An alternative convergent synthesis of silole-core dendrimers¹

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Abstract: Silole-core dendrimers having benzyl-ether-type dendron units in the periphery are readily synthesized by the Ni-catalyzed reaction of benzyloxy-substituted diphenylacetylenes with 1,1,2,2-tetramethyldisilane.

Key words: silole, dendrimer, nickel-catalyzed reaction, convergent synthesis.

Résumé : La synthèse de dendrimères à coeur de silole possédant des dendrones de type éther benzylique à la périphérie peut être réalisée facilement en faisant appel à la réaction du 1,1,2,2-tétraméthyldisilane avec des diphénylacétylènes substitués par un groupe benzyloxy, catalysée par du nickel.

Mots clés : silole, dendrimère, réaction catalysée par le nickel, synthèse convergente.

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Introduction

Dendrimers are a unique class of macromolecules having highly ordered, three-dimensional, and tree-like structures, and they have great potential as building blocks for the construction of functional materials (1). They are generally synthesized by "divergent" or "convergent" approaches. The divergent approach initiates growth at the core, and the generation grows outward by repetition of coupling and activation steps. The convergent method, on the other hand, propagates inward by coupling the focal point of the dendrons to the core. The convergent synthesis allows control over the number and location of functional moieties in the resultant dendrimers. This is a useful and important feature in molecular design. Indeed, quite a few reports on the derivatization of dendrimers have addressed chemical modification of the core and (or) peripheral moieties for a variety of fundamental studies and applications (2).

Recently, many groups reported accelerated approaches that combine the convergent and divergent strategies to reduce the number of tedious and iterative synthetic steps (3). In view of the synthetic improvement of the convergent approach, one-step synthesis of dendrimers, involving simultaneous construction of the core by the reaction of starting materials with the appropriate dendron units, appears promising as compared with the conventional convergent synthesis involving installation of the core in the final step. Hecht and Fréchet (4) reported the cobalt-catalyzed [2+2+2] cyclotrimerization of dendritically substituted alkynes to produce benzene-core dendrimers. This approach successfully yielded highly compact cores. Dehaen and co-workers (5) reported the synthesis of poly(1,2,3-triazolylmethyl)benzene cores via 1,3-dipolar cycloaddition reaction between poly(azidomethyl)benzenes and dendritically disubstituted acetylenedicarboxylates. Sharpless and co-workers (6) and Fokin and co-workers (7) also recently reported, on the basis of their "click chemistry" approach (6), an efficient route to triazole dendrimers by Cu(I)-catalyzed reaction of azides with alkynes (7).

Siloles and silacyclopentadienes have attracted great interest over the past decade because of their unique photophysical and electronic properties (8) and potential applications as organic electroluminescent (EL) devices (9). The silole has a relatively low LUMO energy level, due to the $\sigma^*-\pi^*$ conjugation, in comparison with its carbon analogue, cyclopentadiene. Recently, several reports have addressed synthesis of siloles with a variety of substituent groups (10) and silolebased polymers (11). The silole-core dendrimer systems are envisioned to constitute an interesting class of macromolecule because the silole incorporated at the core acts as a functional conjugated unit and the dendritic framework provides for a site-isolation of chromophores, a light-harvesting antenna, and an energy-transfer interaction (12).

In 1972, Kumada and co-workers (13) reported the nickelcatalyzed reaction of 1,1,2,2-tetramethyldisilane and disubstituted acetylenic compounds to give siloles in good yields

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Sanji et al.

Scheme 1.



(Scheme 1). The reaction is envisioned to proceed with the involvement of an intermediate nickel-silylene complex and its addition to acetylenes. We have found that this reaction works well with heavy acetylenes bearing dendritic substituents, affording silole-core dendrimers. This paper discloses a facile one-pot synthesis of silole-core dendrimers by the alternative convergent method.

Results and discussion

Our synthetic strategy for the silole-core dendrimers is based on the nickel-catalyzed reaction of 1,1,2,2-tetramethyldisilane with disubstituted alkynes, which has proved to work well for dendritic alkynes affording silole-core dendrimers.

The alkynes with poly(benzyl ether) dendrons, 2a-2c, were prepared by the convergent method as shown in Scheme 2.

1,2-Bis(3,5-dihydroxyphenyl)acetylene was readily prepared by deprotection of 1,2-bis(3,5-dimethoxyphenyl)acetylene with boron tribromide. The benzyl ether-type dendritic bromides **1b** and **1c** were obtained according to the previously reported procedures (14). The reaction of bromides **1a**–**1c** (4 equiv.) with 1,2-bis(3,5-dihydroxydiphenyl)acetylene (1 equiv.) in the presence of potassium carbonate and 18-crown-6 proceeded smoothly to give the acetylenes with poly(benzyl ether) dendrons **2a**–**2c**. Table 1 lists the results. The dendritic acetylenes **2a**–**2c** were obtained in good yields even for the higher generation substrates (91%, 62%, and 79%, respectively). The ¹H and ¹³C NMR spectra of **2a**–**2c** showed the high molecular symmetry in these products and conformed to the proposed structures. FAB mass or MALDI-TOF mass spectra were also consistent with the dendritic structures.

Next, the dendritic alkynes 2a-2c were treated with 1,1,2,2-tetramethyldisilane in the presence of NiCl₂(PEt₃)₂

Scheme 3.



Table 1. Synthesis of dendritic acetylene 2a–2c and silole-core dendrimers 3a–3c.

	2	3		
	Yield	Time	Amount of	Yield
Compound (Gn)	(%)	(h)	cat. (mol%)	(%)
a (G1)	91	20	3	50
b (G2)	62	44	3	47
c (G3)	79	136	10	13

Note: Gn = generation number; cat. = catalyst.

(3 mol%) in refluxing toluene (Scheme 3). The reaction, monitored by TLC, was continued until the disappearance of the starting alkynes. The results are also listed in Table 1, which shows that even though longer times are required to complete the reaction, as the generation of the desired dendrimers grows, the silole-forming reaction proceeds satisfactorily. Thus, silole-core dendrimers **3a** and **3b** were obtained in 50% (20 h) and 47% (44 h) yields, respectively. These yields are comparable to that of parent 1,1-dimethyl-2,3,4,5-tetraphenylsilole prepared from diphenylacetylene and tetramethyldisilane under the same conditions (53%, 16 h).³ However, for the even higher generation dendrimer **3c**, the yield decreased to 13%, even after prolonged heating

³ 1,1-Dimethyl-2,3,4,5-tetraphenylsilole was prepared as a reference compound by the nickel-catalyzed reaction of 1,1,2,2-tetramethyldisilane and diphenylacetylene. NMR data for 1,1-dimethyl-2,3,4,5-tetraphenylsilole: ¹H NMR (300 MHz, acetone- d_6) δ : 7.13–6.95 (m, 16H, Ph), 6.94–6.81 (m, 4H, Ph), 0.41 (s, 6H, SiCH₃). ¹³C NMR (75 MHz, acetone- d_6) δ : 154.9 (Ph₄C₄Si), 142.6 (Ph₄C₄Si), 140.6, 139.8, 130.7, 129.5, 128.8, 128.3, 127.1, 126.5, -4.0 (SiCH₃). ²⁹Si NMR (60 MHz, acetone- d_6) δ : 8.2.

(136 h) using an increased amount of the catalyst (10 mol%). This is clearly suggestive of steric crowding around the core hindering the reaction at the higher generation. In addition, the reaction became less clean, although 3c could be readily isolated and purified by column chromatography, as in the other cases.

Silole-core dendrimers 3a-3c were fully characterized by a variety of spectroscopic techniques. The GPC analysis confirmed their monodispersity. The FAB or MALDI-TOF mass spectra showed peaks for m/z 1264 ([M + H]⁺), 2984.5 ([M + Na]⁺), and 6465.0 ([M + Ag]⁺), associated with 3a-**3c**, respectively. The ¹H and ¹³C NMR spectra displayed the signals of methyl on the silole ring at the core along with those of the benzyl ether units (15).³ In the ²⁹Si NMR spectra, the signals assigned to Si–Me on the silole ring core were observed at about 8 ppm for these dendrimers. All these spectral observations support the structure of the silole-core dendrimers.

In conclusion, we have prepared silole-core dendrimers by the nickel-catalyzed reaction of tetramethyldisilane and dendritic acetylenes containing poly(benzyl ether) units through the third generation. This synthetic procedure demonstrates the alternative convergent approach via a one-pot synthesis of the core, for the construction of a precise macromolecular structure. To the best of our knowledge, these are the first examples of silole-core dendrimers. The photophysical properties of the dendrimers will be reported in a forthcoming paper.

Experimental

Measurements

¹H, ¹³C, and ²⁹Si NMR spectra were recorded on a Bruker DPX 300 FT-NMR spectrometer at 300, 75.4, and 59.6 MHz, respectively. The ¹H and ¹³C chemical shifts were referenced to solvent residues (¹H, $\delta = 7.24$ ppm; ¹³C, $\delta = 77.0$ ppm for CDCl₃). The ²⁹Si chemical shift was referenced to external Me₄Si (0 ppm). Mass spectra were measured by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) technique on a Bruker reflex III. Gel permeation chromatography (GPC) was performed on a Shimadzu LC 10 HPLC equipped with PL-gel mixed-C columns calibrated with polystyrene standards.

Materials

All solvents and reagents were of reagent quality, purchased from commercial sources and used without further purification, unless otherwise noted below. Toluene was dried and distilled from sodium–benzophenone just before use. Acetone was distilled from calcium hydride. 1,2-Bis(3,5dihydroxyphenyl)acetylene (16) and poly(benzyl ether)-dendritic bromides (14) were prepared according to the previously reported procedures.

General procedure for synthesis of poly(benzyl ether)type dendritic acetylenes (2a-2c)

A mixture of an appropriate dendritic bromide (4 equiv.), 1,2-bis(3,5-dihydroxydiphenyl)acetylene (1 equiv.), K_2CO_3 (6 equiv.), and 18-crown-6 (0.4 equiv.) in acetone (10–100 mL) was heated under reflux under nitrogen (24–132 h). After the mixture was cooled to room temperature, water

(30 mL) was added to the mixture, and then the mixture was extracted with CH_2Cl_2 (20–100 mL × 3). The combined organic layer was washed successively with water, sat. NH_4Cl solution, and sat. NaCl solution and evaporated after being dried over anhydrous MgSO₄. The residue was chromatographed over silica gel to give the corresponding poly(benzyl ether)-type dendritic acetylene (**2a–2c**).

2a

This was prepared by the reaction of 1,2-bis(3,5dihydroxyphenyl)acetylene and benzyl bromide **1a** and purified from silica gel column chromatography with CH₂Cl₂ to give **2a** as a pale yellow solid. Yield 91%; mp 149–151 °C. ¹H NMR (300 MHz, CDCl₃) δ : 7.44–7.33 (m, 20H, Ar*H*), 6.80 (d, 4H, *J* = 2.2 Hz, Ar*H*), 6.63 (t, 2H, *J* = 2.2 Hz, Ar*H*), 5.04 (s, 8H, -CH₂O-). ¹³C NMR (75 MHz, CDCl₃) δ : 159.7, 136.6, 128.6, 128.0, 127.5, 124.4, 110.6, 103.5, 89.0 (-*C*=C-), 70.1 (-*C*H₂O-). MS (FAB) *m/z*: 603 ([M + H]⁺). Anal. calcd. for C₄₂H₃₄O₄: C 83.70, H 5.69; found: C 83.94, H 6.00.

2b

This was prepared by the reaction of 1,2-bis(3,5dihydroxyphenyl)acetylene and **1b** and purified from silica gel column chromatography with CH₂Cl₂ to give **2b** as a pale yellow solid. Yield 62%; mp 150–154 °C. ¹H NMR (300 MHz, CDCl₃) δ : 7.43–7.30 (m, 40H, Ar*H*), 6.78 (d, 4H, *J* = 2.2 Hz, Ar*H*), 6.68 (d, 8H, *J* = 2.2 Hz, Ar*H*), 6.58 (m, 6H, Ar*H*), 5.02 (s, 16H, -CH₂O-), 4.99 (s, 8H, -CH₂O-). ¹³C NMR (75 MHz, CDCl₃) δ : 160.1, 159.6, 139.0, 136.7, 128.6, 128.0, 127.5, 124.4, 110.6, 106.3, 103.4, 101.6, 89.1 (-C=C-), 70.1 (-CH₂O-), 70.0 (-CH₂O-). MS (FAB) *m/z*: 1451 ([M]⁺). Anal. calcd. for C₉₈H₈₂O₁₂: C 81.08, H 5.69, O 13.23; found: C 80.98, H 5.93, O 13.01.

2c

This was prepared by the reaction of 1,2-bis(3,5dihydroxyphenyl)acetylene and **2c** and purified from silica gel column chromatography with CH₂Cl₂-hexane (1:1) to give **2c** as a pale yellow solid. Yield 62%; mp 59–61 °C. ¹H NMR (300 MHz, CDCl₃) δ : 7.41–7.27 (m, 80H, Ar*H*), 6.80 (d, 4H, *J* = 2.1 Hz, Ar*H*), 6.68–6.65 (m, 24H, Ar*H*), 6.62 (t, 2H, *J* = 2.0 Hz, Ar*H*), 6.57–6.55 (m, 12H, Ar*H*), 5.00 (s, 32H, -CH₂O-), 4.95–4.93 (m, 24H, -CH₂O-). ¹³C NMR (75 MHz, CDCl₃) δ : 160.1, 160.0, 159.6, 139.1, 138.9, 136.7, 128.5, 127.9, 127.5, 124.4, 110.6, 106.4, 106.3, 101.5, 89.1 (-C=C-), 70.0 (-CH₂O-), 69.9 (-CH₂O-). MS (MALDI-TOF) *m/z*: 3172.5 ([M + Na]⁺). Anal. calcd. for C₂₁₀H₁₇₈O₂₈: C 80.08, H 5.70, O 14.22; found: C 80.01, H 5.79, O 14.39.

Synthesis of silole-core dendrimer 3a

A mixture of **2a** (250 mg, 0.42 mmol), 1,1,2,2tetramethyldisilane (72 mg, 0.60 mmol), and Ni(PEt₃)₂Cl₂ (4 mg, 0.01 mmol) in toluene (10 mL) was heated under reflux for 20 h under nitrogen. The mixture was cooled to room temperature and evaporated. The residue was chromatographed over silica gel with toluene–hexane (3:1) to give **3a** (130 mg, 0.103 mmol) as a greenish-yellow glass. Yield 50%. ¹H NMR (300 MHz, acetone- d_6) δ : 7.38–7.20 (m, 40H, ArH), 6.46–6.44 (m, 4H, ArH), 6.35 (d, 4H, J = 2.2 Hz, ArH), 6.32 (d, 4H, J = 2.2 Hz, ArH), 5.00 (s, 8H, -CH₂O-), 4.89 (s, 8H, -CH₂O-), 0.37 (s, 6H, Si-CH₃). ¹³C NMR (75 MHz, acetone- d_6) δ : 160.6, 160.5, 154.9 (Ar₄C₄Si), 142.3 (Ar₄C₄Si), 142.1, 138.3, 138.1, 129.22, 129.18, 128.51, 128.47, 128.3, 128.2, 128.1, 109.8, 108.6, 101.8, 101.4, 70.7 (-CH₂O-), 70.4 (-CH₂O-), -3.7 (Si-CH₃). ²⁹Si NMR (60 MHz, acetone- d_6) δ : 8.1. MS (FAB) *m*/*z*: 1264 ([M + H]⁺). Anal. calcd. for C₈₆H₇₄O₈Si: C 81.74, H 5.90; found: C 81.58, H 6.15.

Synthesis of silole-core dendrimer 3b

A mixture of **2b** (502 mg, 0.34 mmol), 1,1,2,2tetramethyldisilane (72 mg, 0.60 mmol), and Ni(PEt₃)₂Cl₂ (4 mg, 0.01 mmol) in toluene (10 mL) was heated under reflux for 44 h under nitrogen. The mixture was cooled to room temperature and evaporated. The residue was chromatographed over silica gel with toluene-hexane (10:1) to give 3b (240 mg, 0.081 mmol) as a greenish-yellow glass. Yield 47%. ¹H NMR (300 MHz, acetone- d_6) δ : 7.38–7.23 (m, 80H, ArH), 6.65-6.40 (m, 36H, ArH), 5.02-4.74 (m, 48H, -CH₂O-), 0.41 (s, 6H, SiCH₃). ¹³C NMR (75 MHz, acetone- d_6) δ : 160.92, 160.88, 160.7, 160.4, 154.8 (Ar₄C₄Si), 142.4 (Ar₄C₄Si), 142.0, 141.8, 140.6, 140.3, 138.1, 138.0, 129.17, 129.13, 128.53, 128.49, 128.4, 128.1, 108.7, 106.9, 102.1, 101.9, 70.8 (-CH₂O-), 70.4 (-CH₂O-), 70.3 (-CH₂O-), -3.4 (Si-CH₃). ²⁹Si NMR (60 MHz, acetone-d₆) δ: 8.1. MS (MALDI-TOF) m/z: 2984.5 ([M + Na]⁺). Anal. calcd. for C₁₉₈H₁₇₀O₂₄Si: C 80.30, H 5.79; found: C 79.91, H 5.95.

Synthesis of silole-core dendrimer 3c

A mixture of **2c** (501 mg, 0.16 mmol), 1,1,2,2tetramethyldisilane (38 mg, 0.32 mmol), and Ni(PEt₃)₂Cl₂ (6 mg, 0.016 mmol) in toluene (5 mL) was heated under reflux for 136 h under nitrogen. The mixture was cooled to room temperature and evaporated. The residue was chromatographed over silica gel with CH₂Cl₂-hexane (2:1) to give **3c** (68 mg, 0.011 mmol) as a greenish-yellow glass. Yield 13%. ¹H NMR (300 MHz, acetone- d_6) δ : 7.32–7.20 (m, 160H, ArH), 6.68–6.36 (m, 84H, ArH), 4.92–4.64 (m, 112H, -CH₂O-), 0.38 (s, 6H, Si-CH₃). ¹³C NMR (75 MHz, acetone- d_6) δ : 160.9, 160.8, 140.5, 140.4, 138.0, 129.2, 128.5, 128.4, 107.2, 106.8, 102.0, 70.4 (-CH₂O-). ²⁹Si NMR (60 MHz, acetone- d_6) δ : 7.9. MS (MALDI-TOF) m/z: 6465.0 ([M + Ag]⁺). Anal. calcd. for C₄₂₂H₃₆₂O₅₆Si: C 79.73, H 5.74; found: C 79.90, H 6.09.

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