

An alternative convergent synthesis of dendrimers with 2,5-diarylsilole at the core

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Abstract

Dendrimers with 2,5-diarylsilole at the core are readily synthesized by the Ni-catalyzed reaction of 1,1,2,2-tetramethyldisilane and 1,6-diyne having poly(benzyl ether)-dendron units. The dendrimers display, upon excitation of the silole ring, an emission at about 500 nm. The fluorescence quantum yield of the dendrimers increases with increasing the generation of the dendron units. In addition, upon excitation of dendron units in the periphery, the dendrimers also display an emission from the silole ring at the core through the energy transfer from the dendron units to the silole core within the dendrimers.

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1. Introduction

Siloles, silacyclopentadienes, have attracted great interest over the past decade because of their unique photophysical and electronic properties [1] and potential applications as organic electroluminescent devices (OLEDs) [2] and organic field-effect transistors (OFETs) [3]. The silole has a relatively low LUMO energy level due to the $\sigma^*-\pi^*$ conjugation in comparison with a carbon analogue, cyclopentadiene. Recently, several reports have addressed synthesis of siloles with a variety of substituent groups [4] and silole-based polymers [5]. In view of the improvement of the photophysical properties, it is interesting to note that the aggregation leads to efficient enhancement of the emission of a simple tetraphenylsilole [6,7]. The structural tuning of siloles were also described [8,9].

Recently, we have demonstrated a facile one-pot synthesis and photophysical properties of silole-core dendrimers [10]. Dendrimers are a class of highly ordered, three-dimen-

sional, and tree-like macromolecules and potential building blocks for the construction of functional materials [11]. Our synthetic strategy for the silole-core dendrimers was based on the nickel-catalyzed reaction of 1,1,2,2-tetramethyldisilane with disubstituted acetylenes [12] which proved to work well for dendritic acetylenes affording the dendrimers with a tetraarylsilole at the core. As compared with the conventional convergent synthesis involving installation of the core in the final step, the foregoing reaction exemplifies a promising synthetic methodology for dendrimers in one step process, during which the core is constructed by the reaction of starting materials having dendron units. Recently, alternative accelerated synthetic approaches have been reported [13]. Further, we have found that the silole incorporated at the core acts as a functional conjugated unit and the dendritic framework provides a light-harvesting antenna, an energy transfer interaction, and a site-isolation framework for chromophores placed at the core of the dendrimer system.

We have explored synthetically practical structural modifications of siloles to be incorporated in dendritic frameworks. We report herein a facile one-pot synthesis and photophysical properties of dendrimers based on 2,5-diar-

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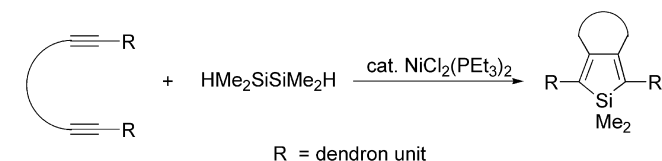
ylsilole at the core. In view of the steric demand of the substituents bound to the silole core, 2,5-diarylsiloles, as compared with tetraarylsiloles, is likely to have a better conjugation between their peripheries and the silole framework, resulting in an improvement of the photophysical properties such as an intense photoluminescence [14].

2. Results and discussion

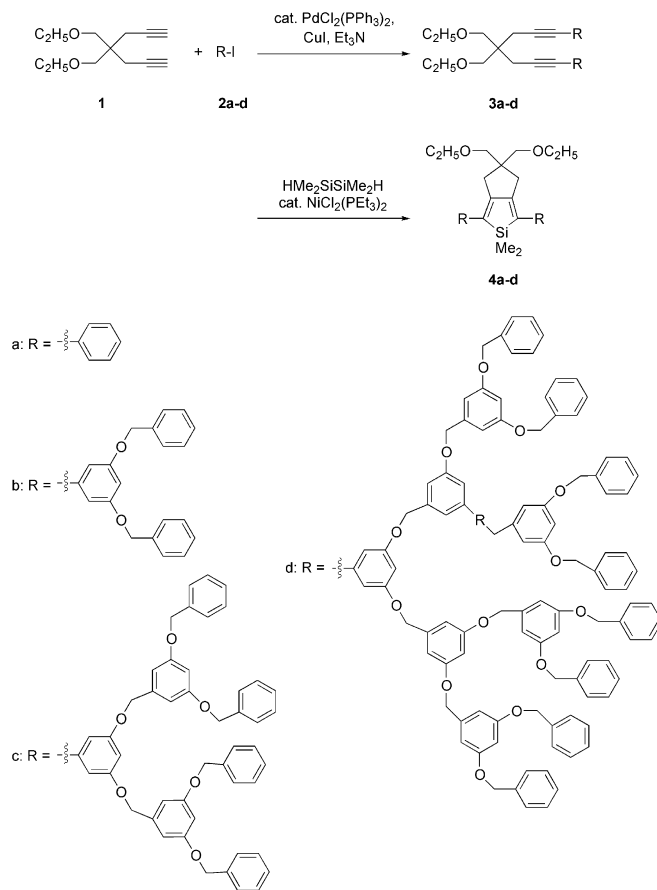
The synthetic strategy for silole-core dendrimers is based on the nickel-catalyzed reaction of 1,1,2,2-tetramethyldisilane with disubstituted alkynes [12], which worked well with dendritic acetylenes [10]. In this study, we applied the Ni-catalyzed reaction to intramolecular cyclization [15] of dendritic 1,6-diyne with the 1,2-dihydrodisilane (Scheme 1).

1,6-Diynes with poly(benzyl ether)-dendrons **3b–d** were prepared by the convergent method, as shown in Scheme 2. Benzyl ether-type dendritic iodides **2b–d** were obtained according to the previously reported procedures [16]. The reaction of 4,4-bis(ethoxymethyl)-1,6-heptadiyne **1** (1 equiv.) with **2b–d** (2 equiv.) in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$, CuI, and triethylamine in THF proceeded smoothly to give 1,6-diynes with poly(benzyl ether) dendrons **3b–d** in good yields even for the higher generation substrates (70%, 68%, and 69%, respectively). The ^1H and ^{13}C NMR spectra of **3b–d** showed the high molecular symmetry in these products and conformed to the structures. Next, dendritic 1,6-diynes **3b–d** were treated with 1,1,2,2-tetramethyldisilane in the presence of catalytic amounts of $\text{NiCl}_2(\text{PEt}_3)_2$ in refluxing toluene. As the generation grows, the time required to complete the reaction increased and the reaction became less clean resulting in lower yields, especially for **4d**. The silole forming reaction, however, proceeded satisfactorily and silole-core dendrimers **4b–d** could be readily purified by column chromatography. Thus, the yield of the higher generation dendrimer **4d** was 28%, even after prolonged heating (58 h) using an increased amount of the catalyst (10 mol%), while the parent silole **4a** was obtained in 46% yield (18 h). This suggests steric crowding around the core hinders the reaction for higher generation materials.

Silole-core dendrimers **4b–d** were fully characterized using a variety of spectroscopic techniques. The ^1H and ^{13}C NMR spectra displayed the signals of methyl on the silole ring at the core along with those of the benzyl ether units [17]. In the ^{29}Si NMR spectra, the signal assigned to Si–Me on the silole ring core was observed at about 15 ppm for these dendrimers. The elemental analyses were



Scheme 1.



Scheme 2.

also satisfactory. All these spectral observations support the structure of the silole-core dendrimers.

The photophysical properties of silole-dendrimers **4b–d** are of interest. The photophysical data in dichloromethane solution, along with those of the parent compound **4a**, are summarized in Table 1 and the absorption and fluorescence spectra of **4a–d** are shown in Fig. 1. In the absorption spectra, silole-core dendrimers **4b–d** displayed two absorption bands at about 280 and 360 nm, assignable to the benzyl ether-type dendrons and the focal silole ring, respectively. The intensity of the absorption of the dendron units increased with increasing the generation of the dendrons, while the intensity and the position of the absorption of the silole ring did not change significantly. When the silole ring was excited at 360 nm, **4b–d** displayed an emission at about 500 nm. The excitation spectra, monitored at 500 nm, reproduced the absorption spectra almost perfectly for **4b–d**.

As expected, the fluorescence quantum yield (Φ_{FL}) increased with increasing the generation of the dendron units, as shown in Table 1. The Φ_{FL} of **4d** was 0.19, while that of the model compound **4a** was 7.0×10^{-3} , suggesting that the dendron units prevent vibrational–rotational events in the excited state to minimize the quenching processes for the silole ring effectively. Further, the Φ_{FL} of **4b–d** is higher than that previously observed for corre-

Table 1
Photophysical properties of silole-core dendrimers **4a–d**

Compound	In solution ^a					Film ^b	
	Absorption		Fluorescence			Absorption λ_{max} (nm)	Fluorescence λ_{FLmax} (nm) ^g
	λ_{max} (nm)	ϵ ($10^4 \text{ cm}^{-1} \text{ M}^{-1}$)	λ_{FLmax} (nm) ^c	$\Phi_{\text{FL}}^{\text{d,e}}$	Φ_{ET} (%) ^f		
4a	250, 365	1.24, 1.86	476	7.0×10^{-3}	– ^h	359	477
4b	283, 372	0.56, 1.27	478	6.9×10^{-2}	52	394	477
4c	278, 366	2.75, 1.31	477	0.11	49	394	477
4d	283, 369	6.57, 1.33	477	0.19	43	401	477

^a In CH_2Cl_2 .

^b A cast film from a toluene solution on a quartz plate.

^c Excited at ca. 370 nm.

^d Determined with quinine sulfate as a standard.

^e Fluorescence quantum yield, when excited at the core silole rings.

^f Energy transfer efficiency from the dendron units to the core silole within the dendrimers, when excited at the dendron units (280 nm).

^g Excited at ca. 390 nm.

^h Not estimated.

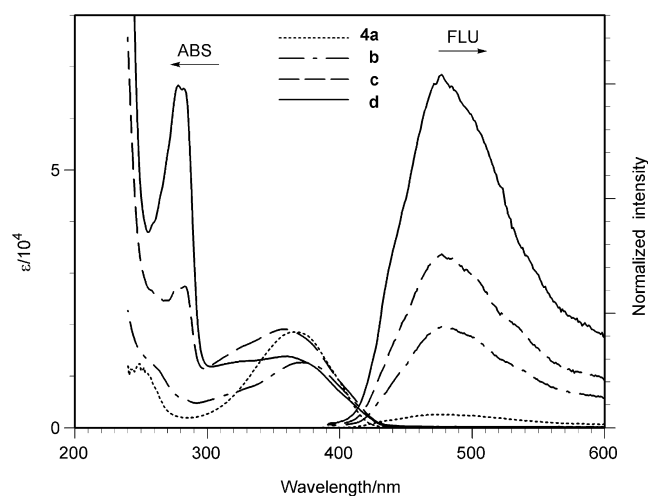


Fig. 1. Absorption and fluorescence (excited at 370 nm) spectra of **4a–d** in CH_2Cl_2 . Intensities of the fluorescence were normalized in the molar concentration.

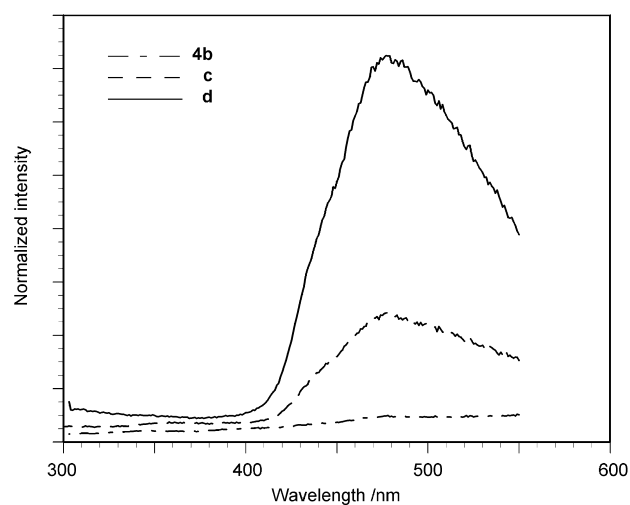


Fig. 2. Fluorescence spectra of **4b–d** in CH_2Cl_2 excited at 280 nm. Intensities of the fluorescence were normalized in the molar concentration.

sponding tetraaryl-type silole dendrimers [10]. In addition, the Φ_{FL} of the dendrimers **4b–d** is dependent on solvent. For example, the Φ_{FL} of **4c** in dichloromethane was 0.11, but much higher in cyclohexane (0.46), where the position of absorption and emission did not change. This is due presumably to the shrinkage of the benzyl ether-type dendron around the silole core in cyclohexane [18].

When excited the benzyl ether-type dendron units at 280 nm, the dendrimers also displayed an emission at around 500 nm from the silole ring unit, but no emission from the benzyl ether-type dendron units (310 nm) was observed, as shown in Fig. 2. This clearly indicates that the energy transfer (ET) from the dendron units to the focal silole ring occurred within the dendrimers. The ET efficiency (Φ_{ET}), estimated by a comparison of the absorption spectrum and the excitation spectrum of the silole-core dendrimer by monitoring the emission of the acceptor, i.e., the silole, is also listed in Table 1. The Φ_{ET} was near 50% for **4b–d**. In principle, the Förster-type ET is favored by:

(a) a large spectral overlap between donor emission and acceptor absorption, (b) a high molar absorption coefficient of the acceptor, (c) a high fluorescence quantum yield of the acceptor, and (d) a short interchromophoric distance [19]. The ET efficiency in the present system, however, was not very high, probably because all of the requirements for the efficient Förster-type ET were not necessarily the case. In addition, the dendrimers did not show clear “antenna effect” [20], i.e., the emission intensities observed upon excitation of the dendron units were almost the same as those observed when the focal silole ring was excited. This is because of the low ET efficiencies for the dendrimers.

The solid-state behavior will more likely perform the feasibility of deploying these compounds in electronic devices. Their conformal films on quartz substrate were obtained by casting a toluene solution of the dendrimers. The photophysical data in the solid state are summarized in Table 1. The absorptions were red-shifted to about 390 nm in the solid state relative to the solution absorption spectra. In the emission spectra, the film of the dendrimers

revealed near the same trends in the position of emission as those observed in solution and the intense blue light emission was observed from the thin film of each dendrimer.

3. Conclusion

We have synthesized silole-core dendrimers **4b–d** by the nickel-catalyzed reaction of tetramethyldisilane and dendritic 1,6-diynes having poly(benzyl ether) units through the third generation. This synthetic procedure demonstrates the alternative convergent approach via one-pot synthesis of the core for the construction of precise macromolecular structure. The photophysical properties of the dendrimers are also discussed. In the absorption spectra, **4b–d** have two absorption bands at about 280 and 360 nm, assignable to the benzyl ether-type dendrons and the focal silole ring, respectively. When the silole ring was excited at 360 nm, the silole dendrimers displayed an emission at about 500 nm. The fluorescence quantum yield increased with increasing the generation of the dendron units. In addition, when the benzyl ether-type dendron units were excited at 280 nm, the dendrimers also displayed an emission around 500 nm from the silole ring unit through the energy transfer within the dendrimers. Further, the conformal films of **4b–d** on quartz substrate were obtained by casting a toluene solution of the dendrimers and the film of the dendrimers revealed near the same trends in the absorption and emission as observed in solution. The findings herein reported would be important in view of optoelectronic applications. Further study along the line is currently in progress.

4. Experimental

4.1. Measurements

The data of ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded using a Bruker DPX 300 FT NMR spectrometer at 300, 75.4, and 59.6 MHz, respectively. The ^1H and ^{13}C chemical shifts were referenced to solvent residues (^1H , $\delta = 7.24$ ppm; ^{13}C , $\delta = 77.0$ ppm for CDCl_3). The ^{29}Si chemical shift was referenced to external Me_4Si (0 ppm). The IR spectra were recorded using a HORIBA FT/IR 730 spectrometer. GC–MS was run using a Shimadzu GC–MS 17A/QP-5000 mass spectrometer. The high resolution mass spectra were obtained with JEOL JMS-700 mass spectrometer at an ionization potential of 70 eV. The melting points were measured using a Micro melting point apparatus IA9100 (As One Ltd.).

4.2. Materials

All solvents and reagents were of reagent quality, purchased from commercial sources and used without further purification, unless otherwise noted below. Toluene and THF were dried and distilled from sodium/benzophenone just before use. Triethylamine was distilled from calcium

hydride. Acetone was distilled from CaSO_4 . 4,4-Bis(hydroxymethyl)-1,6-heptadiyne [21] and poly(benzyl ether) dendritic phenyl iodides **2b–d** [22] were prepared according to the previously reported procedures, respectively.

4.3. Synthesis of 4,4-bis(ethoxymethyl)-1,6-heptadiyne (**1**)

A mixture of 4,4-bis(hydroxymethyl)-1,6-heptadiyne (7.9 g, 52 mmol), ethyl bromide (14.3 g, 130 mmol), and KOH (11.7 g, 210 mmol) in DMSO (200 mL) was stirred at room temperature for 24 h. The mixture was, after addition of water, extracted with ether. The combined organic layer was washed successively with water, saturated NH_4Cl solution, and saturated NaCl solution, dried over anhydrous MgSO_4 and was evaporated. The residue was distilled to give **1** (30 mmol, 57% yield) as pale yellow oil.

Compound 1. bp 48.8–49.2 °C/0.1 mm Hg; ^1H NMR (CDCl_3 , 300 MHz) δ 1.14 (t, $J = 7.2$ Hz, 6H, CH_2CH_3), 1.95 (t, $J = 2.6$ Hz, 2H, HCC), 2.33 (d, $J = 2.6$ Hz, 4H, CCH_2C), 3.37 (s, 4H, CCH_2O), 3.45 (q, $J = 7.2$ Hz, 4H, CH_2CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 15.0 (CH_2CH_3), 21.8 (HCC CH_2), 41.5 ($(\text{CH}_2)_2\text{C}(\text{CH}_2)_2$), 66.7 (OCH_2CH_3), 70.2 (HCC), 70.9 (CCH_2O), 80.9 (HCC); IR (neat) 3296 (s, $\text{HC}\equiv\text{C}$), 2975 (s), 2869 (s), 2117(m), 1428 (m), 1276 (m), 1114 (s, C–O–C), 1029 (m), 893 (s), 636 (s, $\text{HC}\equiv\text{C}$); HRMS calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_2$ [M^+]: 208.1463, found: 208.1463. Anal. Calc. for $\text{C}_{13}\text{H}_{20}\text{O}_2$: C, 74.96; H, 9.68. Found: C, 74.81; H, 9.29%.

4.4. General procedure for synthesis of poly(benzyl ether) dendritic acetylenes (**3a–d**)

A mixture of an appropriate dendritic phenyl iodide **2a–d** (2 equiv.), 4,4-bis(ethoxymethyl)-1,6-heptadiyne (1 equiv.), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.005 equiv.), CuI (0.004 equiv.), and triethylamine (12 mL) in THF was stirred at room temperature for 15–66 h. The residue was chromatographed over silica gel to give the corresponding poly(benzyl ether) dendritic acetylene **3a–d**.

Compound 3a. This was prepared by the reaction of **1** and **2a** and purified from silica gel column chromatography with toluene. Yield: 85%; pale yellow oil; ^1H NMR (acetone- d_6 , 300 MHz) δ 1.20 (t, $J = 7.2$ Hz, 6H, CH_2CH_3), 2.68 (s, 4H, CCH_2C), 3.53 (q, $J = 7.2$ Hz, 4H, CH_2CH_3), 3.56 (s, 4H, CCH_2O), 7.30–7.37 (m, 6H, 2,3,4-*ArH*), 7.43–7.48 (m, 4H, 1,5-*ArH*); $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6 , 75 MHz) δ 15.5 (CH_2CH_3), 23.6 (CCH_2C), 43.2 ($(\text{CH}_2)_2\text{C}(\text{CH}_2)_2$), 67.2 (OCH_2CH_3), 72.0 (CCH_2O), 83.3 (ArCC), 87.4 (ArCC), 124.6 (1,5-*Ar*), 128.4, 129.0 (2,3,4-*Ar*), 132.1 (1,5-*Ar*); HRMS calcd. for $\text{C}_{25}\text{H}_{28}\text{O}_2$ [M^+]: 360.2089, found: 360.2094. Anal. Calc. for $\text{C}_{25}\text{H}_{28}\text{O}_2$: C, 83.29; H, 7.83. Found: C, 82.95; H, 8.01%.

Compound 3b. This was prepared by the reaction of **1** and **2b** and purified from silica gel column chromatography with hexane/ CH_2Cl_2 (1/2). Yield: 70%; a pale yellow waxy solid: m.p. 64.2–65.1 °C; ^1H NMR (CDCl_3 , 300 MHz) δ

1.20 (t, $J = 7.2$ Hz, 6H, CH_2CH_3), 2.62 (s, 4H, CCH_2C), 3.50 (s, 4H, CCH_2O), 3.53 (q, $J = 7.2$ Hz, 4H, CCH_2O), 5.00 (s, 8H, ArCH_2O), 6.57 (t, $J = 2.3$ Hz, 2H, ArH), 6.68 (d, $J = 2.3$ Hz, 4H, ArH), 7.30–7.47 (m, 20H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 15.2 (CH_2CH_3), 23.1 (CCH_2C), 42.7 ($(\text{CH}_2)_2\text{C}(\text{CH}_2)_2$), 66.9 (OCH_2CH_3), 70.1 (ArCH_2O), 71.6 (CCH_2O), 82.5 (ArCC), 86.9 (ArCC), 102.4, 110.7, 125.4, 127.5, 128.2, 128.6, 136.6, 159.6 (Ar); HRMS calcd. for $\text{C}_{53}\text{H}_{52}\text{O}_6$ [M^+]: 784.3764, found: 784.3769. Anal. Calc. for $\text{C}_{53}\text{H}_{52}\text{O}_6$: C, 81.09; H, 6.68. Found: C, 82.95; H, 8.01%.

Compound 3c. This was prepared by the reaction of **1** and **2c** and purified from silica gel column chromatography with hexane/ CH_2Cl_2 /(2/1). Yield: 68%; a white solid; m.p. 67.1–67.8 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 1.19 (t, $J = 7.2$ Hz, 6H, CH_2CH_3), 2.63 (s, 4H, CCH_2C), 3.51 (s, 4H, CCH_2O), 3.52 (q, $J = 7.2$ Hz, 4H, OCH_2CH_3), 4.92 (s, 8H, ArCH_2), 5.02 (s, 16H, ArCH_2), 6.52 (s, 2H, ArH), 6.56 (s, 4H, ArH), 6.66 (s, 12H, ArH) 7.28–7.44 (m, 40H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz): δ 15.8 (CH_2CH_3), 23.9 (CCH_2C), 43.4 ($(\text{CH}_2)_2\text{C}(\text{CH}_2)_2$), 67.6 (OCH_2CH_3), 70.6 (ArC), 70.8 (ArC), 72.3 (CCH_2O), 83.2 (ArCC), 87.7 (ArCC), 102.3, 103.1, 107.0, 111.4, 126.1, 128.2, 128.7, 129.3, 137.4, 139.7, 160.2, 160.8 (Ar); IR (KBr): 2867 (m), 1594 (s), 1454 (m), 1375 (m), 1336 (m), 1297 (m), 1155 (m), 1052 (m), 833 (m), 738 (m), 690 (m). Anal. Calc. for $\text{C}_{109}\text{H}_{100}\text{O}_{14}$: C, 80.12; H, 6.17. Found: C, 79.87; H, 6.41%.

Compound 3d. This was prepared by the reaction of **1** and **2d** and purified from silica gel column chromatography with hexane/ CH_2Cl_2 /(1/1). Yield: 69%; a white solid; m.p. 68.2–69.1 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 1.20 (t, $J = 7.2$ Hz, 6H, CH_2CH_3), 2.65 (s, 4H, CCH_2C), 3.43–3.56 (br, 8H, CCH_2O , OCH_2CH_3), 4.87 (s, 8H, ArCH_2), 4.91 (s, 16H, ArCH_2), 4.98 (s, 32H, ArCH_2), 6.49–6.57 (br, 14H, ArH), 6.63–6.71 (m, 28H, ArH), 7.28–7.44 (m, 80H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 15.1 (CH_2CH_3), 23.2 (CCH_2C), 42.6 ($(\text{CH}_2)_2\text{C}(\text{CH}_2)_2$), 66.8 (OCH_2CH_3), 69.85 (ArC), 69.94 (ArC), 71.6 (CCH_2O), 82.5 (ArCCCH_2), 87.0 (CCCH_2), 101.5, 102.3, 106.3, 110.7, 125.2, 125.4, 127.5, 127.9, 128.1, 128.5, 136.7, 139.0, 139.1, 159.5, 159.95, 160.04 (Ar). Anal. Calc. for $\text{C}_{221}\text{H}_{196}\text{O}_{30}$: C, 79.67; H, 5.93. Found: C, 79.70; H, 5.99%.

4.5. Synthesis of 4a

A mixture of **3a** (500 mg, 1.38 mmol), 1,1,2,2-tetramethyldisilane (326 mg, 2.75 mmol), $\text{Ni}(\text{PET}_3)_2\text{Cl}_2$ (5 mg, 0.013 mmol) in toluene (10 mL) was refluxed for 18 h under nitrogen. The mixture was cooled to room temperature and evaporated. The residue was chromatographed over silica gel with hexane/ CH_2Cl_2 (1/2) to give **4a** (266 mg, mmol) as a pale yellow solid in 46% yield.

Compound 4a. M.p. 120–121 °C; ^1H NMR (acetone- d_6 , 300 MHz) δ 0.50 (s, 6H, SiCH_3), 1.12 (t, $J = 7.2$ Hz, 6H, CH_2CH_3), 2.71 (s, 4H, CCH_2C), 3.37 (s, 4H, CCH_2O), 3.42 (q, $J = 7.2$ Hz, 4H, OCH_2CH_3), 7.17–7.21 (m, 2H, p -

ArH), 7.40–7.44 (m, 8H, o,m - ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6 , 75 MHz) δ -1.75 (SiCH_3), 15.4 (CH_2CH_3), 36.9 (CH_2), 50.5 ($(\text{CH}_2)_2\text{CC}$), 67.1 (OCH_2CH_3), 74.0 (CCH_2O), 126.6 (o - ArC), 128.6 (p - Ar), 129.4 (m - Ar), 134.0 ($ipso$ - Ar), 140.3, 158.6; ^{29}Si NMR (acetone- d_6 , 60 MHz) δ 15.6; HRMS calcd. for $\text{C}_{27}\text{H}_{34}\text{O}_2\text{Si}$ [M^+]: 418.2328, found: 418.2337.

4.6. Synthesis of 4b

A mixture of **3b** (450 mg, 0.57 mmol), 1,1,2,2-tetramethyldisilane (203 mg, 1.71 mmol), $\text{Ni}(\text{PET}_3)_2\text{Cl}_2$ (2.1 mg, 6.0×10^{-3} mmol) in toluene (10 mL) was refluxed for 42 h under nitrogen. The mixture was cooled to room temperature and evaporated. The residue was chromatographed over silica gel with hexane/ CH_2Cl_2 (3/1) to give **3b** (170 mg, 0.20 mmol) as a yellow solid in 35% yield.

Compound 3b. M.p. 59.8–62.0 °C; ^1H NMR (CD_2Cl_2 , 300 MHz) δ 0.33 (s, 6H, SiCH_3), 1.15 (t, $J = 7.2$ Hz, 6H, CH_2CH_3), 2.54 (s, 4H, CCH_2C), 3.27 (s, 4H, CCH_2O), 3.44 (q, $J = 7.2$ Hz, 4H, OCH_2CH_3), 5.07 (s, 8H, ArCH_2), 6.47–6.49 (br, 2H, ArH), 6.53 (d, $J = 2.3$ Hz, 4H, ArH), 7.28–7.48 (m, 20H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75 MHz) δ -2.7 (SiCH_3), 14.6 (CH_2CH_3), 35.7, 49.3 ($(\text{CH}_2)_2\text{CC}$), 66.3 (OCH_2CH_3), 69.6 (ArCH_2), 73.1 (CCH_2O), 99.5, 106.7, 127.1, 127.6, 128.2, 133.0, 136.9, 141.1, 158.1, 159.5; ^{29}Si NMR (CD_2Cl_2 , 60 MHz) δ 15.4. Anal. Calc. for $\text{C}_{55}\text{H}_{58}\text{O}_6\text{Si}$: C, 78.35; H, 6.93. Found: C, 78.35; H, 6.86%.

4.7. Synthesis of 4c

A mixture of **3c** (300 mg, 0.18 mmol), 1,1,2,2-tetramethyldisilane (92 mg, 0.78 mmol), $\text{Ni}(\text{PET}_3)_2\text{Cl}_2$ (2.30 mg, 6.0×10^{-3} mmol) in toluene (6 mL) was refluxed for 58 h under nitrogen. The mixture was cooled to room temperature and evaporated. The residue was subjected to preparative TLC with hexane/ CH_2Cl_2 (5/1) to give **4c** (50 mg, 0.03 mmol) as a pale yellow solid in 16% yield.

Compound 4c. M.p. 62.1–64.5 °C; ^1H NMR (CD_2Cl_2 , 300 MHz) δ 0.38 (s, 6H, SiCH_3), 1.10 (t, $J = 7.2$ Hz, 6H, CH_2CH_3), 2.62 (s, 4H, CCH_2C), 3.29 (s, 4H, CCH_2O), 3.40 (q, $J = 7.2$ Hz, 4H, OCH_2CH_3), 4.89–5.02 (br, 8H, ArCH_2), 5.04 (s, 16H, ArCH_2), 6.40–6.45 (br, 2H, ArH), 6.46–6.65 (br, 8H, ArH), 6.66–6.69 (br, 8H, ArH), 7.23–7.48 (m, 40H, ArH); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75 MHz) δ -2.6 (SiCH_3), 14.6 (CH_2CH_3), 35.8, 49.3 ($(\text{CH}_2)_2\text{CC}$), 66.3 (OCH_2CH_3), 69.5 (ArC), 69.7 (ArC), 73.1 (CCH_2O), 99.3, 101.0, 106.8, 127.3, 127.6, 127.9, 128.2, 133.1, 136.6, 139.3, 141.2, 158.2, 159.3, 159.4; ^{29}Si NMR (CD_2Cl_2 , 60 MHz) δ 15.6. Anal. Calc. for $\text{C}_{111}\text{H}_{106}\text{O}_{14}\text{Si}$: C, 78.79; H, 6.31. Found: C, 78.61; H, 6.61%.

4.8. Synthesis of 4d

A mixture of **3d** (630 mg, 0.19 mmol), 1,1,2,2-tetramethyldisilane (67 mg, 0.57 mmol), $\text{Ni}(\text{PET}_3)_2\text{Cl}_2$ (6.90 mg,

0.02 mmol) in toluene (5 mL) was refluxed for 58 h under nitrogen. The mixture was cooled to room temperature and evaporated. The residue was chromatographed over silica gel with hexane/CH₂Cl₂ (1/1–2/1) to give **4d** (180 mg, 0.053 mmol) as a pale yellow solid in 28% yield.

Compound 4d. M.p. 68.2–69.5 °C; ¹H NMR (CD₂Cl₂, 300 MHz) δ 0.54 (s, 6H, SiCH₃), 1.19 (t, *J* = 7.2 Hz, 6H, CH₂CH₃), 2.75 (s, 4H, CCH₂C), 3.40 (s, 4H, CCH₂O), 3.49 (q, *J* = 7.2 Hz, 4H, OCH₂CH₃), 4.76–4.90 (br, 8H, ArCH₂), 4.90–5.00 (br, 16H, ArCH₂), 5.00–5.24 (br, 32H, ArCH₂), 6.36–6.69 (br, 18H, ArH), 6.69–6.94 (br, 24H, ArH), 7.28–7.58 (m, 80H, ArH); ¹³C{¹H} NMR (CD₂Cl₂, 75 MHz) δ –2.4 (SiCH₃), 14.7 (CH₂CH₃), 36.0, 49.4 ((CH₂)₂CC), 66.3 (OCH₂CH₃), 69.6 (ArC), 69.7 (ArC), 73.2 (CCH₂O), 99.5, 101.2, 106.0, 106.9, 125.5, 127.3, 127.6, 128.2, 128.7, 133.2, 136.7, 139.1, 139.4, 141.3, 158.3, 159.6, 159.8, 159.8; ²⁹Si NMR (CD₂Cl₂, 60 MHz) δ 15.7. Anal. Calc. for C₂₂₃H₂₀₂O₃₀Si: C, 79.01; H, 6.01. Found: C, 78.79; H, 6.14%.

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