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Preparation of dendritic carbosilanes containing ethynyl groups and dicobalt hexacarbonyl clusters on the periphery

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Abstract

Dendritic carbosilanes have been prepared by the use of 2,4,6,8-tetramethyl-2,4,6,8-tetravinyl-2,4,6,8-tetrasila-1,3,5,7-tetraoxacyclooctane $(CH_2{=}CHMeSiO)_4$ and 1,2-bis(triallylsilyl)ethane $((CH_2{=}CHCH_2)_3SiCH_2)_2$ as core molecules, diallylmethylsilyl groups $((CH_2{=}CHCH_2)_2MeSi–)$ as building blocks and bisphenylethynylmethylsilyl groups $((PhC{\equiv}C)_2MeSi–)$ as terminating groups. The phenylethynyl-group-containing terminal generation is produced by the reaction of the chlorosilylated generation with lithium phenylacethylide. The reaction of dicobalt octacarbonyl $Co_2(CO)_8$ with phenylethynyl groups gave the corresponding phenylethynyl hexacarbonyl complexes $(2Co_2(CO)_6{\cdot}(PhC{\equiv}C)_2MeSi$–dendimer) on the periphery. The yields of the prepared dendrimers with phenylethynyl terminal groups and their cobalt carbonyl complexes are obtained nearly quantitatively. They are characterized by the use of spectroscopic analyses (^{1}H-, and ^{13}C-NMR, UV and IR) as well as MALDI mass spectroscopy and elemental analysis. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Dendrimer; Dendritic carbosilane; Dendritic cobalt carbonyl cluster

1. Introduction

Recently, the interest in dendritic macromolecules arose from their highly branched structure that has a number of well-defined functional end groups [1]. They are obtained as unique molecules derived from alternating procedures such as protecting and generating steps [2–4]. We observed a few methods for the preparation of carbosilane dendrimers possessing allyl, allyloxy and phenylethynyl groups, by the use of hydrosilation, alcoholysis, alkenylation as well as alkynylation [3,5c]. The dendrimers with propylenes on the inner shell and phenylethynyl groups on the terminal generation provided access to macromolecular materials having special functions such as metal carbonyl groups [6,7a]. A number of metal-containing dendrimers such as cobalt carbonyl clusters on the periphery have been described by Seyferth et al. [7]. We prepared the carbosilane dendrimers containing phenylethynyl groups on the periphery based on 2,4,6,8-tetramethyl-2,4,6,8-tetravinyl-2,4,6,8-tetrasila-1,3,5,7-tetraoxacyclooctane $(Me(CH_2{=}CH)SiO)_4$ (GS type dendrimer) and 1,2-bis(triallylsilyl)ethane $((CH_2{=}CHCH_2)_3SiCH_2)_2$ (GH type dendrimer) as core molecules. The propylene-containing generations (inner shell) were obtained by repeating alternative procedures such as hydrosilation with dichloromethylsilane and alkenylation with allylmagnesium bromide [8–10]. All terminal dichloromethylsilyl-group-containing generations (G*n*P) were produced on ethynyl-group-containing dendrimers by the reaction of lithium phenylethynyl [11]. We now report on a simple synthetic method for the bis(phenylethynyl)methylsilyl group $(–MeSi(C{\equiv}CPh)_2)$ containing dendrimers (G*n*-*m*PA) on the outer shell and the preparation of the corresponding bimetal carbonyl complexes $(–MeSi(C{\equiv}CPh)_2{\cdot}2Co_2(CO)_6)$ by the reaction of di-cobalt octacarbonyl $Co_2(CO)_8$ on the periphery of carbosilane dendrimers [3,5c,9c,10b,11,12b] (Scheme 1).

All bis(phenylethynyl)methylsilyl-group-containing dendrimers were characterized by NMR, IR and MALDI mass spectroscopy as well as elemental analysis. But, bimetal carbonyl-group-containing dendrimers

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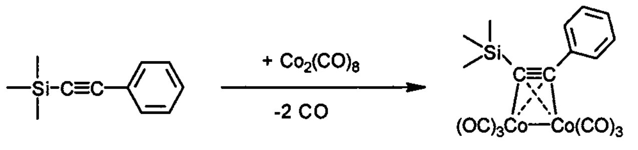


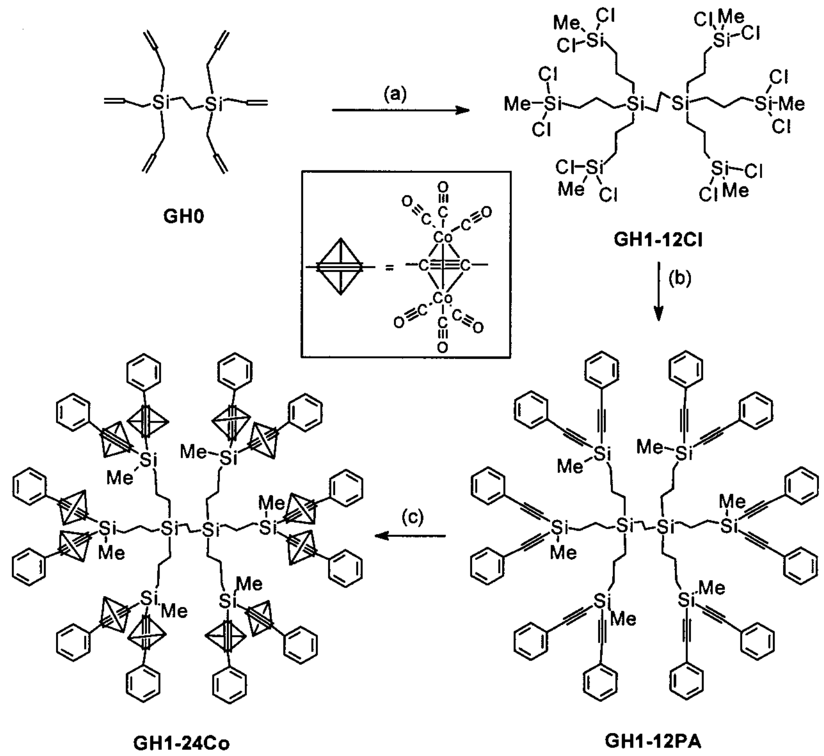
Scheme 1.

were soluble in an organic medium such as toluene, acetone or chloroform and were not observed by the MALDI mass spectroscopy [6,15].

2. Results and discussion

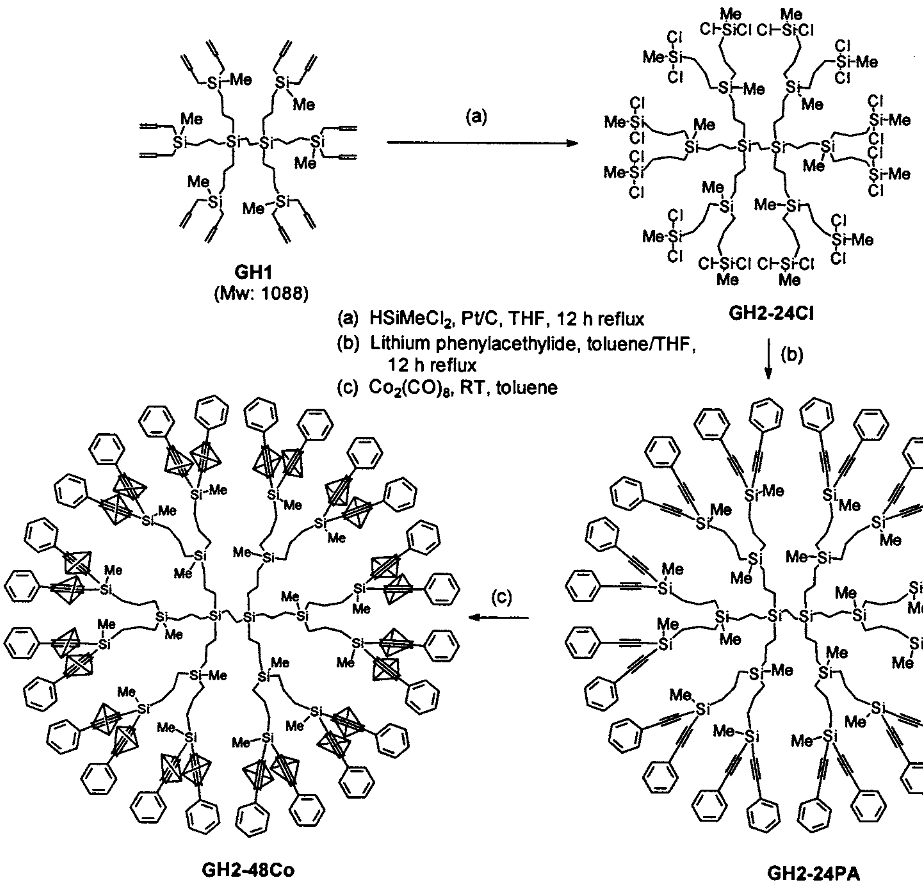
The preparation of dendritic carbosilanes was established with two core molecules [13], which have $(Me(CH_2{=}CH)SiO)_4$ (GS type dendrimers) with a branching degree of four ($N_c = 4$) and $((CH_2{=}CHCH_2)_3SiCH_2)_2$ (GH type dendrimers) with a branching degree of six ($N_c = 6$). The inner shell of the given dendritic molecule used the preparative methods as those of hydrosilation with dichloromethylsilane and alkenylation with allylmagnesium bromide ($N_b = 2$ and $N_l = 3$) [3,8,9,14]. The terminated outer shell of dendritic molecules containing bis(phenylethynyl)methylsilyl groups was prepared by the use of alkynylation with lithium phenylacethylide and the Si–Cl group contained generation (G*n*P) as shown in Schemes 2–5.

GH type dendrimers are synthesised by the use of 1,2-bis(triallylsilyl)ethane as core molecule and dichloromethylsilane and allylmagnesium bromide ($N_b = 2$, $N_l = 3$) as emanating steps. The two steps provided almost quantitative yields [3]. The reaction of GH*n*P ($n = 1$–3), containing 12, 24 and 48 Si–Cl bonds, with lithium phenylacethylide in THF proceeds readily and completely to phenylethynyl-group-containing dendrimers GH*n*-*m*PA ($n = 1$–3; $m = 12$, 24, 48, see Schemes 2–4) as a light yellow solid. The prepared dendrimers were first characterized by NMR (^{1}H and ^{13}C) spectroscopy. From the NMR spectrum of the reaction mixture, we did not observe side products (see Figs. 1–3). The reaction of phenylethynyl groups on the periphery of carbosilane dendrimers GH*n*–*m*PA ($n = 1$–3; $m = 12$, 24, 48) with dicobalt octacarbonyl proceeds to carbonyl clusters at the terminal triple bonds on each arm (Schemes 2–4). Thus, one molar equivalent of dendrimer GH1–12PA reacts with 12



(a) HSiMeCl2, Pt/C, THF, 12 h reflux
(b) Lithium phenylacethylide, toluene/THF, 12 h reflux
(c) Co2(CO)8, RT, toluene

Scheme 2. Synthetic routes for GH1–12PA and GH1–24Co.



Scheme 3. Synthetic routes for GH2–24PA and GH2–48Co.

molar equivalents of $Co_2(CO)_8$ in toluene for 24 h at room temperature by the elimination of CO gas, after simple column chromatographic purification through silica gel and the removal of a solvent, to give a dark red solid. A similar reaction of GHn–mPA ($n = 1$–3; $m = 12$, 24, 48) with $Co_2(CO)_8$ using the same workup gave GHn–mCo ($n = 1$–3; $m = 24$, 48 and 96) as a dark red solid.

The synthesis of GS type dendrimers is based on $(Me(CH_2{=}CH)SiO)_4$ as core molecules and methyldichlorosilane and allyl groups were used as generating groups ($N_c = 4$, $N_b = 2$, $N_l = 3$). By repeating the hydrosilation and alkenylation steps, this siloxane core dendrimer can be converted to G4 with 64 allylic end groups [3b–c]. The reaction of GSnP ($n = 1$–4), containing 8, 16, 32 and 64 Si–Cl bonds, with lithium phenylacethylide in THF proceeds readily and completely to GSn–mPA ($n = 1$–4; $m = 8$, 16, 32, 64; see Scheme 5). The products with the phenylethynyl group containing dendrimers were obtained as a light yellow solid. The reaction of carbosilane dendrimers that contain phenylethynyl groups on the periphery such as GSn–mPA ($n = 1$–4; $m = 8$, 16, 32 and 64) with dicobalt octacarbonyl proceeds readily and completely, provided that the terminal ethynyl groups on each arm are substituted as above (Scheme 5). Thus, one molar equivalent of dendrimer GS1–8PA reacts with eight molar equivalents of $Co_2(CO)_8$ in toluene for 24 h at room temperature by the elimination of CO gas, after simple column chromatographic purification through silica gel and the removal of a solvent, to give a dark red solid. A similar reaction of GSn–mPA ($n = 1$–4; $m = 8$, 16, 32 and 64) with $Co_2(CO)_8$ using the same work-up gave GSn–mCo ($n = 1$–4; $m = 16$, 32, 64 and 128) as a dark red solid. The synthetic methods and spectroscopic views of GSn–mPA and GHn–mPA type dendrimers and their cobalt clusters have practically the same tendency.

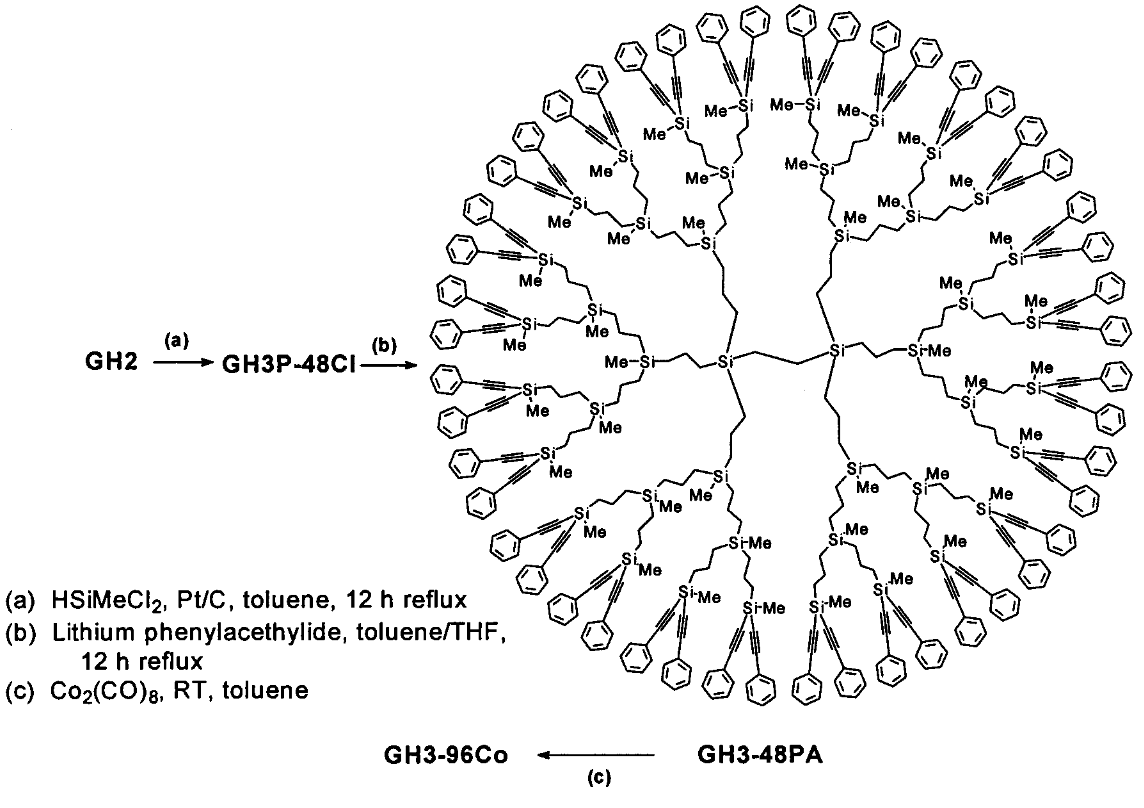
The purification of GSn–mPA and GHn–mPA type dendrimers was carried out by column chromatography after each alkynylation for each terminal steps. The purification of chlorosilylated GS–nP and GH–nP type dendrimers was unsuccessful because of their sensitivity to moisture. But, the NMR spectroscopic view of them showed a perfect formation in all generations.

The dendrimers (Gn–mPA and Gn–2mCo) were structurally characterized by the ^{1}H- and ^{13}C-NMR spectroscopy, elemental analysis, MALDI mass, IR, and UV–vis spectroscopy. All hydrosilation processes with H–SiMeCl_2 and double bonds in the inner shell seemed to be free of side reaction except the small amount of dehydrogenative couplings branches [16]. The ^{1}H- and ^{13}C-NMR spectroscopic analyses of GH*n*–*m*PA, GH*n*–2*m*Co ($n = 1$–3), GS*n*–*m*PA, GS*n*–2*m*Co ($n = 1$–4) type dendrimers showed no defect structure of dendrimers (Figs. 1 and 2). The ^{13}C-NMR spectral shifts were observed in the conversion of G*n*–*m*PA into G*n*–2*m*Co: 90.0 and 106.2 ppm in GH1–12PA to 75.0 and 106.0 ppm in GH1–24Co. The transition of G*n*–*m*PA to G*n*–2*m*Co by the reaction of cobalt carbonyls has been observed as the same evidence in the NMR spectrum (see Figs. 1 and 2).

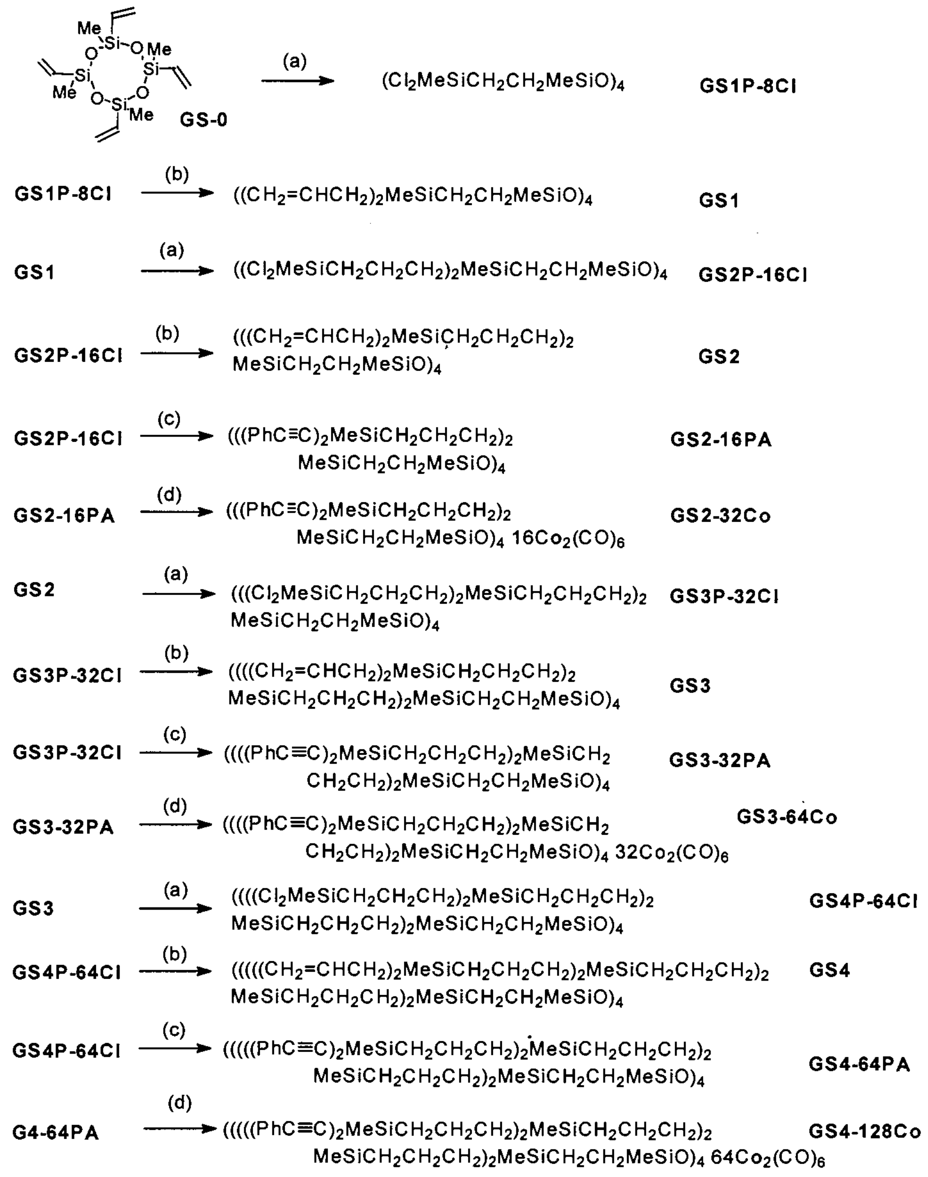
The MALDI mass spectrum of G*n*–*m*PA type dendrimers mainly shows the M^+ of the given dendrimers. The m/z value of the dominant signal for dendrimers corresponds to the calculated value of m/z for GH*n*–mPA and GS*n*–*m*PA (see Figs. 3 and 4). But, the MALDI mass spectrometry was not useful for GS4–64PA and G*n*–2*m*Co due to their unusual formation of matrix as well as heavier molecular weight. However, this may be a consequence of aggregation as we have observed a similar behavior with GS–*n* and GH–*n* type dendrimers.

The determination of molecular mass and the unified character of the prepared dendrimers are very difficult. GPC and MALDI mass spectroscopic measurements were used for this purpose [15]. In order to define dendritic carbosilanes, MALDI mass spectrometry was employed. So far, the high generation of carbosilane dendrimers without the determination of molecular mass has been carried out. We observed the phenomenon that the molar absorbities of GH*n*–*m*PA and GS*n*–*m*PA type dendrimers were proportional to the increasing number of triple bonds in the UV spectroscopy. The spectra of the given compounds are similar and consist of a broad band with a maximum wave length (λ_{max}) at 283 nm for GH*n*–*m*PA ($n = 1$–3) and 284 nm for GS*n*–*m*PA ($n = 1$–4) type dendrimers. The molar absorbances (ε_{max}) of all dendrimers are approximately increasing according to the number of triple bonds (see Table 1 and Fig. 5). We expect the possibility of determining the molecular mass of these types of dendrimers from the increasing molar absorbances.

In conclusion, G*n*–*m*PA dendrimers are obtained by the reaction of the chlorosilylated dendrimer G*n*–*m*P with lithium phenylacethylide as quantitative yields. The phenylethynyl group-containing dendrimers were reacted with cobalt octacarbonyl to form cobalt hexacarbonyl-containing noble dendritic carbosilanes. The yields of two products G*n*–*m*PA and G*n*–2*m*Co were quantitative. Using MALDI mass spectroscopy we have directly measured the molecular weight for the prepared dendrimers. We expected the possibility of a determining method for the molecular mass of G*n*–*m*PA type dendrimers by the use of UV spectroscopy.



Scheme 4. Synthetic routes for GH3–48PA and GH3–96Co.



(a) $HSiMeCl_2$, Pt/C, Et_2O, RT ~ reflux, (b) Allylmagnesium bromide, THF/Et_2O, reflux
(c) Lithiumphenylacethylide, THF, reflux, (d) $Co_2(CO)_8$, toluene, RT

Scheme 5. Synthetic routes for GS*n*–*m*PA and GS*n*–2*m*Co.

3. Experimental

All reactions were carried out under a dried N_2 atmosphere. Ether and THF were dried by sodium–benzophenone ketyl, while solvents such as toluene were dried and distilled from sodium metal. The NMR spectra were recorded on a Bruker AC-200 spectrometer. The FT-IR spectra were measured by an IFS 55 (Bruker). The UV spectra were measured by HP 8452A diode array UV–visible spectrophotometer (HP). Elemental analysis and MALDI mass spectroscopy (KRATOS KOMPACKT MALDI 2) attachments were performed by the Pusan and Taejon Branches of the Korean Basic Science Institute.

The following abbreviations are used in the experiments: GS–*n* refers to each generation of dendritic silanes with siloxane tetramer $(Me(CH_2{=}CH)SiO)_4$ in the core molecule. GS–*n*P and GS*n*–*m*Cl refers to the generation of dendritic silanes with dichloromethylsilyl groups in GS–*n* type dendrimers. GS*n*–*m*PA refers to the generation of dendritic silanes with phenylethynyl groups generated from GS*n*P–*m*Cl type dendrimers by the reaction of lithium phenylacethylide. GH–*n* refers to each generation of dendritic silanes with 1,2-bis(triallylsilyl)ethane in the core molecule. GH–*n*P and GH*n*P–*m*Cl refer to the generation of dendritic silanes with dichloromethylsilyl groups in GH–*n* type dendrimers. GH*n*–*m*PA refers to the generation of den-

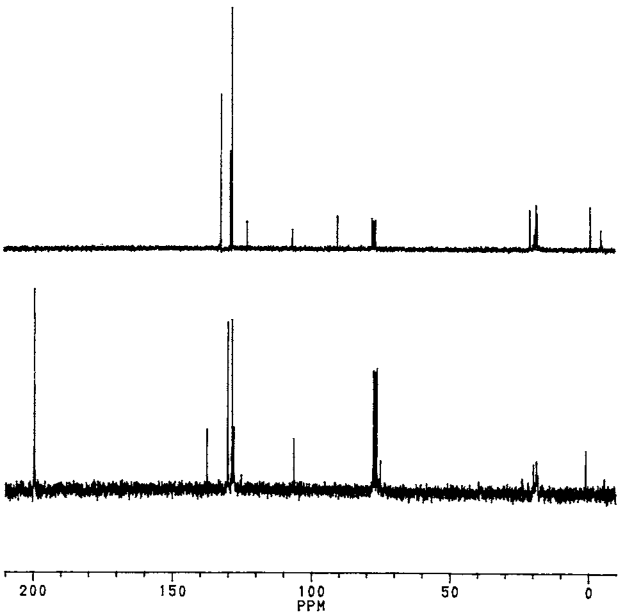


Fig. 1. ^{13}C-NMR spectra of GH3–48PA (top) and GH3–96Co (bottom).

dritic silanes with phenylethynyl groups generated from GH*n*P–*m*Cl type dendrimers by the reaction of lithium phenylacetylide. G–*n* refers to each generation of dendritic silanes with all GH–*n* and GS–*n* types. G*n*–P refers to each generation of dendritic silanes with Si–Cl bonds in GH*n*P–*m*Cl and GS*n*P–*m*Cl. N_c refers to the number of the initial core (in the case of GS–*n*, $N_c = 4$; GH–*n*, $N_c = 6$). N_b refers to the number of branching for each new layer. N_l refers to the number of carbon segments between silicon atoms.

3.1. GH–0

A solution of 9.00g (30.30 mmol) GH–0P, $(Cl_3SiCH_2)_2$ in 50 ml THF was slowly added to 200 ml of allylmagnesium bromide (200 mmol). The reaction mixture was refluxed for 2 h. Solvents were removed under reduced pressure. The salt was precipitated in pentane and filtered off. The volatile components were removed under reduced pressure, leaving 9 g of a colorless liquid. The product, GH–0 $(CH_2{=}CH\text{-}CH_2)_3SiCH_2)_2$, was obtained by distillation at 80°C vacuum as a clear colorless liquid. Yield: 8.61 g (26.03 mmol, 86%) of GH–0. Anal. Calc. for $C_{20}H_{34}Si_2$: C, 72.65; H, 10.36. Found: C, 72.26; H, 10.33. UV–vis (in hexane); λ_{max}: 224 nm, ε_{max}: 218 1 mol^{-1} per cm. ^{1}H-NMR (ppm, $CDCl_3$); $\delta = 0.53$ (s, 4H, CH_2 (G0P)), 1.60 (d, 12H, CH_2, $J = 8$ Hz), 4.73–5.02 (m, 12H, $=CH_2$), 5.64–5.91 (m, 6H, CH=). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = 3.29$ (CH_2 (G0P)), 19.32 (CH_2), 113.55 ($=CH_2$), 134.30 (CH=). For the characterization of GH–*n* ($n = 0$–3) type dendrimers, see ref. [3a].

3.2. GH1P–12Cl

A mixture of 7.64 g (23.12 mmol) of GH-0, 18.00 g (157.47 mmol) of $HSiMeCl_2$ and hydrosilation catalyst (Pt/C, 10% content on activated carbon) in 50 ml toluene was refluxed for 24 h. The solvent and excess dichloromethylsilane were removed by vacuum. The catalyst was filtered off and volatile components were removed by vacuum, leaving 22.72 g of pure GH–1P as a white precipitate. Further purification was not available because of the sensitivity to moisture. By the NMR spectroscopy the yielded compound was only one dendrimer. Yield: 22.72 g (22.41 mmol, 97%) of pure GH1P–12Cl $((Cl_2MeSi(CH_2)_3)_3SiCH_2)_2$. ^{1}H-NMR (ppm, $CDCl_3$); $\delta = 0.77$ (s, 18H, MeSi (G1P)), 0.43 (s, 4H, CH_2 (G0P)), 0.65–0.76 (m, 12H, CH_2), 1.15–1.24 (m, 12H, CH_2), 1.43–1.64 (m, 12H, CH_2). ^{13}C-NMR (ppm, $CDCl_3$); $\delta =$ 5.53 (MeSi (G1P)), 4.28 (CH_2 (G0P)), 15.45, 17.34, 25.89 (CH_2). For the characterization, see reference [3a].

3.3. GH1–12PA

A total of 15ml (15 mmol) of a lithium phenylacetylide solution in THF was slowly added to 1.00 g (0.99 mmol) of GH–1P in 50 ml toluene. After addition was finished, the reaction mixture was refluxed for 4 h. Volatile components were removed under reduced pressure, leaving a yellow precipitate and the salt was precipitated in toluene and filtered off. The prepared compounds were chromatographed on silica gel with chloroform. The product GH1–12PA was obtained as a clear, yellow–brown glass (1.68 g, 0.93 mmol, 95%). Anal. Calc. for $C_{122}H_{118}Si_8$: C, 81.00; H, 6.57. Found: C, 81.18; H, 6.51. IR (KBr, cm^{-1}): 2165 (s, $\nu_{C\equiv C}$), 1584 (w, $\nu_{C=C\ aromatic}$), 3068 (w, $\nu_{C\text{–}H\ aromatic}$). UV–vis (in toluene); λ_{max}: 283nm, ε_{max}: 6158 l mol^{-1} per cm. ^{1}H-NMR (ppm, $CDCl_3$); $\delta = 0.40$ (s, 18H, MeSi (G1P)), 0.48 (s, 4H, CH_2 (G0)), 0.62–0.81 (m, 12H, CH_2 (G0)), 0.81–1.09 (m, 12H, CH_2 (G0)), 1.48–1.80 (m, 12H, CH_2 (G0)), 7.18–7.68 (m, 60H, Ph). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = -1.19$ (MeSi (G1P)), 4.82 (CH_2 (G0)), 16.05, 18.30, 20.69 (CH_2 (G0)), 90.03 (SiC≡), 106.26 (≡CPh), 122.66 ($C_{\text{-}quart}$), 128.12 ($C_{\text{-}o}$), 128.68 ($C_{\text{-}p}$), 132.02 ($C_{\text{-}m}$). MALDI mass *m*/*z* calculated for $C_{122}H_{118}Si_8$, 1809, measured, 1876 (M + Na and K ion).

3.4. GH1–24Co

A mixture of 0.30 g (0.17 mmol) of GH1–12PA and 0.82 g (2.40 mmol) of $Co_2(CO)_8$ in 50 ml toluene was stirred for 12 h at room temperature. The reaction, which was accompanied by the initial evolution of CO, was carried out at room temperature for 12 h. The reaction mixture was evaporated at high vacuum. A dark red powder type solid was dissolved in a minimum

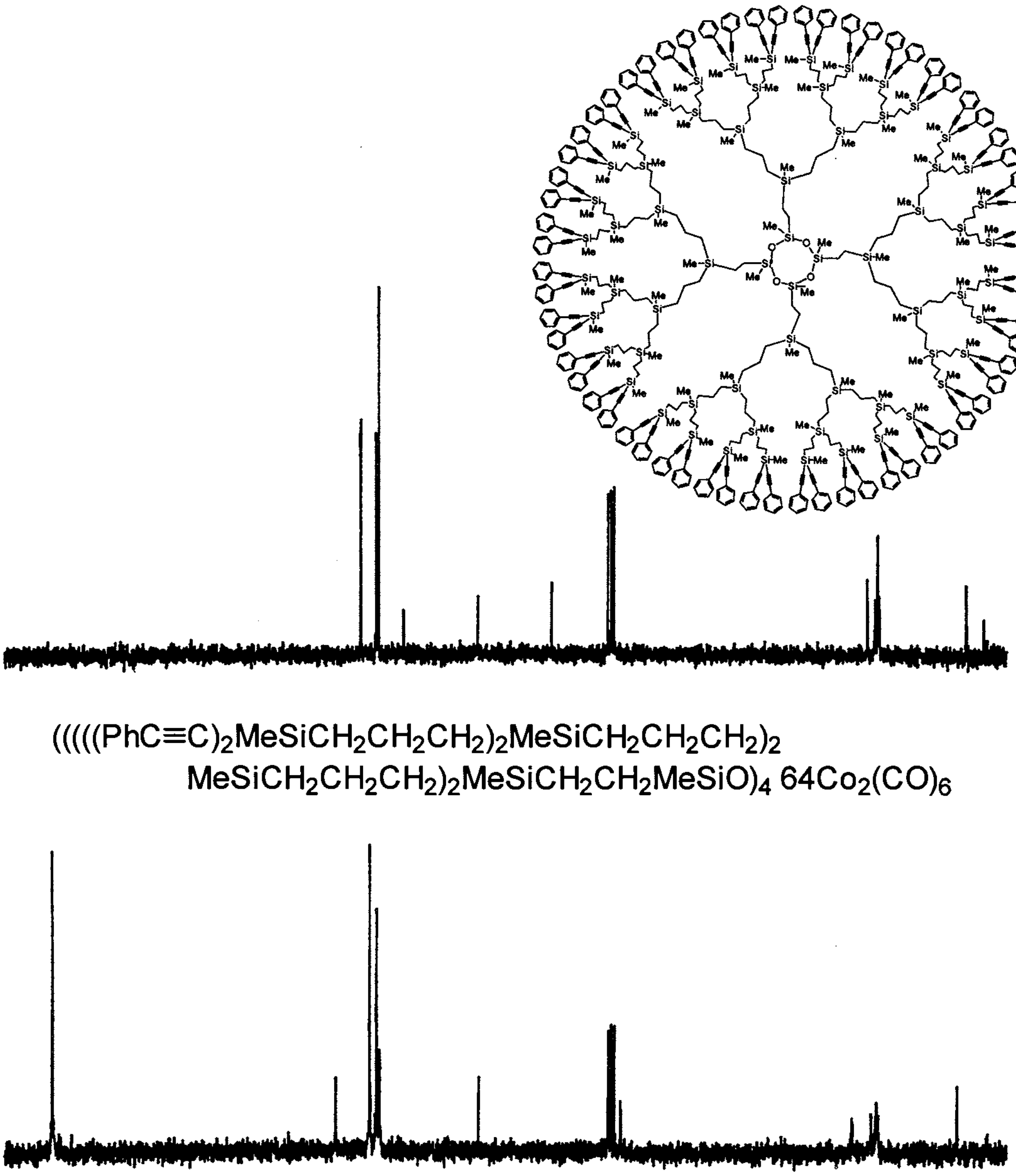


Fig. 2. ^{13}C-NMR spectra of GS4–64PA (top) and GS4–128Co (bottom).

volume of toluene and subjected to column chromatography (silica gel). Recrystallization from acetone, GH1·24Co was obtained as a clear, yellow–brown glass (0.83 g, 0.16 mmol, 96%). Anal. Calc. for $C_{194}H_{118}O_{72}Si_8Co_{24}$: C, 44.45; H, 2.27. Found: C, 43.57; H, 2.33. IR ($\nu_{C\equiv O}$, KBr, cm^{-1}): 2091 (s, CO), 2049 (s, CO), 2024 (s, CO). ^{1}H-NMR (ppm, $CDCl_3$); $\delta = 0.01$–0.18 (m, 4H, CH_2 (G0)), 0.44–0.67 (m, 12H, CH_2 (G0)), 0.92 (s, 18H, MeSi (G1P)), 1.40–1.65 (m, 12H, CH_2 (G0)), 1.65–2.05 (m, 12H, CH_2 (G0)), 7.00–7.81(m, 30H, Ph). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = 1.03$ (MeSi (G1P)), 16.98, 19.94, 24.16 (CH_2 (G0)), 75.02 (SiC≡), 106.28 (≡CPh), 128.09 ($C_{\text{-}m}$), 128.76 ($C_{\text{-}p}$), 130.17 ($C_{\text{-}o}$), 137.62 ($C_{\text{-}quart}$), 199.66 (C≡O).

3.5. GH2–24PA

The same procedure was used in the reaction of 3.70 g (1.52 mmol) of GH2–24Cl and 40 ml (40 mmol) of lithium phenylacethylide in 25 ml THF for 4 h at reflux temperature. Anal. Calc. for $C_{266}H_{286}Si_{20}$: C, 79.01; H, 7.13. Found: C, 78.00; H, 7.29. IR (KBr, cm^{-1}): 2160 (s, $\nu_{C\equiv C}$), 1582 (w, $\nu_{C=C\ \text{aromatic}}$), 3061 (w, $\nu_{C\text{–}H\ \text{aromatic}}$). UV–vis (in toluene); λ_{max}: 283 nm, ε_{max}: 13623 l mol^{-1} per cm. ^{1}H-NMR (ppm, $CDCl_3$); $\delta = 0.00$ (s, 18H, MeSi(G1)), 0.32 (s, 4H, CH_2 (G0)), 0.43 (s, 36H, MeSi (G2P)), 0.50–0.67 (m, 24H, CH_2 (G0)), 0.67–0.82 (m, 24H, CH_2 (G1)), 0.82–1.12 (m, 24H, CH_2 (G1)), 1.12–1.45 (m, 12H, CH_2 (G0)), 1.45–1.79 (m, 24H, CH_2

(G1)), 7.18–7.64 (m, 120H, Ph). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = -4.96$ (MeSi (G1)), -1.04 (MeSi (G2P)), 5.00 (CH_2 (G0)), 17.16, 18.36, 20.66 (CH_2 (G1)), 18.07, 18.59, 19.19 (CH_2 (G0)), 90.09 (SiC≡), 106.37 (≡CPh), 122.73 (C_{-quart}), 128.20 (C_{-o}), 128.77 (C_{-p}), 132.10 (C_{-m}). MALDI mass m/z calculated for $C_{266}H_{286}Si_{20}$, 4040, measured, 4063 (M + Na ion).

3.6. GH2–48Co

The same procedure was used in the reaction of 0.88 g (2.58 mmol) of $Co_2(CO)_8$ and 0.34 g (0.08 mmol) of GH2–24PA in 25 ml of toluene for 1 day at room temperature. Anal. Calc. for $C_{410}H_{286}O_{144}Si_{20}Co_{48}$: C, 45.14; H, 2.64. Found: C, 45.31; H, 2.78. IR ($\nu_{c\equiv o}$, KBr, cm^{-1}): 2091 (s, CO), 2049 (s, CO), 2024 (s, CO). ^{1}H-NMR (ppm, $CDCl_3$); $\delta = -0.01$ (s, 18H, MeSi (G1)), 0.22–0.43 (m, 4H, CH_2 (G0)), 0.45–0.62 (m, 24H, CH_2 (G0)), 0.62–0.80 (m, 24H, CH_2 (G0)), 0.83 (s, 36H, MeSi (G2P)), 1.10–1.55 (m, 12H, CH_2 (G0), 24H, CH_2 (G1)), 1.55–1.92 (m, 24H, CH_2 (G1)), 6.92–7.75 (m, 120H, Ph). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = -7.75$ (MeSi (G1)), 1.13 (MeSi (G2P)), 18.87, 19.92, 24.02 (CH_2 (G0 ~ G1)), 75.08 (SiC≡), 106.34 (≡CPh), 128.65 (C_{-m}), 128.69 (C_{-p}), 130.18 (C_{-o}), 137.64 (C_{-quart}), 199.65 (C≡O).

3.7. GH3–48PA

Anal. Calc. for $C_{554}H_{622}Si_{44}$: C, 78.16; H, 7.37. Found: C, 77.70; H, 7.49. IR (KBr, cm^{-1}): 2159 (s, $\nu_{C\equiv C}$), 1610 (w, $\nu_{C=C\ \mathrm{aromatic}}$), 3057 (w, $\nu_{C-H\ \mathrm{aromatic}}$). UV–vis (in toluene); λ_{max}: 283 nm, ε_{max}: 35674 l mol^{-1} per cm. ^{1}H-NMR (ppm, $CDCl_3$); $\delta = -0.12$ (s, 18H, MeSi (G1)), -0.03 (s, 36H, MeSi (G2)), 0.09 (s, 4H, CH_2 (G0)), 0.39 (s, 72H, MeSi (G3P)), 0.49–0.63 (m, 72H, CH_2 (G0–G1)), 0.63–0.80 (m, 48H, CH_2 (G2)), 0.80–1.10 (m, 48H, CH_2 (G2)), 1.11–1.46 (m, 36H, CH_2 (G0–G1)), 1.47–1.88 (m, 48H, CH_2 (G2)), 7.10–7.58 (m, 240H, Ph). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = -4.90$ (MeSi (G1)), -4.80 (MeSi (G2)), -0.99 (MeSi (G3P)), 18.07, 18.41, 20.69 (CH_2 (G2)), 18.54, 19.04, 19.57 (CH_2 (G0–G1)), 90.17 (SiC≡), 106.41 (≡CPh), 122.79 (C_{-quart}), 128.19 (C_{-o}), 128.75 (C_{-p}), 132.11 (C_{-m}). MALDI mass m/z calculated for $C_{554}H_{622}Si_{44}$, 8506, measured, 8529 (M + Na ion).

3.8. GH3–96Co

Anal. Calc. for $C_{842}H_{622}O_{288}Si_{44}Co_{96}$: C, 45.46; H, 2.82. Found: C, 45.29; H, 2.90. IR($\nu_{c\equiv o}$, KBr, cm^{-1}): 2091(s, CO), 2049 (s, CO), 2024 (s, CO). ^{1}H-NMR (ppm, $CDCl_3$); $\delta = 0.08$ (s, 36H, MeSi (G2)), 0.19 (s, 18H, MeSi (G1)), 0.29–0.42 (m, 4H, CH_2 (G0)), 0.42–0.70 (m, 72H, CH_2 (G0–G1)), 0.70–0.90 (m, 48H, CH_2 (G2)), 0.94 (s, 72H, MeSi (G3P)), 1.20–1.65 (m, 36H, CH_2 (G0–G1), 48H, CH_2 (G2)), 1.65–2.10 (m, 48H, CH_2 (G2)), 7.10–7.80 (m, 240H, Ph). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = -5.49$ (MeSi (G1–G2)), 1.16 (MeSi (G3P)), 18.82, 19.94 (CH_2 (G0 ~ G2)), 75.04 (SiC≡), 106.38 (≡CPh), 128.03 (C_{-m}), 128.68 (C_{-p}), 130.19 (C_{-o}), 137.64 (C_{-quart}), 199.66 (C≡O).

3.9. GS1–8PA

Anal. Calc. for $C_{80}H_{80}Si_8O_4$: C, 72.24; H, 6.06. Found: C, 71.05; H, 6.12. IR (KBr, cm^{-1}): 2159 (s, $\nu_{C\equiv C}$), 1599 (w, $\nu_{C=C\ \mathrm{aromatic}}$), 3075 (w, $\nu_{C-H\ \mathrm{aromatic}}$). UV–vis (in toluene); λ_{max}: 284 nm, ε_{max}: 4826 l mol^{-1}

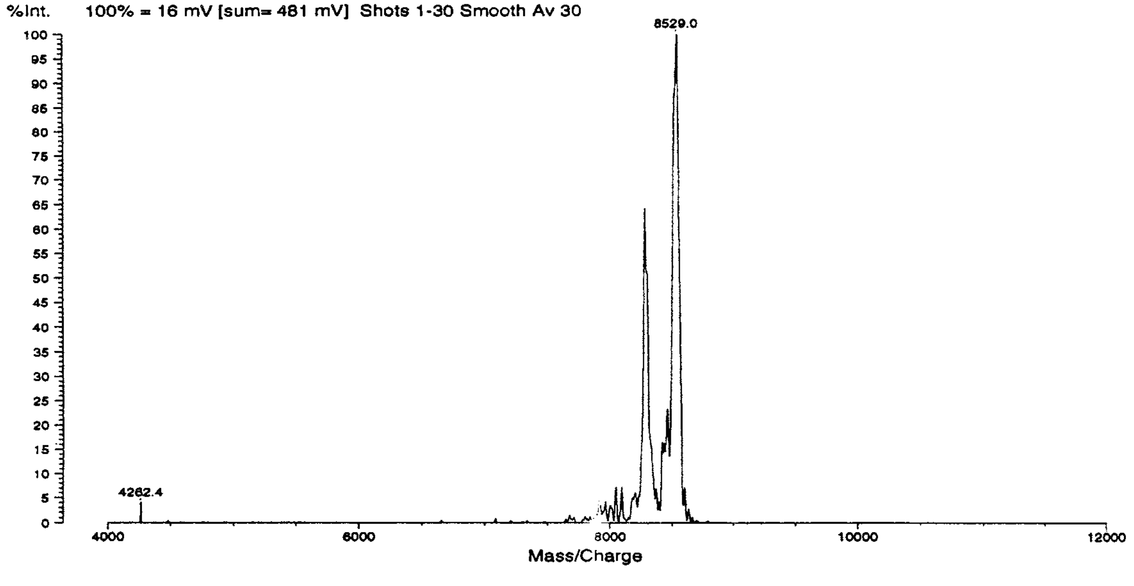


Fig. 3. MALDI mass spectrum of GH3–48PA.

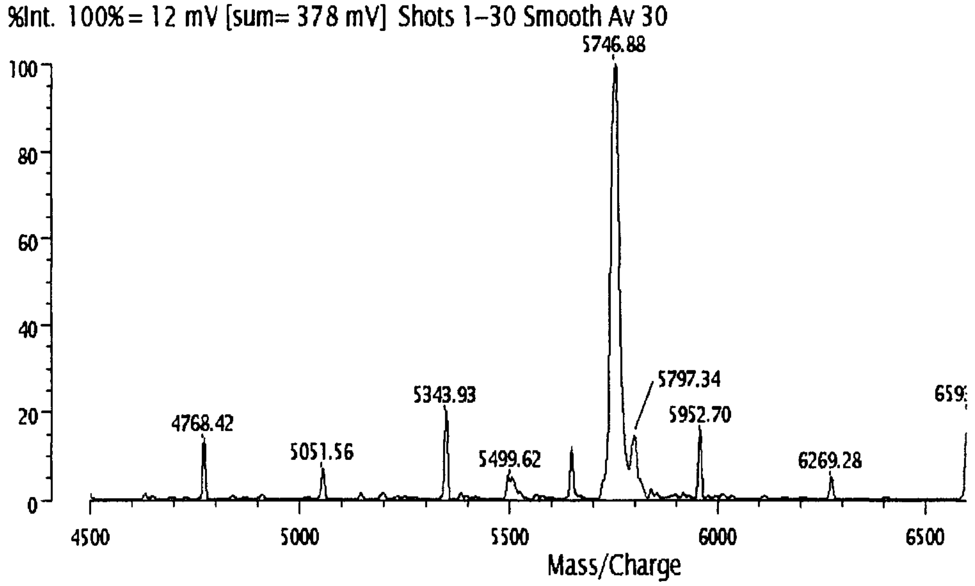


Fig. 4. MALDI mass spectrum of GS3–32PA.

per cm. ^{1}H-NMR (ppm, $CDCl_3$); $\delta = 0.13$ (s, 12H, MeSi (G0)), 0.40 (s, 12H, MeSi (G1P)), 0.61–0.93 (m, 16H, CH_2 (G0)), 7.07–7.52 (m, 40H, Ph). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = -1.81$ (MeSi (G0)), -1.32 (MeSi (G1P)), 8.02, 9.06 (CH_2 (G0)), 89.82 (SiC≡), 106.33 (≡C–Ph), 128.16 (C_{-quart}), 128.73 (C_{-o}), 128.83 (C_{-p}), 132.17 (C_{-m}). MALDI mass m/z calculated for $C_{80}H_{80}Si_8O_4$, 1330, measured, 1373 (M + K ion).

3.10. GS2–16PA

Anal. Calc. for $C_{176}H_{192}Si_{16}O_4$: C, 74.94; H, 6.86. Found: C, 74.30; H, 6.97. IR(KBr, cm^{-1}): 2157 (s, $\nu_{C\equiv C}$), 1596 (w, $\nu_{C=C\ aromatic}$), 3079 (w, $\nu_{C-H\ aromatic}$). UV–vis (in toluene); λ_{max}: 284 nm, ε_{max}: 10426 l mol^{-1} per cm. ^{1}H-NMR (ppm, $CDCl_3$); $\delta = -0.023$ (s, 12H, MeSi (G1)), -0.020 (s, 12H, MeSi (G0)), 0.22 (s, 16H, CH_2 (G0)), 0.39 (s, 24H, MeSi (G2P)), 0.61–0.75 (m, 16H, CH_2 (G1)), 0.75–0.99 (m, 16H, CH_2 (G1)), 1.41–1.70 (m, 16H, CH_2 (G1)), 7.18–7.55 (m, 80H, Ph). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = -4.54$ (MeSi (G1)), -1.01 (MeSi (G0)), -1.07 (MeSi (G2P)), 5.91, 9.98 (CH_2 (G0)), 17.42, 18.34, 20.67 (CH_2 (G1)), 90.05 (SiC≡), 106.35 (≡CPh), 122.71 (C_{-quart}), 128.19 (C_{-o}), 128.77 (C_{-p}), 132.10 (C_{-m}). MALDI mass m/z calculated for $C_{176}H_{192}Si_{16}O_4$, 2821, measured, 2844 (M + Na ion).

3.11. GS2–32Co

IR ($\nu_{C\equiv O}$, KBr, cm^{-1}): 2091 (s, CO), 2049 (s, CO), 2024 (s, CO). ^{1}H-NMR (ppm, $CDCl_3$); $\delta = 0.04$ (s, 12H, MeSi (G1)), 0.15 (s, 12H, MeSi (G0)), 0.40 (s, 16H, CH_2 (G0)), 0.67–0.83 (m, 16H, CH_2 (G1)), 0.91 (s, 24H, SiMe (G2P)), 1.31–1.58 (m, 16H, CH_2 (G1)), 1.58–1.92 (m, 16H, CH_2 (G1)), 7.09–7.71 (m, 80H, Ph). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = 1.05$ (SiMe (G2P)), 5.90, 8.90 (CH_2 (G0)), 17.9, 19.29, 20.81 (CH_2, (G0–G1)), 74.92 (SiC≡), 106.27 (≡CPh), 128.05 (C_{-m}), 128.71 (C_{-p}), 130.16 (C_{-o}), 137.62 (C_{-quart}), 199.64 (C≡O).

3.12. GS3–32PA

Anal. Calc. for $C_{368}H_{416}Si_{32}O_4$: C, 76.18; H, 7.23. Found: C, 76.04; H, 7.17. IR (KBr, cm^{-1}): 2161 (s, $\nu_{C\equiv C}$), 1595 (w, $\nu_{C=C\ aromatic}$), 3079 (w, $\nu_{C-H\ aromatic}$). UV–vis (in toluene); λ_{max}: 284 nm, ε_{max}: 18 241 l mol^{-1} per cm. ^{1}H-NMR (ppm, $CDCl_3$); $\delta = -0.15$ (s, 12H, MeSi (G1)), -0.03 (s, 24H, MeSi (G2)), 0.05 (s, 12H, MeSi (G0)), 0.35 (s, 16H, CH_2 (G0)), 0.39 (s, 48H, MeSi (G3P)), 0.49–0.67 (m, 32H, CH_2 (G1)), 0.67–0.81 (m, 32H, CH_2 (G2)), 0.88–1.03 (m, 32H, CH_2 (G2)), 1.18–1.39 (m, 16H, CH_2 (G1)), 1.50–1.72 (m, 32H, CH_2 (G2)), 7.18–7.52 (m, 160H, Ph). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = -5.08$ (MeSi (G1–G2)), -1.05 (MeSi (G0)), -1.03 (MeSi (G3P)), 5.41, 9.01 (CH_2 (G0)), 18.05, 18.38, 20.67 (CH_2 (G2)), 18.54, 18.92 (CH_2

Table 1
UV spectroscopic data of G*n*–*m*PA type dendrimers

	χ [a]	λ_{max}	ε_{max}	ε_{max}/χ
GS1–8PA	8	284	4826	603
GS2–16PA	16	284	10 426	651
GS3–32PA	32	284	24241	757
GH1–12PA	12	283	6158	513
GH2–24PA	24	283	13 623	567
GH3–48PA	48	283	35674	743

[a] χ, number of triple bonds.

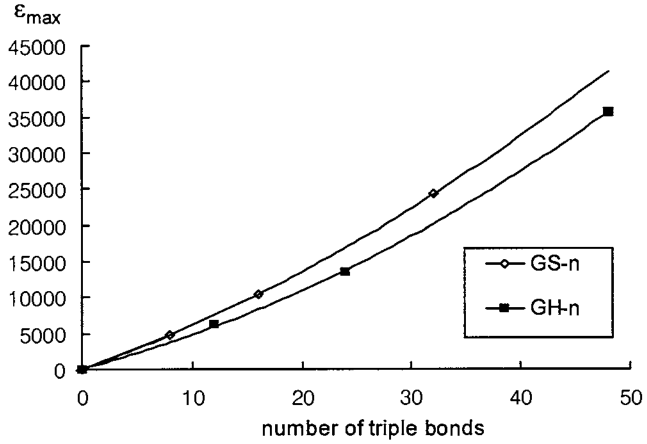


Fig. 5. Plots of ε_{max} vs. number of triple bonds of G*n*–*m*PA dendrimers.

(G1)), 90.12 (SiC≡), 106.38 (≡CPh), 122.76 (C_{-quart}), 128.19 (C_{-o}), 128.76 (C_{-p}), 132.10 (C_{-m}). MALDI mass *m*/*z* calculated for $C_{368}H_{416}Si_{32}O_4$, 5802, measured, 5797 (M ion).

3.13. GS3–64Co

Anal. Calc. for $C_{560}H_{416}O_{196}Si_{32}Co_{64}$: C, 44.99; H, 2.80. Found: C, 42.45; H, 2.78. IR ($\nu_{C\equiv O}$, KBr, cm^{-1}): 2091 (s, CO), 2049 (s, CO), 2024 (s, CO). ^{1}H-NMR (ppm, $CDCl_3$); $\delta = -0.06$ (s, 24H, MeSi (G2)), -0.02 (s, 12H, MeSi (G1)), 0.07 (s, 12H, SiMe (G0)), 0.40 (s, 16H, CH_2 (G0)), 0.49–0.61 (m, 32H, CH_2 (G1)), 0.61–0.79 (m, 32H, CH_2 (G2)), 0.84 (s, 48H, SiMe (G3P)), 1.21–1.55 (m, 16H, CH_2 (G1), 32H, CH_2 (G2)), 1.55–1.81 (m, 32H, CH_2 (G2)), 7.06–7.55 (m, 160H, Ph). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = -5.10$ (MeSi (G1–G2)), -2.52 (MeSi (G0)), 1.06 (SiMe (G3P)), 18.74, 19.88, 24.10 (CH_2, (G0–G2)), 74.94 (SiC≡), 106.26 (≡CPh), 128.00 (C_{-m}), 128.66 (C_{-p}), 130.13 (C_{-o}), 137.59 (C_{-quart}), 199.62 (C≡O).

3.14. GS4–64PA

Anal. Calc. for $C_{752}H_{864}Si_{64}O_4$: C, 76.77; H, 7.40. Found: C, 76.46; H, 7.41. ^{1}H-NMR (ppm, $CDCl_3$); $\delta = -0.16$ (s, 12H, MeSi (G1)), -0.05 (s, 48H, MeSi (G3)), -0.02 (s, 24H, MeSi (G2)), 0.06 (s, 12H, MeSi (G0)), 0.38 (s, 16H, CH_2 (G0)), 0.41 (s, 96H, MeSi (G4P)), 0.42–0.61 (m, 96H, CH_2 (G1–G2)), 0.61–0.80 (m, 64H, CH_2 (G3)), 0.80–0.99 (m, 64H, CH_2 (G3)), 1.08–1.39 (m, 48H, CH_2 (G1–G2)), 1.47–1.70 (m, 64H, CH_2 (G3)), 7.15–7.58 (m, 320H, Ph). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = -4.94$ (MeSi (G1–G3)), -1.01 (MeSi (G0)), -1.02 (MeSi (G4P)), 18.05, 18.37, 20.65 (CH_2 (G3)), 18.91, 19.45 (CH_2 (G1–G2)), 90.08 (SiC≡), 106.36 (≡CPh), 122.73 (C_{-quart}), 128.19 (C_{-o}), 128.77 (C_{-p}), 132.09 (C_{-m}).

3.15. GS4–128Co

Anal. Calc. for $C_{1136}H_{864}O_{388}Si_{64}Co_{128}$: C, 45.38; H, 2.90. Found: C, 43.96; H, 2.89. IR ($\nu_{C\equiv O}$, KBr, cm^{-1}): 2091 (s, CO), 2049 (s, CO), 2024 (s, CO). ^{1}H-NMR (ppm, $CDCl_3$); $\delta = -0.20$ (s, 48H, MeSi (G3)), -0.19 (s, 36H, MeSi (G1–G2)), -0.09 (s, 12H, MeSi (G0)), 0.15–0.30 (m, 16H, CH_2 (G0)), 0.30–0.48 (m, 96H, CH_2 (G1–G2)), 0.48–0.64 (m, 64H, CH_2 (G3)), 0.68 (s, 96H, MeSi (G4P)), 1.01–1.39 (m, 48H, CH_2 (G1–G2), 64H, CH_2 (G3)), 1.39–1.62 (m, 64H, CH_2 (G3)), 6.81–7.38 (m, 320H, Ph). ^{13}C-NMR (ppm, $CDCl_3$); $\delta = -5.92$ (MeSi (G1–G3)), 1.08 (MeSi (G4P)), 18.76, 19.95, 25.90 (CH_2 (G0–G3)), 74.94 (SiC≡), 106.28 (≡CPh), 128.02 (C_{-m}), 129.03 (C_{-p}), 130.16 (C_{-o}), 137.61 (C_{-quart}), 199.64 (C≡O).

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