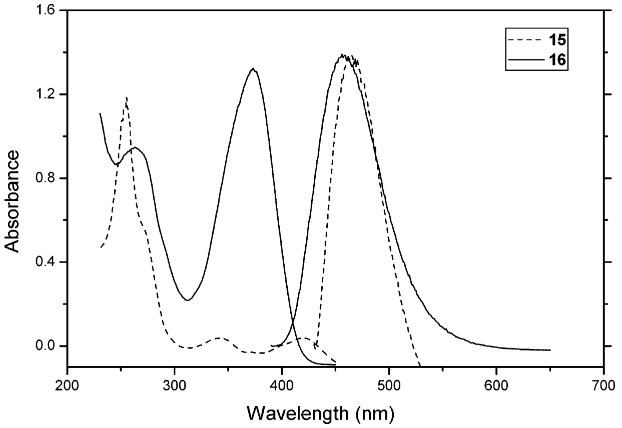


Figure 3. UV−visible spectra and PL spectra of **15** and **16** in CH_2Cl_2.

Such silylene-spaced divinylarene copolymers were recently reported by Luh,[6] Mori,[19] and Neckers.[17]

In summary, the first general hydrosilylation of a variety of diyne and triyne π-electron bridges to afford bis- and trissilylvinyl compounds with high regioselectivity is presented. The hydrosilylation product underwent a substitution reaction with a variety of chromophore units to give the bis- and tris-chromophore substituted products. The easy access of the silyl hydride opens the way to a host of potential subsequent transformations for the construction of a large number of copolymers. Additional investigations into the photophysical properties and subsequent synthetic utility of the copolymers are now being undertaken in this laboratory.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. Toluene, ether, and THF were freshly distilled from sodium benzophenone. The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.00 and 75.44 MHz, respectively. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 25 UV−visible spectrophotometer and a Perkin-Elmer LS fluorescence spectrometer, respectively. 1,4-Diethynylbenzene,[20] 1,3,5-triethynylbenzene,[21] 2,7-diethynyl-9,9-dimethylfluorene,[22] 3,6-diethynyl-9-hexylcarbazole,[23] 2,7-dibromo-9,9′-spirobifluorene,[24] 1,3-diethynylazulene,[25] 2,2′-diethoxy-

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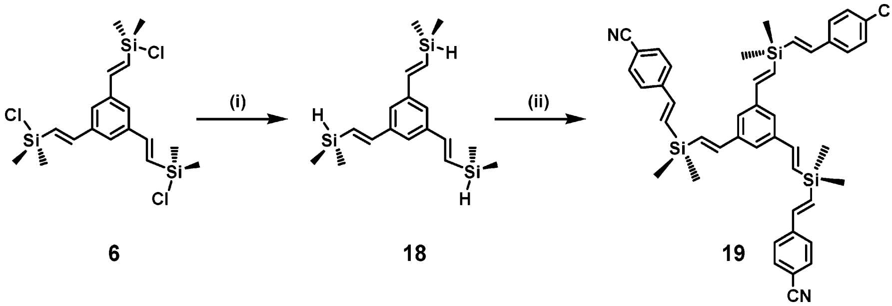
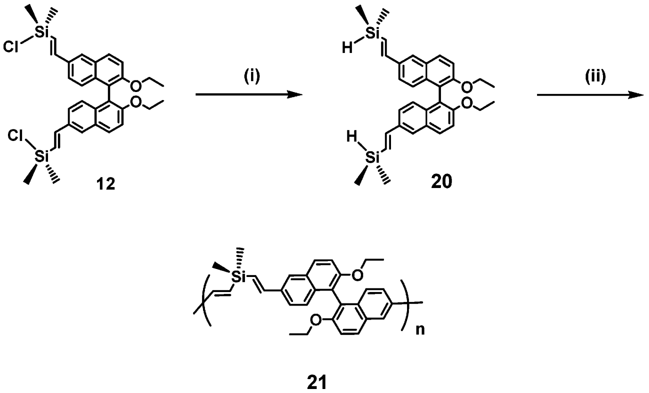
Scheme 3[a]



[a] Reaction conditions: (i) $LiAlH_4$, benzene, reflux, 12 h, 75%; (ii) 4-ethynylbenzonitrile, $RhCl(PPh_3)_3$, CH_2Cl_2, rt, 12 h, 57%.

Scheme 4[a]



[a] Reaction conditions: (i) $LiAlH_4$, benzene, reflux, 12 h, 85%; (ii) 2,2′-diethoxy-6,6′-diethynyl-1,1′-binaphthalene, $RhCl(PPh_3)_3$, NaI, THF, reflux, 6 h, 80%.

6,6′-diethynyl-1,1′-binaphthalene,[26] 4-ethynylbenzonitrile,[20] 1-bromo-3,5-di(*N*-7-azaindolyl)benzene,[27] 9-bromo-10-(dimesitylboryl)anthracene,[28] and 5-bromo-2-{4-[bis(9,9-dimethylfluorene-2-yl)amino]phenyl}thiophene[29] were prepared according to procedures reported in the literature.

General Procedure for Hydrosilylation of Diynes and Triynes. To a stirred ether solution (30 mL) of 1,3,5-triethynylbenzene (0.20 g, 1.30 mmol) was added $SiMe_2ClH$ (0.86 mL, 4.29 mmol) and 1 drop of Karstedt catalyst at room temperature. The solution was stirred for 6 h at that temperature. The solvent was removed in vacuo and extracted with hexane (20 mL). The solution was left in a refrigerator overnight to give a pale yellow product, **6**, in quantitative yield.

6. ^1H NMR ($CDCl_3$): δ 7.51 (s, 3H, Ph-*H*), 7.07 (d, 3H, J_{HH} = 18.6 Hz, Ph-C*H*=), 6.53 (d, 3H, J_{HH} = 18.6 Hz, =C*H*-Si), 0.59 (s, 18H, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.6, 138.4, 128.1, 126.3, 1.3. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 13.2. MS: *m/z* 434 [M^+]. Anal. Calcd for $C_{18}H_{27}Cl_3Si_3$: C, 49.81; H, 6.27. Found: C, 49.58; H, 6.16.

7. ^1H NMR ($CDCl_3$): δ 7.46 (s, 4H, Ph-*H*), 7.06 (d, 2H, J_{HH} = 18.9 Hz, Ph-C*H*=), 6.48 (d, 2H, J_{HH} = 18.9 Hz, =C*H*-Si), 0.59 (s, 12H, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.2, 137.9, 126.4, 125.5, 1.2. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 12.5. MS: *m/z* 314 [M^+]. Anal. Calcd for $C_{14}H_{20}Cl_2Si_2$: C, 53.32; H, 6.39. Found: C, 53.16; H, 6.25.

8. ^1H NMR ($CDCl_3$): δ 8.52 (s, 1H, Ph-*H*), 8.44 (d, 2H, *J* = 9.3 Hz), 7.60 (t, 1H, *J* = 8.4 Hz), 7.20 (dd, 2H, *J* = 9.3 Hz, *J* = 8.4 Hz), 6.98 (d, 2H, J_{HH} = 19.2 Hz, Ph-C*H*=), 6.54 (d, 2H, J_{HH} = 19.2 Hz, =C*H*-Si), 0.64 (s, 12H, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.9, 137.7, 137.4, 134.2, 133.9, 127.6, 123.5, 122.4, 1.6. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 14.1. MS: *m/z* 365 [M^+]. Anal. Calcd for $C_{18}H_{22}Cl_2Si_2$: C, 59.16; H, 6.07. Found: C, 58.95; H, 5.96.

9. ^1H NMR ($CDCl_3$): δ 7.70 (d, 2H, *J* = 7.8 Hz), 7.60 (s, 2H, Ph-*H*), 7.48 (d, 2H, *J* = 7.8 Hz), 7.20 (d, 2H, J_{HH} = 19.2 Hz, Ph-C*H*=), 6.56 (d, 2H, J_{HH} = 19.2 Hz, =C*H*-Si), 1.55 (s, 6H), 0.65 (s, 12H, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.6, 139.7, 136.8, 126.9, 126.4, 124.7, 121.1, 120.7, 46.9, 27.2, 1.4. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 11.8. MS: *m/z* 431 [M^+]. Anal. Calcd for $C_{23}H_{28}Cl_2Si_2$: C, 64.01; H, 6.54. Found: C, 63.78; H, 6.36.

10. ^1H NMR ($CDCl_3$): δ 8.24 (s, 2H, Ph-*H*), 7.64 (d, 2H, *J* = 8.4 Hz), 7.35 (d, 2H, *J* = 8.4 Hz), 7.32 (d, 2H, J_{HH} = 18.9 Hz, Ph-C*H*=), 6.53 (d, 2H, J_{HH} = 18.9 Hz, =C*H*-Si), 4.25 (t, 2H, *J* = 6.6 Hz), 1.49−0.85 (m, 11H), 0.69 (s, 12H, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.8, 137.2, 136.1, 128.3, 127.2, 125.8, 123.9, 122.2, 55.3, 34.6, 33.0, 27.6, 25.4, 13.2, 1.6. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 15.6. MS: *m/z* 488 [M^+]. Anal. Calcd for $C_{26}H_{35}Cl_2NSi_2$: C, 63.91; H, 7.22. Found: C, 63.68; H, 7.01.

11. ^1H NMR ($CDCl_3$): δ 7.95 (d, 2H, *J* = 7.8 Hz), 7.87 (d, 2H, *J* = 8.1 Hz), 7.55 (d, 2H, *J* = 7.2 Hz), 7.44 (t, 2H, *J* = 7.5 Hz), 7.18 (t, 2H, *J* = 7.5 Hz), 6.97 (d, 2H, J_{HH} = 19.2 Hz, Ph-C*H*=), 6.86 (d, 2H, *J* = 7.5 Hz), 6.80 (d, 2H, *J* = 7.2 Hz), 6.33 (d, 2H, J_{HH} = 19.2 Hz, =C*H*-Si), 0.53 (s, 12H, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.9, 148.3, 147.0, 142.1, 141.8, 128.7, 128.3, 127.9, 127.3, 127.0, 124.9, 123.9, 121.9, 120.3, 65.8, 2.1. MS: *m/z* 553 [M^+]. Anal. Calcd for $C_{33}H_{30}Cl_2Si_2$: C, 71.59; H, 5.46. Found: C, 71.38; H, 5.26.

12. ^1H NMR ($CDCl_3$): δ 7.93 (d, 2H, J_{HH} = 9.0 Hz), 7.86 (s, 2H), 7.42 (d, 2H, J_{HH} = 9.0 Hz), 7.40 (s, 2H), 7.20 (d, 2H, J_{HH} = 19.2 Hz, Ph-C*H*=), 7.10 (d, 2H, J_{HH} = 9.0 Hz), 6.45 (d, 2H, J_{HH} = 19.2 Hz, =C*H*-Si), 4.05 (m, 4H, OCH_2), 1.07 (t, 6H, *J* = 6.9 Hz, OCH_2CH_3), 0.59 (s, 12H, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.1, 134.6, 132.6, 129.9, 129.2, 128.0, 126.7, 125.5, 124.5, 120.5, 116.4, 115.8, 65.2, 15.1, 2.3. MS: *m/z* 578 [M^+]. Anal. Calcd for $C_{32}H_{36}Cl_2O_2Si_2$: C, 66.30; H, 6.26. Found: C, 65.98; H, 6.07.

1,4-Bis[(pyrenyldimethylsilyl)vinyl]benzene (13). To a stirred THF solution (20 mL) of 1-bromopyrene (commercially available, 0.42 g, 1.5 mmol) was added *n*-BuLi (1.6 M in hexane, 1.0 mL, 1.65 mmol) at −78 °C. The solution was warmed to room temperature and stirred for 1 h at that temperature. The solution was again chilled to −78 °C, and then **7** (0.21 g, 0.68 mmol) dissolved in THF (10 mL) was added dropwise. The solution was slowly warmed to room

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temperature and stirred for 8 h. H_2O and brine were added to the solution, and the product was extracted with CH_2Cl_2 (20 mL). The pure product **13** was isolated by chromatography (eluent: EA/hexane, 1:15 ($R_f = 0.4$)) in 55% yield. Mp: 215 °C. ^1H NMR ($CDCl_3$): δ 8.47 (d, 2H, $J = 7.8$ Hz), 8.29 (d, 2H, $J = 7.8$ Hz), 8.21−7.98 (m, 14H), 7.43 (s, 4H, Ph-*H*), 7.08 (d, 2H, $J_{HH} = 19.2$ Hz, Ph-C*H*═), 6.90 (d, 2H, $J_{HH} = 19.2$ Hz, ═C*H*-Si), 0.77 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.5, 139.0, 136.0, 133.4, 133.0, 132.4, 131.3, 130.7, 128.1, 127.9, 127.7, 127.5, 127.2, 125.8, 125.4, 124.9, 124.7, 124.4, 124.1, −0.6. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −16.3. MS: *m/z* 646 [M$^+$]. Anal. Calcd for $C_{46}H_{38}Si_2$: C, 85.40; H, 5.92. Found: C, 85.26; H, 5.72.

1,4-Bis{[3,5-di(*N*-7-azaindolyl)phenyldimethylsilyl]vinyl}benzene (14). Compound **14** was prepared using the same procedure as that described for **13** except 1-bromo-3,5-di(*N*-7-azaindolyl)benzene was used instead of 1-bromopyrene. Pure **14** was isolated by chromatographic workup (eluent: EA/hexane, 1:3 ($R_f = 0.35$)) in 50% yield. Mp: 288 °C. ^1H NMR ($CDCl_3$): δ 8.37 (dd, 4H, $J = 7.8$ Hz, $J = 5.8$ Hz), 8.32 (dd, 4H, $J = 3.6$ Hz, $J = 1.5$ Hz), 7.94 (dd, 4H, $J = 5.8$ Hz, $J = 1.5$ Hz), 7.83 (s, 2H, Ph-*H*), 7.59 (d, 4H, $J = 3.6$ Hz), 7.54 (s, 4H, Ph-*H*), 7.10 (d, 4H, $J = 7.8$ Hz), 7.07 (d, 2H, $J_{HH} = 19.2$ Hz, Ph-C*H*═), 6.70 (d, 2H, $J_{HH} = 19.2$ Hz, ═C*H*-Si), 6.62 (d, 4H, $J = 3.6$ Hz), 0.53 (s, 12H, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.7, 143.7, 141.6, 138.9, 138.7, 129.1, 128.1, 127.1, 124.9, 121.6, 121.1, 117.4, 116.2, 102.6, 101.1, −2.4. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −11.2. MS: *m/z* 862 [M$^+$]. Anal. Calcd for $C_{54}H_{46}N_8Si_2$: C, 75.14; H, 5.37. Found: C, 74.95; H, 5.18.

1,3,5-Tris[(10-dimesitylboryl-9-anthryldimethylsilyl)vinyl]benzene (15). To a stirred THF solution (20 mL) of 9-bromo-10-(dimesitylboryl)anthracene (0.76 g, 1.5 mmol) was added *n*-BuLi (1.6 M in hexane, 1.0 mL, 1.65 mmol) at −78 °C. The solution was warmed to room temperature and stirred for 1 h at that temperature. The solution was again chilled to −78 °C, and then **6** (0.2 g, 0.45 mmol) dissolved in THF (10 mL) was added dropwise. The solution was slowly warmed to room temperature and stirred overnight. H_2O and brine were added to the solution, and the product was extracted with CH_2Cl_2 (20 mL). Pure product **15** was obtained by chromatography (eluent: EA/hexane, 1:20 ($R_f = 0.5$)) in 51% yield. Mp: 283 °C. ^1H NMR ($CDCl_3$): δ 8.45 (d, 6H, $J = 9.2$ Hz, anthryl-*H*), 8.08 (d, 6H, $J = 9.0$ Hz, anthryl-*H*), 7.50 (s, 3H, Ph-*H*), 7.29 (dd, 6H, $J = 9.2$ Hz, $J = 5.4$ Hz, anthryl-*H*), 7.13 (dd, 6H, $J = 9.0$ Hz, $J = 5.4$ Hz, anthryl-*H*), 7.09 (d, 3H, $J_{HH} = 19.2$ Hz, Ph-C*H*═), 6.74 (br s, 12H, mesityl-*H*), 6.70 (d, 3H, $J_{HH} = 19.2$ Hz, ═C*H*-Si), 2.26 (s, 18H, mesityl-CH_3), 1.86 (br s, 36H, mesityl-CH_3), 0.79 (s, 18H, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.4, 145.7, 140.9, 139.8, 139.1, 138.4, 136.9, 134.1, 133.5, 131.3, 130.3, 129.3, 128.5, 128.2, 125.8, 124.9, 123.8, 122.9, 22.7, 20.8, 2.6. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −8.5. Anal. Calcd for $C_{114}H_{117}B_3Si_3$: C, 85.37; H, 7.35. Found: C, 85.02; H, 7.22.

1,3,5-Tris{2-[4-(bis(9,9-dimethylfluoren-2-yl)amino)phenylthiophenyldimethylsilyl]vinyl}benzene (16). Compound **16** was prepared using the same procedure as that described for **15** except 2-{4-[bis(9,9-dimethylfluoren-2-yl)amino]phenyl}thiophene was used instead of 9-bromo-10-(dimesitylboryl)anthracene. Pure **16** was isolated by chromatography (eluent: EA/hexane, 1:15 ($R_f = 0.45$)) in 48% yield. Mp: 266 °C. ^1H NMR ($CDCl_3$): δ 7.70−7.06 (m, 63H, aromatic and vinyl-*H*), 7.01 (d, 3H, $J_{HH} = 19.2$ Hz, Ph-C*H*═), 6.64 (d, 3H, $J_{HH} = 19.2$ Hz, ═C*H*-Si), 1.40 (s, 36H, fluoren-CH_3), 0.50 (s, 18H, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.2, 153.7, 152.6, 150.3, 148.2, 147.6, 147.2, 144.6, 142.8, 139.1, 138.7, 137.0, 135.4, 134.4, 128.7, 127.2, 126.8, 124.0, 122.9, 122.9, 122.3, 120.6, 119.7, 119.4, 118.5, 47.0, 8.1, 0.11. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −20.1. Anal. Calcd for $C_{138}H_{123}N_3S_3Si_3$: C, 82.71; H, 6.19. Found: C, 82.42; H, 6.01.

1,3,5-Tris[(dimethylsilyl)vinyl]benzene (18). To a benzene solution (30 mL) of **6** (0.43 g, 1 mmol) was added $LiAlH_4$ (0.22 g, 6 mmol). The solution was refluxed for 12 h. To that solution was slowly added water (10 mL) to give a white precipitate. After filtration, a benzene solution was obtained by decantation and added $MgSO_4$. Pure **17** was obtained by chromatographic workup (eluent: hexane ($R_f = 0.7$)) as a colorless oil in 75% yield. ^1H NMR ($CDCl_3$): δ 7.42 (s, 3H, Ph-*H*), 6.97 (d, 3H, $J_{HH} = 18.9$ Hz, Ph-C*H*═), 6.51 (dd, 3H, $J_{HH} = 18.9$ Hz, $J = 3.0$ Hz, ═C*H*-Si), 4.21 (m, 3H, Si-*H*), 0.24 (d, 18H, $J = 3.9$ Hz, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.9, 138.8, 125.5, 124.1, −4.3. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −26.6. MS: *m/z* 330 [M$^+$]. Anal. Calcd for $C_{18}H_{30}Si_3$: C, 65.38; H, 9.14. Found: C, 65.04; H, 9.02.

1,3,5-Tris{[(4-benzonitrile)vinyldimethylsilyl]vinyl}benzene (19). To a stirred CH_2Cl_2 solution (15 mL) of **17** (0.10 g, 0.3 mmol) and 4-ethynylbenzonitrile (0.11 g, 0.9 mmol) was added $RhCl(PPh_3)_3$ (0.004 g, 0.5 mol %). The solution was stirred for 12 h at room temperature. The solution was dried in vacuo. Pure **18** was obtained by chromatographic workup (eluent: EA/hexane, 1:4) as a white solid in 57% yield. Mp: 145 °C. ^1H NMR ($CDCl_3$): δ 7.61 (d, 6H, $J = 8.10$ Hz, *Ph*-CN), 7.51 (d, 6H, $J = 8.10$ Hz, *Ph*-CN), 7.46 (s, 3H, Ph-*H*), 6.95 (d, 3H, $J_{HH} = 19.2$ Hz), 6.93 (d, 3H, $J_{HH} = 19.2$ Hz), 6.67 (d, 3H, $J_{HH} = 19.2$ Hz), 6.65 (d, 3H, $J_{HH} = 19.2$ Hz), 0.33 (s, 18H, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 218.4, 142.5, 138.8, 132.7, 132.4, 127.3, 126.8, 119.0, 111.4, −2.9. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −9.4. IR (KBr pellet, cm^{-1}): ν 2164 (C≡N). MS: *m/z* 712 [M$^+$]. Anal. Calcd for $C_{45}H_{45}N_3Si_3$: C, 75.90; H, 6.37. Found: C, 75.62; H, 6.16.

2,2′-Diethoxy-[6,6′-bis(hydridedimethylsilyl)vinyl]-1,1′-binaphthalene (20). To a benzene solution (30 mL) of **12** (0.48 g, 0.84 mmol) was added $LiAlH_4$ (0.22 g, 6 mmol). The solution was refluxed for 12 h. On cooling to room temperature, the mixture was quenched carefully with water. After the filtration, a benzene solution was obtained by decantation and added $MgSO_4$. Pure **19** was obtained by chromatographic workup (eluent: EA/hexane, 1:4 ($R_f = 0.5$)) as a pale yellow product in 85% yield. ^1H NMR ($CDCl_3$): δ 7.91 (d, 2H, $J = 9.9$ Hz), 7.80 (s, 2H), 7.39 (d, 4H, $J = 9.0$ Hz), 7.10 (d, 2H, $J_{HH} = 18.9$ Hz, Ph-C*H*═), 7.08 (d, 2H, $J = 9.0$ Hz), 6.44 (d, 2H, $J_{HH} = 18.9$ Hz, ═C*H*-Si), 4.22 (m, 2H, Si-*H*), 4.03 (m, 4H, OCH_2), 1.07 (t, 6H, $J = 6.9$ Hz, OCH$_2$CH_3), 0.27 (d, 12H, $J = 3.3$ Hz, Si-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.7, 137.8, 136.4, 134.0, 132.9, 129.4, 126.5, 125.3, 123.8, 120.7, 116.5, 115.9, 65.3, 15.1, 1.2. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −24.2. MS: *m/z* 510 (M$^+$). Anal. Calcd for $C_{32}H_{38}O_2Si_2$: C, 75.24; H, 7.50. Found: C, 74.99; H, 7.25.

2,2′-Diethoxy-6,6′-bis(dimethylsilylvinyl)-1,1′-binaphthalene polymer (21). To a mixture of **19** (0.2 g, 0.39 mmol) and 2,2′-diethoxy-6,6′-diethynyl-1,1′-binaphthalene (0.15 g, 0.39 mmol) in THF (1 mL) were added $RhCl(PPh_3)_3$ (4 μg, 0.1 mol %) and NaI (2.92 μg, 5 mol %) in THF (1 mL) in an inert atmosphere, and the reaction mixture was refluxed until its viscosity increased like a gum. The resulting mixture was dissolved in 5 mL of chloroform, and the solution was poured into a catalytic amount (100 mL) of methanol with vigorous stirring to form a precipitate. Filtration, washing with methanol, and drying under reduced pressure afforded the corresponding polymer in 80% yield. Reprecipitation was repeated several times if necessary. ^1H NMR ($CDCl_3$): δ 7.88 (br, 2H), 7.81 (br, 2H), 7.39 (br, 4H), 7.08 (br, 2H), 7.07 (br, 2H), 6.50 (d, 2H, $J_{HH} = 19.2$ Hz, ═C*H*-Si), 4.08 (m, 4H, OCH_2), 1.03 (br, 6H, OCH$_2$CH_3), 0.32 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.8, 134.2, 133.6, 129.7, 129.4, 127.2, 125.4, 123.9, 123.5, 120.7, 116.4, 115.9, 65.2, 15.4, −0.2. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −18.8. $M_w = 14\,500$, $M_w/M_n = 3.15$.

X-ray Crystallography. Suitable crystals of **13** and **14** were grown by CH_2Cl_2/hexane and EA/hexane, respectively. All X-ray data of compounds **13** and **14** were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.7173$ Å) with a Bruker AXS SMART CCD area-detector diffractometer. The orientation matrix and unit cell parameters of **13** and **14** were determined by least-squares analyses of the setting angles of 28 reflections in the ranges 2.20° $< 2\theta <$ 28.28° and 1.73° $< 2\theta <$ 28.22°, respectively. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were collected with Ψ-scan data. All calculations were carried out with the SHELXL-97 program.[30] The structure was solved by the direct method. All non-hydrogen atoms in compounds **13** and **14** were refined anisotropically. All hydrogen atoms were included in the calculated positions.

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Supporting Information Available: Tables listing crystallographic information, atomic coordinates and B_{eq} values, anisotropic thermal parameters, intramolecular bond distances and angles, and torsion angles for **13** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[30] Sheldrick, G. M. *SHELXL-97*, program for crystal structure refinement; University of Göttingen: Göttingen, Germany, 1997.