

Convergent Synthesis of Platinum–Acetylide Dendrimers

Kiyotaka Onitsuka,* Masanori Fujimoto, Hotaka Kitajima, Nobuaki Ohshiro, Fumie Takei, and Shigetoshi Takahashi^[a]

Abstract: An efficient convergent route to the main chain type of organometallic dendrimers, in which platinum moieties are linked by 1,3,5-triethynylbenzene, has been developed. The synthesis of platinum–acetylide dendrons involved the use of two types of trialkylsilyl groups for protection of the terminal acetylene. The platinum–acety-

lide dendrimers were prepared up to the third generation by reacting dendrons with a triplatinum core and a tetraplatinum core. Spectroscopic characterization and trace experiments by gel

Keywords: acetylene • acetylide complex • dendrimers • platinum

permeation chromatography indicated that the dendrimer molecules have no structural defects. Although a π -conjugated system was used as the bridging ligand, electronic and fluorescence spectra suggested that the interaction among the platinum–acetylide moieties in the dendrimers was small.

Introduction

Dendrimers possessing a regularly branched architecture and large spherical dimensions have attracted significant attention because of their unique and tunable properties as well as their potential applications.^[1] Recently, organometallic dendrimers have been the focus of considerable interest because the organometallic species may introduce new functionalities, such as catalysis, multiredox systems, and molecular recognition ability, to the dendritic molecule.^[2] Organometallic dendrimers offer the advantage of molecular design of dendrimers with desirable functionalities, not only because of the availability of a wide variety of organic compounds that coordinate to many types of metal atoms, but also the flexibility of the coordination modes of organic ligands to the metal. Thus, a variety of organometallic dendrimers have been prepared so far. However, most of them contain metal species at specific positions in the molecule, such as at the core or at the periphery. Such organometallic dendrimers can be prepared by a combination of successive organic reactions and a single organometallic reaction, as their dendritic skeletons consist of organic compounds. On the other hand, dendrimers composed of organometallic complexes in each generation are still limited in number, although they are expected to emerge as a new type of hybrid

material.^[3–6] Because of the intrinsic low stability of organometallic complexes compared to organic compounds, the appropriate choice of the repeating unit is very important for the construction of organometallic dendrimers.

We have long been interested in the chemistry of organometallic macromolecules composed of transition-metal–acetylide complexes,^[7] which are fairly stable and easily prepared by well-established reactions.^[8] As it is well known that some metal acetylides show unique properties, metal–acetylide dendrimers are expected to have potential use in the fabrication of new materials.^[9–12] Using triethynylmesitylene as the bridging ligand, we have previously reported the synthesis of platinum–acetylide dendrimers up to the second generation.^[13] However, extension to higher generation dendrimers was difficult, because in the absence of protecting groups, much effort was required to isolate the resulting dendrimer from the reaction mixture. We report herein an efficient synthesis of platinum–acetylide dendrimers through a convergent route. The preliminary results have been reported elsewhere.^[14]

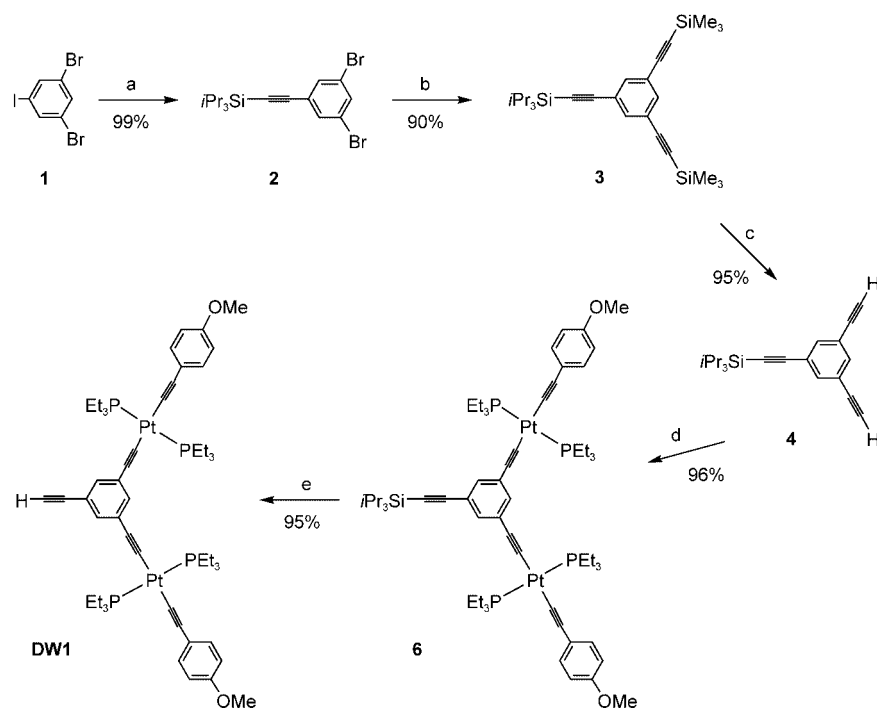
Results and Discussion

There are two key points for the efficient synthesis of platinum–acetylide dendrimers. One is that two types of trialkylsilyl groups—trimethylsilyl and triisopropylsilyl—are used as the protecting group of the terminal acetylene.^[15] The other is that the formation and/or cleavage of the Pt–C bond is controlled by the ratio of the terminal acetylene to the platinum complex as well as by the reaction temperature.^[16] The reaction of a chloroplatinum complex with terminal acety-

[a] Dr. K. Onitsuka, M. Fujimoto, H. Kitajima, Dr. N. Ohshiro, Dr. F. Takei, Prof. Dr. S. Takahashi
The Institute of Scientific and Industrial Research
Osaka University, Mihogaoka, Ibaraki, Osaka 567-0047 (Japan)
Fax: (+81) 6-6879-8459
E-mail: onitsuka@sanken.osaka-u.ac.jp

lene at room temperature in the presence of a copper(i) catalyst led to the formation of a new Pt–C bond, but no cleavage took place. On the other hand, a chloro(ethynyl)platinum complex was formed in the reaction of a dichloroplatinum complex with one equivalent of terminal acetylene through the proportionation between dichloroplatinum and diethynylplatinum complexes.

The synthetic route to the first-generation dendron (**DW1**) is shown in Scheme 1. Treatment of 1,3-dibromo-5-iodobenzene (**1**), which was prepared from 2,6-dibromo-4-nitroaniline in three steps (see the Experimental Section)



Scheme 1. Synthesis of first-generation dendron **DW1**. a) $\text{HC}\equiv\text{CSi-}i\text{Pr}_3$, $[\text{PdCl}_2(\text{PPh}_3)_2]$ (cat.), CuI (cat.), Et_2NH , room temperature, 2 days; b) $\text{HC}\equiv\text{CSiMe}_3$, $[\text{PdCl}_2(\text{PPh}_3)_2]$ (cat.), CuI (cat.), Et_3N , benzene, reflux, overnight; c) K_2CO_3 (aq), acetone, room temperature, overnight; d) $[\text{Pt}(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-}p)\text{Cl}(\text{PEt}_3)_2]$ (**5**) (2 equiv), CuI (cat.), Et_2NH , room temperature, overnight; e) Bu_4NF , THF, -78°C to room temperature, 3 h.

with one equivalent of triisopropylsilylacetylene at room temperature in the presence of $[\text{PdCl}_2(\text{PPh}_3)_2]/\text{CuI}$ catalysts in diethylamine, led to the selective formation of the mono-(silylethynyl) derivative (**2**).^[17] The reaction of **2** with excess trimethylsilylacetylene in triethylamine under reflux gave trisilylethynyl derivative **3** quantitatively. The two trimethylsilyl groups in **3** were selectively removed by treatment with K_2CO_3 in acetone to give **4** that has two terminal acetylenic groups in the molecule. The surface groups of the dendrimer, (*p*-methoxyphenyl)ethynylplatinum moieties, were introduced by reacting **4** with two equivalents of platinum complex **5** in the presence of a CuI catalyst at room temperature to give the dinuclear acetylide complex (**6**). Removal of the triisopropylsilyl group in **6** by treatment with Bu_4NF gave the first-generation dendron **DW1**, the molecular structure of which was determined by using X-ray analysis.^[14]

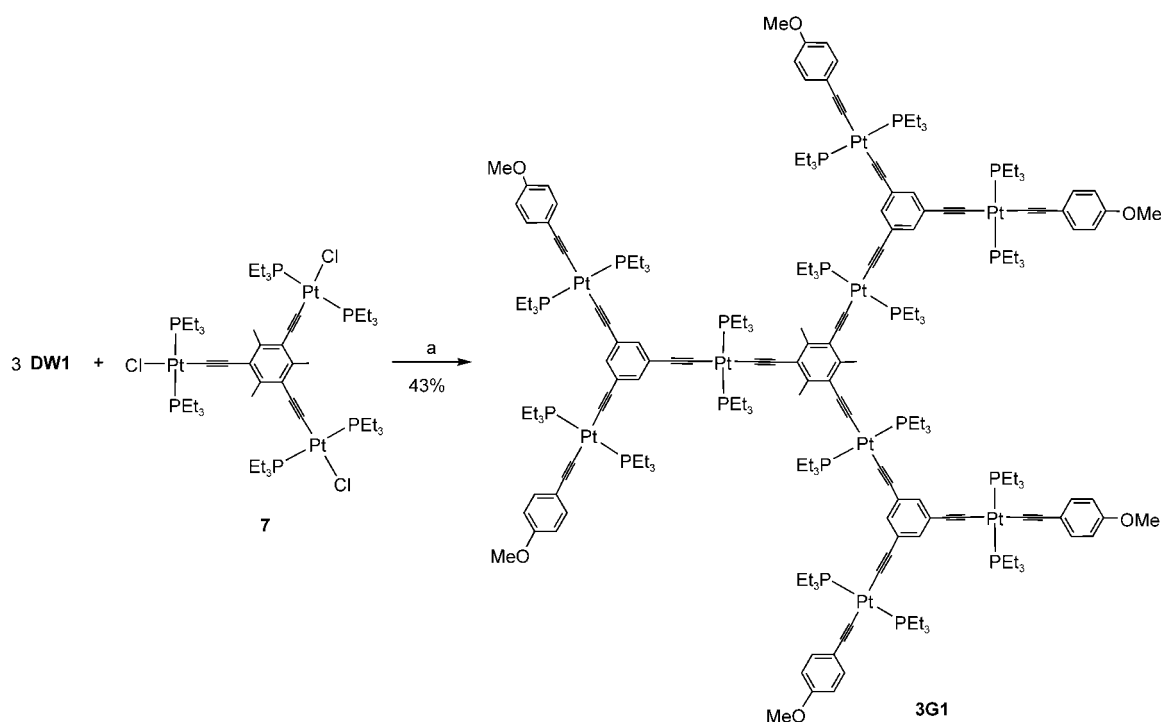
The trinuclear platinum–acetylide complex (**7**) bridged by 1,3,5-triethynylmesitylene was used as the core of the convergent synthesis.^[13] The three methyl groups on the bridging ligand played an important role in the characterization of the dendrimers by using ^1H NMR spectroscopy (see later). The reaction of core **7** with three equivalents of **DW1** gave the first-generation dendrimer (**3G1**) containing nine platinum atoms per molecule (Scheme 2). Characterization of **3G1** was performed by using gel permeation chromatography (GPC) analysis as well as ^1H and ^{31}P NMR spectroscopic methods. As core **7** and **DW1** had fairly large molecular

sizes, it was easy to detect whether product **3G1** contained impurities consisting of different ratios of **7** to **DW1** by using GPC analysis. The narrow single GPC profile clearly indicated that **3G1** was isolated as a pure form. The ^{31}P NMR spectrum of **3G1** exhibited two singlets at $\delta = 10.9$ ($J_{\text{P-Pt}} = 2381$ Hz) and 11.1 ppm ($J_{\text{P-Pt}} = 2392$ Hz) in a 2:1 integral ratio, which were due to phosphine ligands bound to six outer and three inner platinum atoms, respectively. The signals lay in the typical region for the $(-\text{C}\equiv\text{C})_2\text{Pt}(\text{PEt}_3)_2$ moiety, whereas no signal was observed at approximately $\delta = 15$ ppm, which is a typical chemical shift for the $(-\text{C}\equiv\text{C})\text{PtCl}(\text{PEt}_3)_2$ moiety (**7**: $\delta = 15.3$ ppm). The ^1H NMR spectrum of **3G1** showed two singlets at $\delta = 2.57$ and 3.78 ppm in a 1:2 integral ratio; the former signal was assignable to the methyl protons of the central mesitylene and the latter to the methoxy protons of the end group. These data

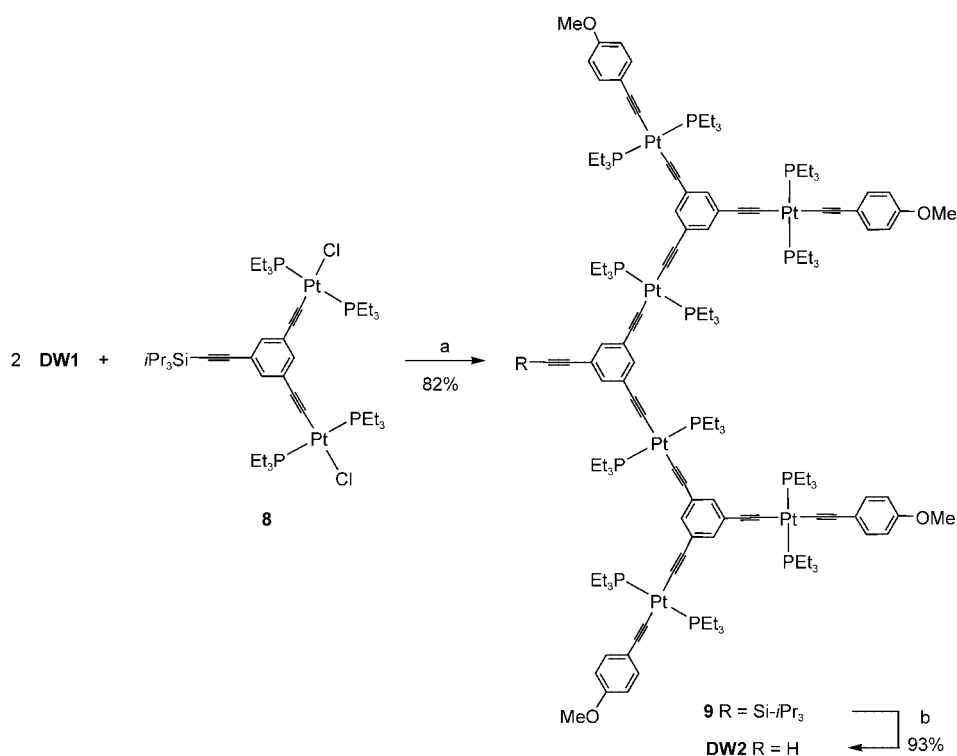
are consistent with the expected structure of **3G1**, which is also supported by elemental analysis.

To grow **DW1** into higher generation dendrons, a building block (**8**) having two chloro(ethynyl)platinum moieties and one protected acetylene moiety was required. Building block **8** was prepared by reacting **4** with a slight excess of $[\text{PtCl}_2(\text{PEt}_3)_2]$ in refluxing piperidine in the presence of a CuI catalyst. The reaction of **DW1** with **8** in a 2:1 ratio gave the protected second-generation dendron (**9**), which was converted into the second-generation dendron (**DW2**) by desilylation with Bu_4NF (Scheme 3). As shown in Scheme 4, similar treatments of **DW2** led to the formation of the third-generation dendron (**DW3**), and further treatments led to the fourth-generation dendron (**DW4**).

The treatment of **DW2** or **DW3** with core **7** in a 3:1 ratio gave the second-generation dendrimer (**3G2**) or the third-generation dendrimer (**3G3**), respectively (Scheme 5). In



Scheme 2. Synthesis of first-generation dendrimer **3G1**. a) CuI (cat.), Et₂NH, room temperature, overnight.



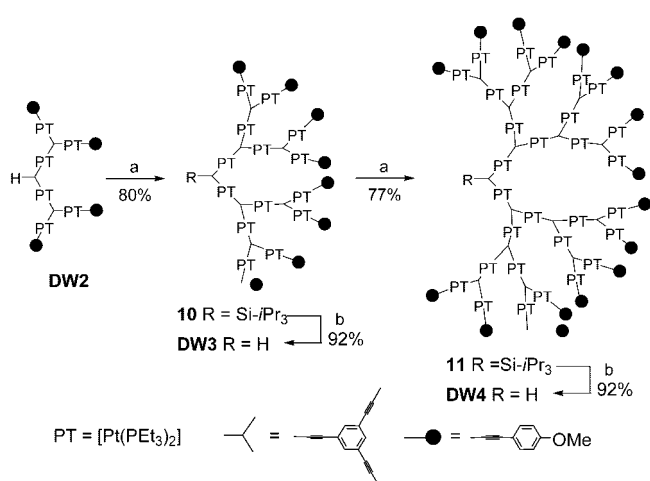
Scheme 3. Synthesis of second-generation dendron **DW2**. a) CuI (cat.), Et₂NH, room temperature, overnight; b) Bu₄NF, THF, –78 °C to room temperature, 3 h.

these cases, dendrons **DW2** and **DW3** were completely consumed at the end of the reactions. However, a considerable amount of unreacted **DW4** was detected in the reaction of **DW4** with **7** under similar conditions (Scheme 6). GPC anal-

ysis suggested that not only the fourth-generation dendrimer (**3G4**) but also another product (**10**) having a smaller molecular size than **3G4** was formed in this reaction. Although we were unable to separate them, product **10** must be an incomplete dendritic complex that consisted of one molecule of **7** and two molecules of **DW4**, as a small signal was observed at approximately $\delta = 15$ ppm in the ³¹P NMR spectrum of the product. Although we attempted to prepare **3G4** under severe conditions, all our efforts were unsuccessful. For example, the reaction at a higher temperature led to give polymers with a fairly wide molecular distribution along with smaller platinum–acetylide complexes.

Steric repulsion among dendrons of **DW4** might be one of the possible reasons for the difficulty in the synthesis of **3G4**.

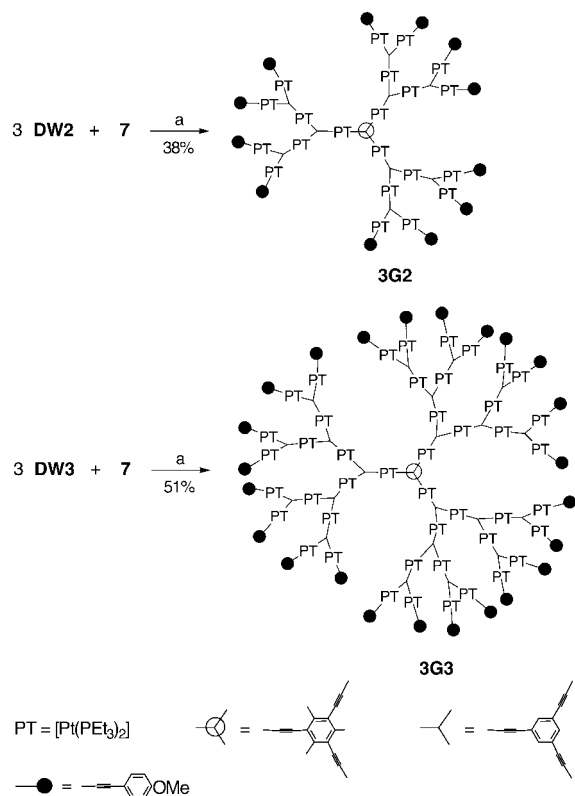
In order to decrease the steric repulsion, we designed a new core (**18**), the three platinum atoms of which were linked by an acetylene ligand with long tethers, as shown in Scheme 7. The treatment of core **18** with three equivalents of **DW4** led to the formation of **3G4**



Scheme 4. Synthesis of third- and fourth-generation dendrons **DW3** and **DW4**. a) 1/2 **8**, CuI (cat.), Et₂NH, room temperature, overnight; b) Bu₄NF, THF, -78 °C to room temperature, 3 h.

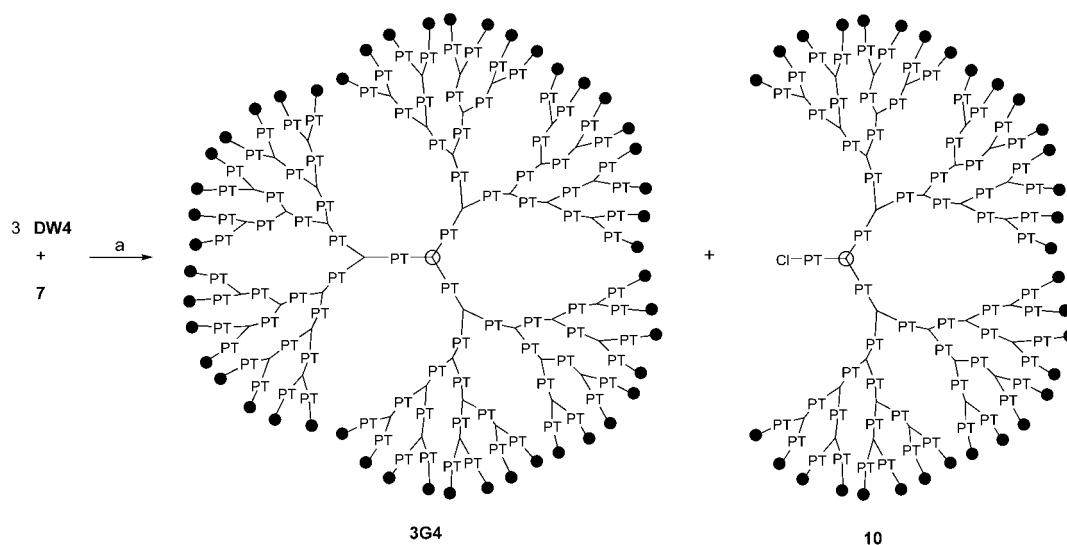
as well as defective dendrimer (**19**) in which two units of dendron **DW4** were attached to **18** (Scheme 8). The reaction using six equivalents of **DW4** relative to **18** did not result in the selective formation of **3G4'**. When we examined the reaction using diplatinum core **20**,^[18] the desired dendrimer (**3G4''**) was partially formed, but fairly large amounts of **DW4** and monosubstituted product (**21**) remained (Scheme 9). Although cores **18** and **20** might not provide a solution to the steric repulsion among dendrons of **DW4**, another reason for the difficulty in the synthesis of fourth-generation dendrimers should be taken into account. As dendron **DW4** has 30 platinum moieties per molecule, the terminal acetylene group at the focal point (the reaction point with the core) might be covered by the platinum–acetylide moieties.

Mass spectrometry is a powerful tool for the characterization of large dendrimers. However, no molecular ion peaks

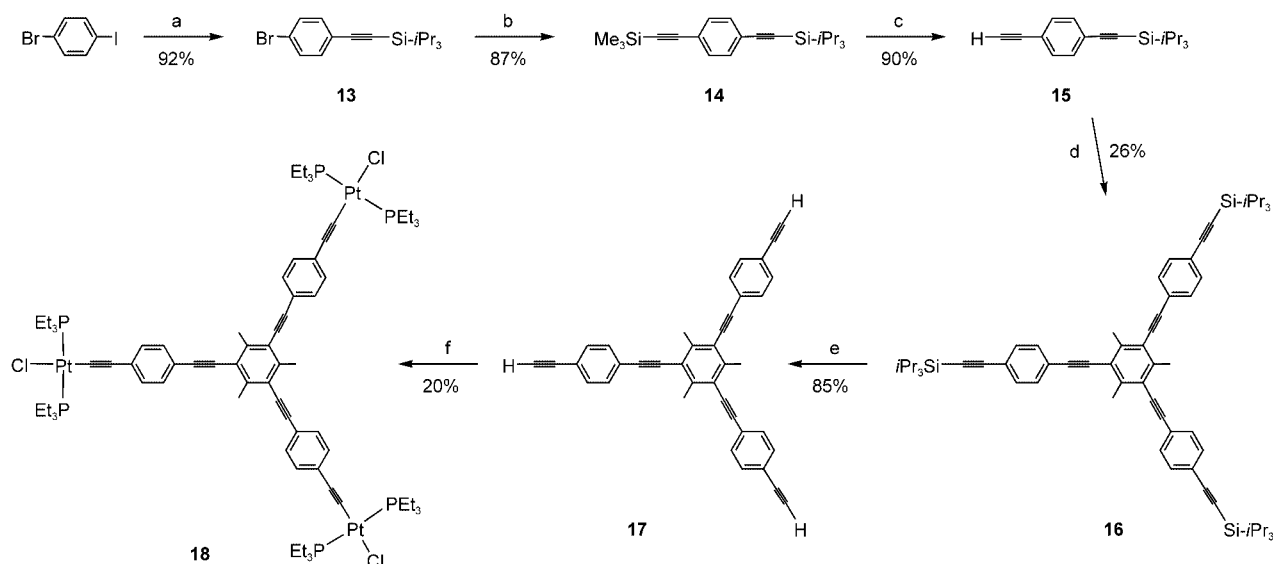


Scheme 5. Synthesis of second- and third-generation dendrons **3G2** and **3G3**. a) CuI (cat.), Et₂NH, room temperature, overnight.

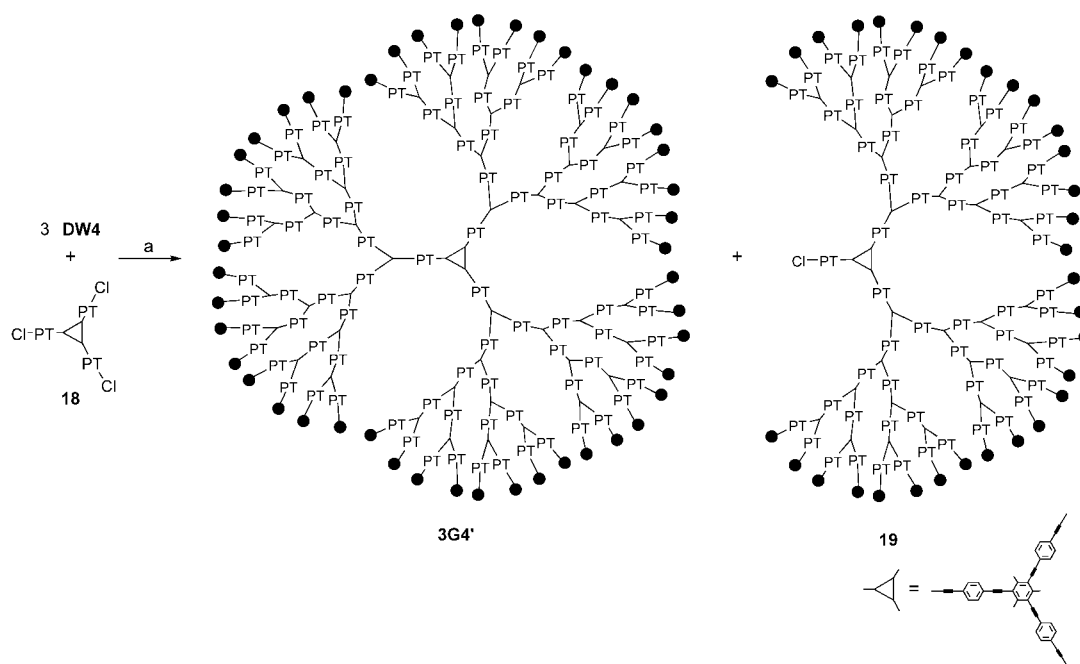
were detected even in matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) and electrospray ionization (ESI) mass spectra. Therefore, the third-generation dendrimer was characterized by using ¹H and ³¹P NMR spectroscopic methods. The ¹H NMR spectrum of **3G3** is given in Figure 1, which is very simple in spite of being an extremely large molecule (*M_r* = 25 840), indicating the highly symmetric structure of **3G3**. Two singlets were observed at



Scheme 6. Reaction of fourth-generation dendron **DW4** with **7**. a) CuI (cat.), Et₂NH, room temperature.



Scheme 7. Synthesis of triplatinum core **18** with long tethers. a) $\text{HC}\equiv\text{CSi-}i\text{Pr}_3$, $[\text{PdCl}_2(\text{PPh}_3)_2]$ (cat.), CuI (cat.), Et_2NH , room temperature, 2 days; b) $\text{HC}\equiv\text{CSiMe}_3$, $[\text{PdCl}_2(\text{PPh}_3)_2]$ (cat.), CuI (cat.), Et_3N , benzene, reflux, overnight; c) K_2CO_3 (aq), acetone, room temperature, overnight; d) 2,4,6-triiodomesitylene (1/3 equiv), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (cat.), CuI (cat.), Et_2NH , THF, reflux, 1 week; e) Bu_4NF , THF, -78°C to room temperature, 3 h; f) $[\text{PtCl}_2(\text{PEt}_3)_2]$ (3.3 equiv), CuI (cat.), piperidine, toluene, reflux, 1 week.



Scheme 8. Reaction of fourth-generation dendron **DW4** with **18**. a) CuI (cat.), Et_2NH , room temperature.

$\delta = 2.57$ and 3.77 ppm, which were due to the central methyl groups and the methoxy end groups, respectively, in a 1:8 integral ratio. The ^{31}P NMR spectrum of **3G3** showed only two signals at $\delta = 10.8$ ($J_{\text{P-Pt}} = 2381$ Hz) and 11.0 ppm (coupling constant $J_{\text{P-Pt}}$ could not be determined because the satellite signals were too weak to be detected) in an approximately 14:1 integral ratio, the latter of which was assigned to the six central phosphine ligands, and the former, to the other eighty-four phosphine ligands. These spectral data

clearly supported the proposed structure of **3G3**. The narrow profile obtained by using GPC analysis unequivocally excluded the interfusion of defective dendrimers because the cleavage of the Pt–C bond does not take place at room temperature.

Following this, we tried to prepare the platinum–acetylide dendrimers by using a tetraplatinum core (**22**), the bridging ligand of which was derived from tetraphenylmethane.^[19] The molecular structure of **22** was determined by using X-

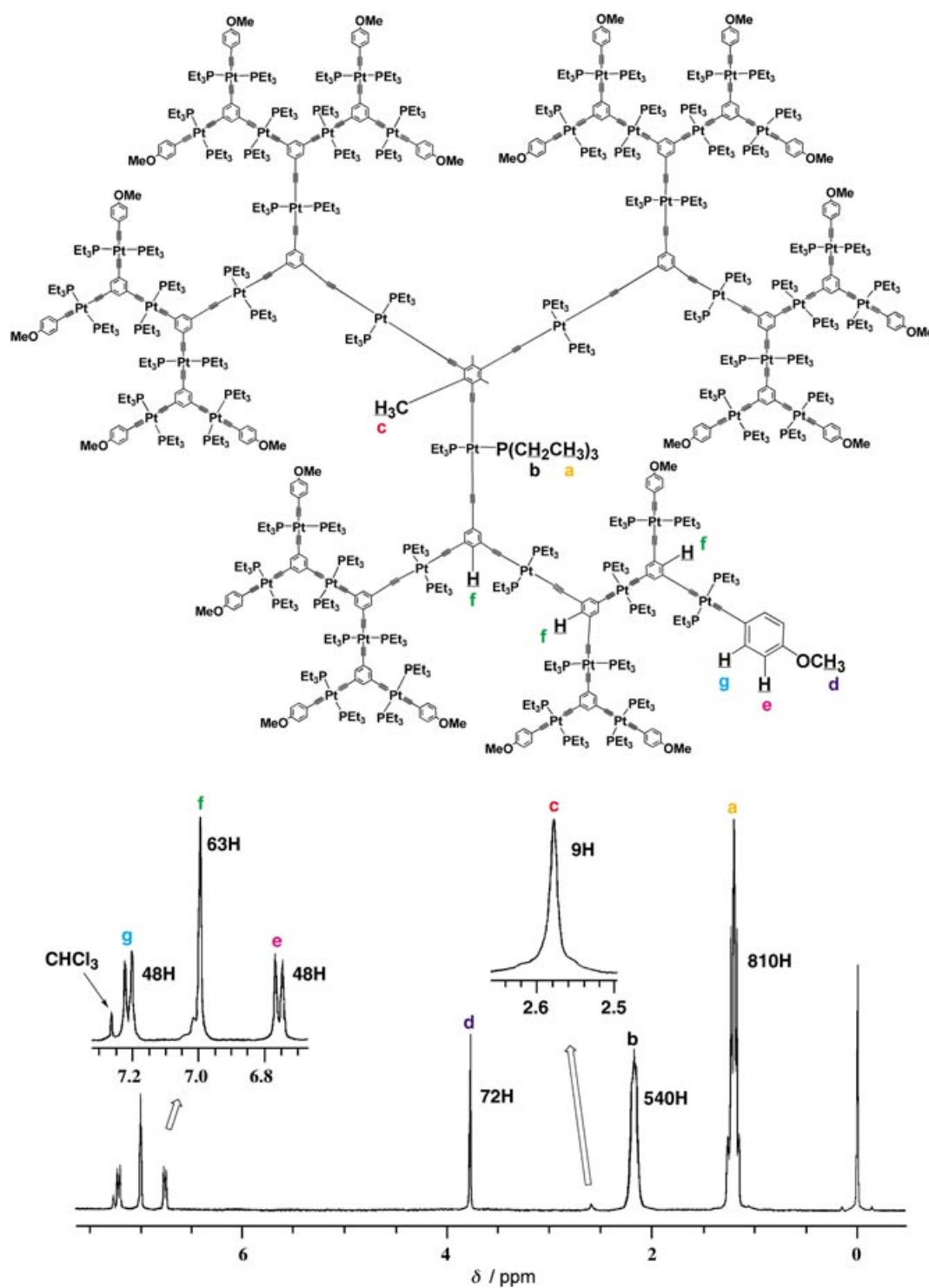
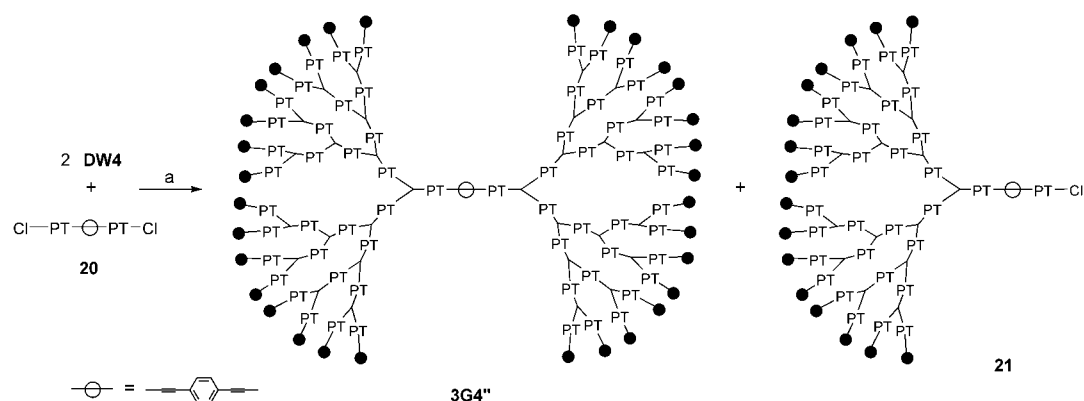
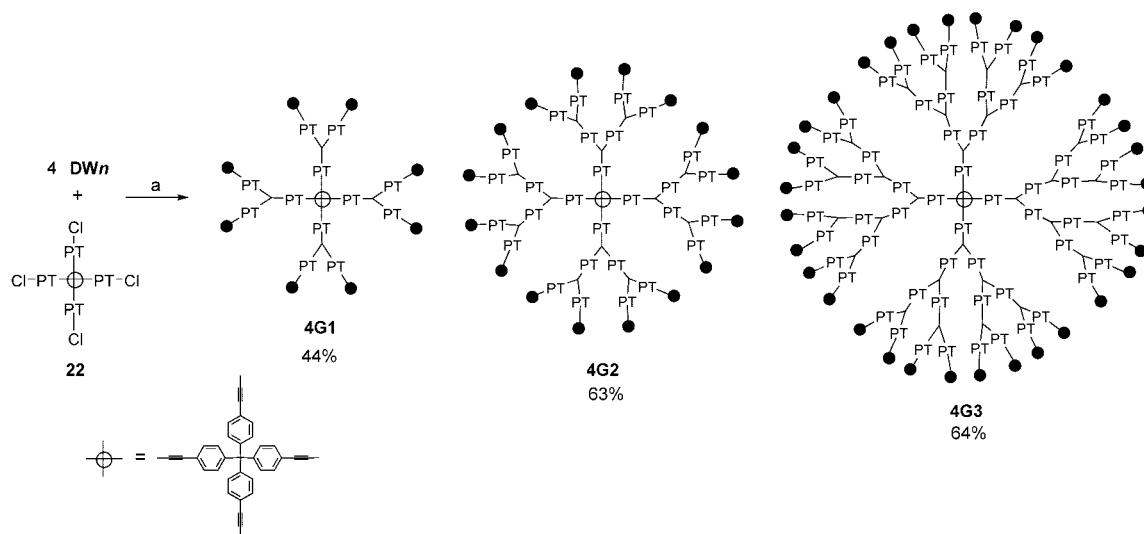
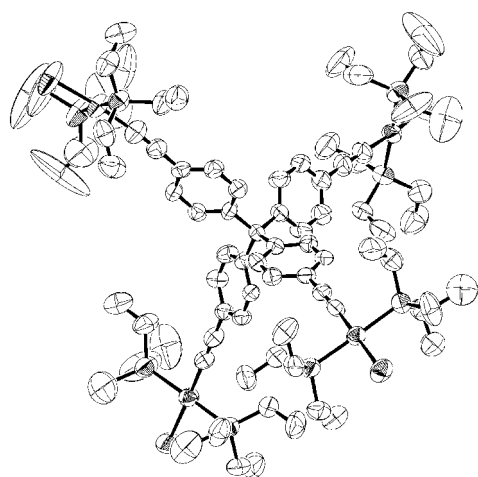


Figure 1. ^1H NMR spectrum of third-generation dendrimer **3G3** in CDCl_3 .

ray analysis. The unit cell contained two independent molecules with essentially the same structure; one of them is given in Figure 2. Although core **22** has four reaction points for dendrimer construction, they are positioned sufficiently far apart from each other. Thus, the treatment of **22** with four equivalents of dendrons **DW1**, **DW2**, and **DW3** led to the selective formation of dendrimers **4G1**, **4G2**, and **4G3**, respectively (Scheme 10).

The relative molecular sizes of these dendrons and dendrimers were examined by using GPC analysis and the results are shown in Table 1. The number averaged molecular weight (M_n) of **DW1** is consistent with the formula weight (fw). The M_n value of the dendrons doubles with increasing number of generations, which seems to be reasonable because **DW n** have been prepared from two equivalents of **DW($n-1$)** with **7**. The M_n values of **3G1** and **4G1** are approx-

Scheme 9. Reaction of fourth-generation dendron **DW4** with **20**. a) CuI (cat.), Et₂NH, room temperature.Scheme 10. Synthesis of dendrimers **4Gn** using tetraplatinum core **22**. a) CuI (cat.), Et₂NH, room temperature.Figure 2. Molecular structure of tetraplatinum core **22**. Hydrogen atoms are omitted for clarity.

imately three and four times larger than those of **DW1**, respectively. These results are consistent with the number of **DW1** dendrons for constructing these dendrimers. Although

Table 1. GPC data for dendrons **DWn** and dendrimers **3Gn** and **4Gn**.

Compound	$M_n^{[a]}$	fw	M_n/fw
DW1	1200	1273	0.94
DW2	2900	3555	0.82
DW3	6000	8120	0.74
DW4	11 400	17 249	0.66
3G1	3800	5300	0.72
3G2	7700	12 147	0.63
3G3	16 200	25 840	0.63
4G1	5300	7227	0.73
4G2	9700	16 356	0.59
4G3	16 600	34 614	0.48

[a] Determined by using polystyrene standards.

the M_n values of **3Gn** and **4Gn** increase with an increase in the number of generations, their proportions relative to the fw decrease, suggesting that higher generation dendrimers have spherical structures. It may be of interest that the molecular size of **4G3** is approximately equal to that of **3G3** as the M_n values estimated by GPC analysis of these dendrimers are close to each other.

Platinum–acetylide dendrimers **3Gn** and **4Gn** are soluble in common organic solvents such as toluene, dichlorome-

thane, THF, and acetone, but not methanol. Macromolecules containing unsaturated repeating units such as aromatic and acetylenic groups are, in general, insoluble in common organic solvents due to the strong intermolecular interaction among the macromolecules. The high solubility of the present platinum–acetylide dendrimers is due to the spherical shape of the dendrimer molecules as well as the presence of bis(trialkylphosphine) platinum units, the sterically large phosphine ligands of which prevent intermolecular interaction, as also seen for linear platinum–acetylide polymers.^[7] The high solubility must be favorable for the preparation, purification, and characterization of the dendrimers. Although during the synthesis of organometallic macromolecules serious problems are frequently encountered in purification and characterization due to their insolubility, the platinum–acetylide dendrimers may be easily purified by means of conventional column chromatography and recrystallization. Thus, the prepared dendrons and dendrimers may be well characterized by using GPC and conventional spectroscopic analyses as a result of their good solubility and the existence of useful probes, such as phosphorus nuclei on platinum and independent methyl groups on the benzene ring in the molecule (see earlier).

It is well recognized that transition metal–carbon sigma bonds are generally unstable, whereas group 10 metal acetylides are fairly stable due to $d\pi$ – $p\pi$ interaction and the ionic character of the metal–carbon bond as well as the absence of β -hydrogen atoms in the acetylene ligand. As expected, platinum–acetylide dendrimers **3Gn** and **4Gn** show high thermal stability up to temperatures as high as 200 °C, and the decomposition temperatures of the dendrons and the dendrimers increase with an increase in the number of platinum–acetylide units in the molecule.

To obtain information on the conformational change dynamics of our dendrimers, ¹H NMR spin–lattice relaxation times (T_1) were measured in CDCl₃ at 25 °C (Figure 3).^[20] In the series of **3Gn**, the T_1 value of the signal due to the methyl groups at the core was slightly decreased with an increase in the number of generations, whereas the exterior methoxy signal kept virtually a constant T_1 value regardless of the number of generations. Similar phenomena were also observed in the series of **4Gn**. These results were consistent with the ¹H NMR spectra, in which no broadening of signals was observed even for **3G3** and **4G3** dendrimers, suggesting that the exterior of our dendrimer is not restricted in terms of conformational motion.

Because a π -conjugated system was employed as the bridging ligand in our dendrimers, interaction among platinum moieties was expected for the dendrimers as well as the dendrons. Figure 4a shows the electronic spectra of the dendrons **DWn** in CHCl₃. The higher energy bands ($\lambda < 300$ nm) are due to π – π^* transitions of the bridging ligands, and the λ_{\max} values are 265 and 290 nm. The absorption at approximately 345 nm is assignable to the metal–ligand charge transfer (MLCT) band of the platinum–acetylide units. That the molar absorptivity (ϵ) of these absorptions markedly increased with an increase in the number of generations is due to the increase in the number of platinum moieties in the molecules, because the spectra based on plati-

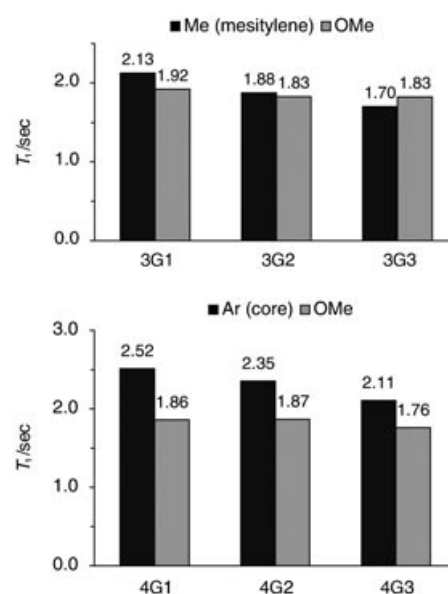


Figure 3. ¹H NMR spin–lattice relaxation times (T_1) of Me, MeO, and Ar signals in the series of platinum–acetylide dendrimers **3Gn** and **4Gn** in CDCl₃ at 25 °C.

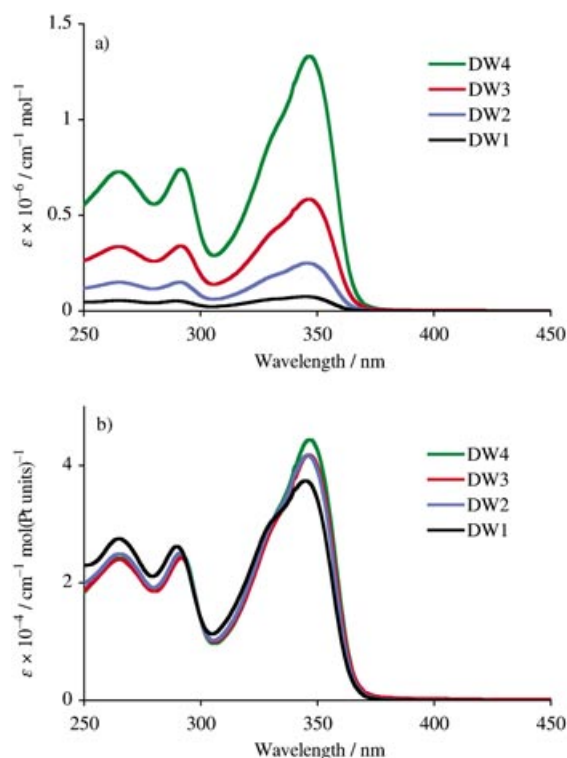


Figure 4. Electronic spectra of dendrons **DWn** in CHCl₃. a) Intensity is shown in molar absorptivity. b) Intensity is based on the molar absorptivity of the platinum–acetylide units.

num units resemble each other very closely (Figure 4b). The electronic spectra of **3Gn** and **4Gn** shown in Figures 5 and 6 reveal no significant shifts of the λ_{\max} values. These results contrast sharply with the finding that the MLCT band of the platinum–acetylide oligomers bridged by *p*-diethynylbenzene shows a redshift with an increase in the number of

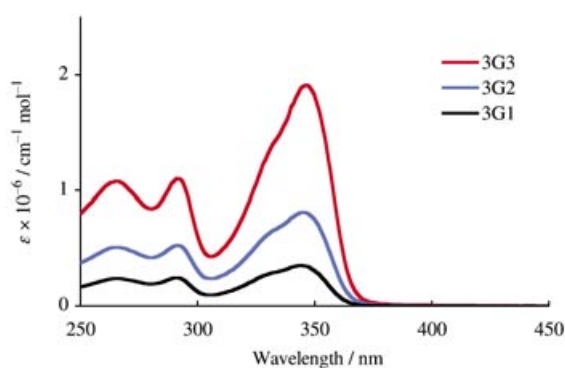


Figure 5. Electronic spectra of dendrimers **3Gn** in CHCl_3 .

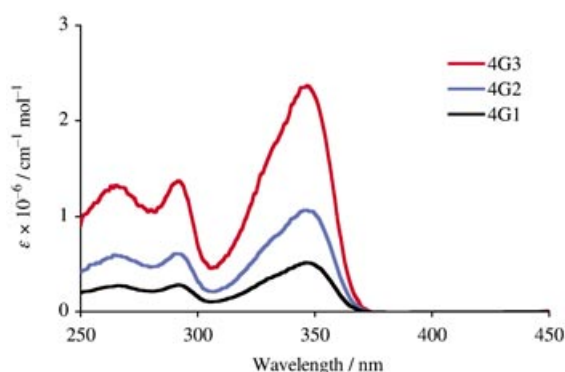


Figure 6. Electronic spectra of dendrimers **4Gn** in CHCl_3 .

units,^[21] and suggest that the interaction among platinum moieties is small in these dendritic molecules.

The fluorescence spectra of dendrons **DWn** and dendrimers **3Gn**, obtained by exciting the MLCT band, were also measured. As shown in Figure 7, the fluorescence bands at $\lambda_{\text{max}} = 384 \text{ nm}$, which were Stokes-shifted very slightly from the MLCT bands, were observed in all of the spectra.^[22] Although the fluorescence spectra of dendrons **DW2** and **DW3** (not shown in Figure 7) were essentially the same as that of dendron **DW1**, the fluorescence of dendrimer **3G1** was much weaker than that of dendron **DW1** (Figure 7a). In contrast, **3G2** and **3G3** exhibited approximately twofold higher intensities compared to **3G1** (Figure 7b). Although we have no good explanation for this phenomenon, we believe that the fluorescence of the platinum–acetylide units is affected by the morphology of the molecules.

Conclusion

In summary, large platinum–acetylide dendrimers containing up to sixty platinum atoms have been synthesized by a convergent method that uses two types of trialkylsilyl groups for protection of the terminal acetylene. The formation of dendritic molecules was demonstrated by the reaction of platinum–acetylide dendrons with not only the triplatinum core but also the tetraplatinum core. It is unfortunate that the third generation is the synthetic limit of the convergent

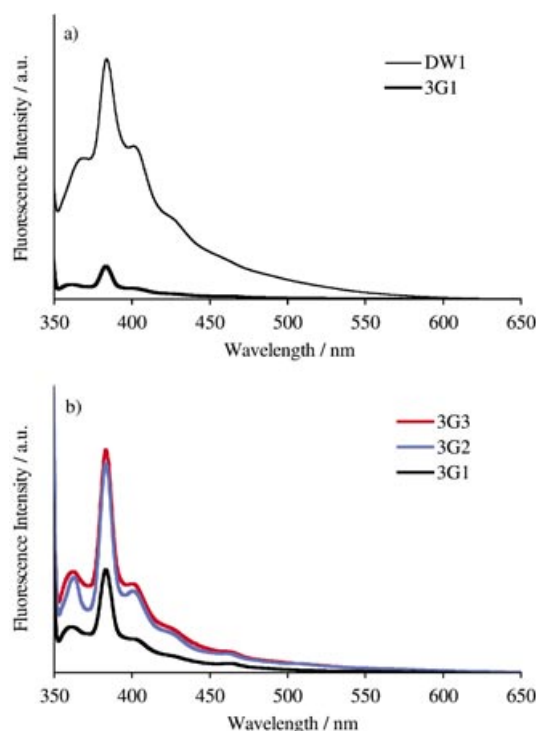


Figure 7. Fluorescence spectra of dendron **DW1** and dendrimers **3G1** (excited at 343 nm) and **3G2** and **3G3** (both excited at 344 nm) in THF. The spectra are normalized to a constant absorbance at the excitation wavelength.

route; nevertheless, the method presented here is expected to be useful for the precise synthesis of nanosized organo-metallic molecules.

Experimental Section

General: All reactions involving transition-metal complexes were carried out under an argon atmosphere, whereas the other reactions were performed in air. THF was distilled over benzophenone ketyl under argon immediately before use. All other chemicals commercially available were used without further purification. Triplatinum core **7**,^[13] diplatinum core **20**,^[18] and tetra(4-ethynylphenyl)methane^[19] were prepared according to methods in the literature. NMR spectra were measured in CDCl_3 on JEOL JNM-LA400 and Bruker ARX400 spectrometers using SiMe_4 as the internal standard for ^1H and ^{13}C NMR, and 85% aqueous H_3PO_4 as the external standard for ^{31}P NMR. IR, electronic, and fluorescence spectra were recorded on Perkin-Elmer System 2000 FT-IR, JASCO V-560, and Shimadzu RF-5300PC instruments, respectively. Gel permeation chromatography analyses were performed with the Shimadzu LC-6AD and SPD-10A using Shimadzu GPC-805, 804, and 8025 columns. Melting points were measured with a Yamato MP-21 instrument, and no corrections were made. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University.

Synthesis of 1,3-dibromo-5-nitrobenzene: 2,6-Dibromo-4-nitroaniline (20.00 g, 67.6 mmol) was dissolved in concentrated H_2SO_4 (200 mL) and the solution was cooled over an ice bath. NaNO_2 (6.10 g, 88.4 mmol) was added in small portions, and then aqueous H_3PO_4 (85%, 200 mL) was added. After stirring the mixture over the ice bath for 1 h, the reaction mixture was allowed to warm to room temperature and stirred for an additional 1 h. The reaction mixture was poured into ice water and water was added to make a total volume of approximately 1 L. After urea (7.81 g, 130 mmol) was added in small portions, the reaction mixture was left overnight at room temperature. Aqueous H_3PO_2 (30%, 80 mL) was

added in small portions at 0°C, and the reaction mixture was stirred for 30 min. The stirring was continued overnight at room temperature. The precipitate was collected by filtration and dissolved in CH₂Cl₂. The solution was washed with brine several times and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by alumina column chromatography (hexane/benzene 3:1) to give a pale-yellow solid (16.20 g, 85%). ¹H NMR: δ = 8.00 (t, *J* = 2 Hz, 1H; Ar), 8.33 ppm (d, *J* = 2 Hz, 2H; Ar). This compound was used for the next reaction without further purification.

Synthesis of 3,5-dibromoaniline: To a solution of concentrated HCl (250 mL) containing 1,3-dibromo-5-nitrobenzene (16.20 g, 57.7 mmol), powdered tin (20.54 g, 173 mmol) was added in small portions and the reaction mixture was stirred at 90°C for 7 h. After water (ca. 300 mL) was added, dilute aqueous NaOH was added until the pH of the solution was approximately 9. The solution was extracted with diethyl ether and the extract was dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using benzene as eluent to give a pale-yellow solid (14.28 g, 99%). ¹H NMR: δ = 3.77 (s, 2H; NH₂), 6.74 (d, *J* = 2 Hz, 2H; Ar), 7.02 ppm (t, *J* = 2 Hz, 1H; Ar); IR (KBr): $\tilde{\nu}$ = 3296, 3419 cm⁻¹ (N–H). This compound was also used for the next reaction without further purification.

Synthesis of 1,3-dibromo-5-iodobenzene (1): 3,5-Dibromoaniline (14.28 g, 56.9 mmol) was dissolved in concentrated H₂SO₄ (200 mL) then NaNO₂ (5.13 g, 74.4 mmol) was added in small portions at 0°C. After the addition of aqueous H₃PO₄ (85%, 100 mL), the reaction mixture was stirred at 0°C for 1 h. The reaction mixture was allowed to warm at room temperature and to stand overnight, and was then poured into ice water and water was added until the total volume was about 300 mL. To the solution, urea (6.57 g, 109 mmol) and KI (13.08 g, 78.8 mmol) were added in that order in small portions, and the reaction mixture was stirred until gas evolution stopped. The reaction mixture was then heated to 50°C and stirred overnight. After cooling to room temperature, NaHSO₃ (ca. 9 g) was added. The precipitate was collected by filtration and dissolved in CH₂Cl₂. The solution was washed with brine several times and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by alumina column chromatography with hexane. Recrystallization from ethanol gave colorless needles (14.75 g, 72%). M.p. 123°C; ¹H NMR: δ = 7.64 (t, *J* = 2 Hz, 1H; Ar), 7.80 ppm (d, *J* = 2 Hz, 2H; Ar); elemental analysis calcd (%) for C₆H₃Br₂I (361.80): C 19.92, H 0.84, Br and I 79.25; found: C 19.83, H 0.67, Br and I 79.07.

Synthesis of 1,3-dibromo-5-(triisopropylsilylethynyl)benzene (2): A solution of diethylamine (100 mL) containing 1,3-dibromo-5-iodobenzene **1** (3.62 g, 10 mmol), triisopropylsilylacetylene (2.37 g, 13 mmol), and catalytic amounts (ca. 5 mol%) of [PdCl₂(PPh₃)₂] and CuI was stirred at room temperature for 2 days. After removal of the solvent, the residue was extracted with diethyl ether and the extract was dried over Na₂SO₄. The solvent was evaporated again and the residue was purified by alumina column chromatography with hexane to give a colorless oil (4.16 g, 99%). ¹H NMR: δ = 1.12 (s, 21H; C₃H₇), 7.53 (d, *J* = 2 Hz, 2H; Ar), 7.61 ppm (t, *J* = 2 Hz, 1H; Ar); IR (neat): $\tilde{\nu}$ = 2164 cm⁻¹ (C≡C). This compound was used for the next reaction without further purification.

Synthesis of 1-(triisopropylsilylethynyl)-3,5-bis(trimethylsilylethynyl)benzene (3): 1,3-Dibromo-5-(triisopropylsilylethynyl)benzene **2** (2.00 g, 4.80 mmol) and trimethylsilylacetylene (2.83 g, 28.8 mmol) were dissolved in benzene (50 mL), and triethylamine (50 mL) was added. After the addition of catalytic amounts (ca. 5 mol%) of [PdCl₂(PPh₃)₂], PPh₃, and CuI, the reaction mixture was stirred overnight under reflux. The solvent was evaporated and the residue was extracted with diethyl ether. The extract was dried over Na₂SO₄ and the solvent was evaporated again. The residue was purified by silica-gel column chromatography with hexane and the resulting oil was dissolved in hot ethanol. Cooling to room temperature led to phase separation. The liquid supernatant was removed by decantation and the remaining solvent was removed in vacuo to give a colorless oil (1.95 g, 90%). ¹H NMR: δ = 0.23 (s, 18H; SiCH₃), 1.11 (s, 21H; SiC₃H₇), 7.48 (d, *J* = 2 Hz, 2H; Ar), 7.50 ppm (t, *J* = 2 Hz, 1H; Ar); IR (neat): $\tilde{\nu}$ = 2164 cm⁻¹ (C≡C); elemental analysis calcd (%) for C₂₇H₄₂Si₃ (450.89): C 71.92, H 9.39; found: C 72.01, H 9.58.

Synthesis of 1,3-diethynyl-5-(triisopropylsilylethynyl)benzene (4): To a solution of 1-(triisopropylsilylethynyl)-3,5-bis(trimethylsilylethynyl)ben-

zene **3** (1.95 g, 4.32 mmol) in acetone (100 mL), an aqueous K₂CO₃ solution (10 mL; 1.38 g, 10 mmol) was added, and the reaction mixture was stirred overnight at room temperature. After removal of the solvent, the residue was extracted with diethyl ether and the extract was dried over Na₂SO₄. The solvent was evaporated again and the residue was purified by alumina column chromatography using hexane as eluent to give a yellow oil (0.87 g, 66%). ¹H NMR: δ = 1.12 (s, 21H; SiC₃H₇), 3.09 (s, 2H; ≡CH), 7.53 (t, *J* = 2 Hz, 1H; Ar), 7.55 ppm (d, *J* = 2 Hz, 2H; Ar); IR (neat): $\tilde{\nu}$ = 2160 (C≡C), 3303 cm⁻¹ (≡C–H); elemental analysis calcd (%) for C₂₁H₂₆Si (306.52): C 82.29, H 8.55; found: C 82.25, H 8.27.

Synthesis of mononuclear platinum-acetylide complex (5): To a solution of [PtCl₂(PEt₃)₂] (19.02 g, 37.86 mmol) and (4-methoxyphenyl)acetylene (4.17 g, 31.55 mmol) in a mixture of piperidine (250 mL) and toluene (250 mL), a catalytic amount of CuI (ca. 5 mol%) was added, and the reaction mixture was stirred under reflux for one week. After removal of the solvent, the residue was extracted with diethyl ether and the extract was dried over Na₂SO₄. The solvent was evaporated again and the residue was passed through a short alumina column with hexane as eluent. The crude product was purified by alumina column chromatography, the eluent of which was gradually changed from hexane/benzene (3:1) to benzene, and then to dichloromethane. Recrystallization from hexane gave yellow needles (12.84 g, 68%). M.p. 83°C; ¹H NMR: δ = 1.20 (dt, *J*_{H–P} = 17, *J*_{H–H} = 8 Hz, 18H; PCH₂CH₃), 2.03–2.10 (m, 12H; PCH₂CH₃), 3.78 (s, 3H; OCH₃), 6.77 (d, *J* = 9 Hz, 2H; Ar), 7.18 ppm (d, *J* = 9 Hz, 2H; Ar); ¹³C NMR: δ = 8.0 (s, PCH₂CH₃), 14.5 (vt, *N* = 17 Hz; PCH₂CH₃), 55.2 (s, OCH₃), 79.1 (t, *J*_{C–P} = 14 Hz, *J*_{C–Pt} = 714 Hz; PtC≡), 100.9 (s, PtC≡C), 113.6 (s, Ar), 121.2 (s, Ar C_{ipso}–C≡), 131.9 (s, Ar), 157.5 ppm (s, Ar C_{ipso}–OMe); ³¹P NMR: δ = 14.7 ppm (s, *J*_{P–Pt} = 2396 Hz); IR (KBr): $\tilde{\nu}$ = 2118 cm⁻¹ (C≡C); elemental analysis calcd (%) for C₂₁H₂₇OP₂ClPt (598.00): C 42.18, H 6.24, P 10.36, Cl 5.93; found: C 42.38, H 6.04, P 10.63, Cl 5.88.

Synthesis of protected first-generation dendron (6): A mixture of platinum-acetylide complex **5** (12.55 g, 20.99 mmol) and protected building block **4** (3.22 g, 10.50 mmol) in diethylamine (500 mL) was stirred overnight at room temperature in the presence of a catalytic amount of CuI (ca. 5 mol%). The solvent was evaporated under reduced pressure, the residue was extracted with diethyl ether, and the extract was dried over Na₂SO₄. The solvent was evaporated again and the residue was purified by column chromatography on alumina using benzene/CH₂Cl₂ (3:1) as eluent. Recrystallization from toluene/hexane gave a pale-yellow solid (14.40 g, 96%). M.p. 46°C; ¹H NMR: δ = 1.12 (s, 21H; SiC₃H₇), 1.21 (dt, *J*_{H–P} = 16, *J*_{H–H} = 8 Hz, 36H; PCH₂CH₃), 2.13–2.19 (m, 24H; PCH₂CH₃), 3.78 (s, 6H; OCH₃), 6.76 (d, *J* = 9 Hz, 4H; C₆H₄OMe), 7.12 (s, 2H; Ar), 7.13 (s, 1H; Ar), 7.21 ppm (d, *J* = 9 Hz, 4H; C₆H₄OMe); ¹³C NMR: δ = 8.4 (s, PCH₂CH₃), 11.4 (s, *J*_{C–Si} = 57 Hz; SiCH(CH₃)₂), 16.3 (vt, *N* = 17 Hz; PCH₂CH₃), 18.7 (s, SiCH(CH₃)₂), 55.2 (s, OCH₃), 89.4 (s, SiC≡), 104.6 (t, *J*_{C–P} = 15 Hz; PtC≡), 107.6 (s, SiC≡C), 108.4 (t, *J*_{C–P} = 15 Hz; PtC≡), 108.6 (s, *J*_{C–Pt} = 270 Hz; PtC≡C), 108.8 (s, *J*_{C–Pt} = 270 Hz; PtC≡C), 113.5 (s, C₆H₄OMe), 121.4 (s, Ar C_{ipso}–C≡), 122.8 (s, Ar C_{ipso}–C≡), 128.6 (s, Ar C_{ipso}–C≡), 131.0 (s, Ar), 131.9 (s, C₆H₄OMe), 133.5 (s, Ar), 157.3 ppm (s, Ar C_{ipso}–OMe); ³¹P NMR: δ = 11.0 ppm (s, *J*_{P–Pt} = 2375 Hz); IR (KBr): $\tilde{\nu}$ = 2098 cm⁻¹ (C≡C); elemental analysis calcd (%) for C₆₃H₉₈O₂Si₄Pt₂ (1429.61): C 52.93, H 6.91, P 8.67; found: C 53.13, H 7.15, P 8.47.

Synthesis of first-generation dendron (DW1): A solution of the protected first-generation dendron **6** (14.18 g, 9.92 mmol) in THF (200 mL) was cooled in a dry ice/acetone bath, and a solution of Bu₄NF (11.9 mL, 11.9 mmol) in THF (1.0 M) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The solvent was removed under reduced pressure and the residue was purified by alumina column chromatography with benzene/CH₂Cl₂ (2:1) as eluent. Recrystallization from ethanol gave yellow needles (12.05 g, 95%). M.p. 151°C; ¹H NMR: δ = 1.21 (dt, *J*_{H–P} = 16, *J*_{H–H} = 8 Hz, 36H; PCH₂CH₃), 2.13–2.20 (m, 24H; PCH₂CH₃), 3.00 (s, 1H; ≡CH), 3.78 (s, 6H; OCH₃), 6.76 (d, *J* = 9 Hz, 4H; C₆H₄OMe), 7.15 (s, 2H; Ar), 7.18 (s, 1H; Ar), 7.21 ppm (d, *J* = 9 Hz, 4H; C₆H₄OMe); ¹³C NMR: δ = 8.4 (s, PCH₂CH₃), 16.3 (vt, *N* = 17 Hz; PCH₂CH₃), 55.2 (s, OCH₃), 76.2 (s, ≡CH), 84.0 (s, C≡CH), 104.6 (t, *J*_{C–P} = 15 Hz; PtC≡), 108.3 (s, *J*_{C–Pt} = 269 Hz; PtC≡C), 108.7 (t, *J*_{C–P} = 15 Hz; PtC≡), 108.9 (s, *J*_{C–Pt} = 269 Hz; PtC≡C), 113.5 (s, C₆H₄OMe), 121.3 (s, Ar C_{ipso}–C≡), 121.4 (s, Ar C_{ipso}–C≡), 128.7 (s, Ar C_{ipso}–C≡), 131.1 (s, Ar), 131.9 (s, C₆H₄OMe), 134.0 (s, Ar), 157.3 ppm (s, Ar C_{ipso}–OMe); ³¹P NMR: δ = 11.0 ppm (s, *J*_{P–Pt} = 2374 Hz); IR (KBr):

$\bar{\nu}$ = 2101 cm⁻¹ (C≡C); elemental analysis calcd (%) for C₅₄H₇₈O₂Pt₄ (1273.27): C 50.94, H 6.17, P 9.73; found: C 51.10, H 6.02, P 9.62.

Synthesis of first-generation dendrimer (3G1): A solution of first-generation dendron **DW1** (382 mg, 0.30 mmol) and core **7** (159 mg, 0.10 mmol) in diethylamine (50 mL) was stirred in the presence of a catalytic amount of CuI (ca. 5 mol%) overnight at room temperature. After removal of the solvent, the residue was extracted with diethyl ether and the extract was dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by alumina column chromatography using dichloromethane as eluent. Recrystallization from dichloromethane/hexane afforded a yellow solid (230 mg, 43%). M.p. 175 °C (decomp); ¹H NMR: δ = 1.20 (dt, $J_{\text{H-P}} = 17$, $J_{\text{H-H}} = 8$ Hz, 162H; PCH₂CH₃), 2.13–2.19 (m, 108H; PCH₂CH₃), 2.57 (s, 9H; C₆H₄), 3.78 (s, 18H; OCH₃), 6.76 (d, $J = 9$ Hz, 12H; C₆H₄OMe), 6.99 (s, 3H; Ar), 7.01 (s, 6H; Ar), 7.21 ppm (d, $J = 9$ Hz, 12H; C₆H₄OMe); ¹³C NMR: δ = 8.4 (s, PCH₂CH₃), 16.3 (vt, $N = 17$ Hz; PCH₂CH₃), 20.6 (s, C₆H₄), 55.2 (s, OCH₃), 105.0 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 106.1 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 106.7 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 107.5 (s, PtC≡C), 108.7 (s, PtC≡C), 109.4 (s, PtC≡C), 109.7 (s, PtC≡C), 113.5 (s, C₆H₄OMe), 114.4 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 121.5 (s, Ar C_{ipso}-C≡), 125.4 (s, Ar C_{ipso}-C≡), 127.9 (s, Ar C_{ipso}-C≡), 128.1 (s, Ar C_{ipso}-C≡), 130.4 (s, Ar), 130.6 (s, Ar), 131.9 (s, C₆H₄OMe), 135.6 (s, Ar C_{ipso}-CH₃), 157.2 ppm (s, Ar C_{ipso}-OMe); ³¹P NMR: δ = 10.9 (s, $J_{\text{P-Pt}} = 2381$ Hz, 12P), 11.1 ppm (s, $J_{\text{P-Pt}} = 2392$ Hz, 6P); IR (KBr): $\bar{\nu}$ = 2095 cm⁻¹ (C≡C); elemental analysis calcd (%) for C₆₈₄H₁₀₅₈O₁₆P₆₀Pt₃₀ (5300.21): C 48.27, H 6.28, P 10.52; found: C 48.37, H 6.14, P 10.26.

Synthesis of building block (8): 1,3-Diethynyl-5-(triisopropylsilyl)ethynylbenzene **4** (5.57 g, 18.17 mmol) and [PtCl₂(PET₃)₂] (22.82 g, 45.43 mmol) were dissolved in piperidine (600 mL). After a catalytic amount of CuI (ca. 5 mol%) was added, the reaction mixture was placed under reflux for one week. The solvent was evaporated and the residue was extracted with diethyl ether. The extract was dried over Na₂SO₄ and the solvent was evaporated again. The residue was purified by alumina column chromatography with benzene followed by recrystallization from ethanol to give pale-yellow needles (16.63 g, 74%). ¹H NMR: δ = 1.13 (s, 21H; SiC₃H₇), 1.20 (dt, $J_{\text{H-P}} = 16$, $J_{\text{H-H}} = 8$ Hz, 36H; PCH₂CH₃), 2.02–2.09 (m, 24H; PCH₂CH₃), 7.07 (b, 1H; Ar), 7.11 ppm (d, $J = 1$ Hz, 2H; Ar); ¹³C NMR: δ = 8.0 (s, PCH₂CH₃), 11.3 (s, $J_{\text{C-Si}} = 56$ Hz; SiCH(CH₃)₂), 14.5 (vt, $N = 17$ Hz; PCH₂CH₃), 18.7 (s, SiCH(CH₃)₂), 83.2 (t, $J_{\text{C-P}} = 15$, $J_{\text{C-Pt}} = 1437$ Hz; PtC≡), 90.0 (s, SiC≡), 100.9 (t, $J_{\text{C-P}} = 2$, $J_{\text{C-Pt}} = 408$ Hz; PtC≡C), 107.2 (s, SiC≡C), 123.0 (s, Ar C_{ipso}-C≡), 128.50 (s, $J_{\text{C-Pt}} = 35$ Hz; Ar C_{ipso}-C≡), 131.2 (s, Ar), 133.3 ppm (s, Ar); ³¹P NMR: δ = 14.9 ppm (s, $J_{\text{P-Pt}} = 2385$ Hz); IR (KBr): $\bar{\nu}$ = 2111 cm⁻¹ (C≡C); elemental analysis calcd (%) for C₄₅H₈₈Si₃P₄Cl₂Pt₂ (1238.21): C 43.65, H 6.84, P 10.01, Cl 5.73; found: C 43.94, H 6.83, P 10.24, Cl 5.63.

Synthesis of protected second-generation dendron (9): First-generation dendron **DW1** (10.06 g, 7.90 mmol) and building block **8** (4.89 g, 3.95 mmol) were reacted in a similar manner to that of the preparation of the protected first-generation dendron **6**. Alumina column chromatography was performed with benzene/CH₂Cl₂ (1:1) as eluent. Recrystallization from dichloromethane/hexane gave a pale-yellow solid (12.08 g, 82%). M.p. 148 °C; ¹H NMR: δ = 1.12 (s, 21H; SiC₃H₇), 1.21 (dt, $J_{\text{H-P}} = 16$, $J_{\text{H-H}} = 8$ Hz, 108H; PCH₂CH₃), 2.15–2.19 (m, 72H; PCH₂CH₃), 3.78 (s, 12H; OCH₃), 6.76 (d, $J = 9$ Hz, 8H; C₆H₄OMe), 6.98 (s, 6H; Ar), 7.12 (s, 3H; Ar), 7.21 ppm (d, $J = 9$ Hz, 8H; C₆H₄OMe); ¹³C NMR: δ = 8.35 (s, PCH₂CH₃), 11.4 (s, $J_{\text{C-Si}} = 56$ Hz; SiCH), 16.3 (vt, $N = 17$ Hz; PCH₂CH₃), 18.7 (s, SiCH(CH₃)₂), 55.2 (s, OCH₃), 89.4 (s, SiC≡), 104.9 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 106.0 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 106.3 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 107.6 (s, SiC≡C), 108.4 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 108.7 (s, PtC≡C), 109.4 (s, PtC≡C), 109.6 (s, PtC≡C), 113.5 (s, C₆H₄OMe), 121.5 (s, Ar C_{ipso}-C≡), 122.8 (s, Ar C_{ipso}-C≡), 127.9 (s, Ar C_{ipso}-C≡), 128.0 (s, Ar C_{ipso}-C≡), 128.5 (s, Ar C_{ipso}-C≡), 130.5 (s, Ar), 131.0 (s, Ar), 131.9 (s, C₆H₄OMe), 133.5 (s, Ar), 157.3 ppm (s, Ar C_{ipso}-OMe); ³¹P NMR: δ = 10.8 (s, $J_{\text{P-Pt}} = 2381$ Hz, 8P), 11.0 ppm (s, $J_{\text{P-Pt}} = 2374$ Hz, 4P); IR (KBr): $\bar{\nu}$ = 2095 cm⁻¹ (C≡C); elemental analysis calcd (%) for C₁₅₃H₂₃₈O₈Si₃P₁₂Pt₆ (3711.82): C 49.51, H 6.46, P 10.01; found: C 49.61, H 6.29, P 10.12.

Synthesis of second-generation dendron (DW2): Protected second-generation dendron **9** (11.91 g, 3.21 mmol) was treated with a solution of Bu₄NF (3.9 mL, 3.9 mmol) in THF (1.0 M) in a similar manner to that of preparation of the first-generation dendron **DW1**. The crude product was purified by alumina column chromatography with benzene/dichloromethane (1:9) as eluent, and recrystallization from dichloromethane/ethanol

gave a pale-yellow solid (10.64 g, 93%). M.p. 180 °C (decomp); ¹H NMR: δ = 1.21 (dt, $J_{\text{H-P}} = 16$, $J_{\text{H-H}} = 8$ Hz, 108H; PCH₂CH₃), 2.14–2.19 (m, 72H; PCH₂CH₃), 2.99 (s, 1H; ≡CH), 3.78 (s, 12H; OCH₃), 6.76 (d, $J = 9$ Hz, 8H; C₆H₄OMe), 6.99 (s, 6H; Ar), 7.14 (s, 2H; Ar), 7.17 (s, 1H; Ar), 7.21 ppm (d, $J = 9$ Hz, 8H; C₆H₄OMe); ¹³C NMR: δ = 8.4 (s, PCH₂CH₃), 16.3 (vt, $N = 17$ Hz; PCH₂CH₃), 55.2 (s, OCH₃), 76.2 (s, ≡CH), 84.0 (s, C≡CH), 104.9 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 105.9 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 106.3 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 108.4 (s, PtC≡C), 108.7 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 108.7 (s, PtC≡C), 109.4 (s, PtC≡C), 109.7 (s, PtC≡C), 113.5 (s, C₆H₄OMe), 121.3 (s, Ar C_{ipso}-C≡), 122.5 (s, Ar C_{ipso}-C≡), 127.8 (s, Ar C_{ipso}-C≡), 128.0 (s, Ar C_{ipso}-C≡), 128.7 (s, Ar C_{ipso}-C≡), 130.5 (s, Ar), 130.6 (s, Ar), 131.1 (s, Ar), 131.9 (s, C₆H₄OMe), 134.0 (s, Ar), 157.3 ppm (s, Ar C_{ipso}-OMe); ³¹P NMR: δ = 10.8 (s, $J_{\text{P-Pt}} = 2381$ Hz, 8P), 11.0 ppm (s, $J_{\text{P-Pt}} = 2374$ Hz, 4P); IR (KBr): $\bar{\nu}$ = 2095 cm⁻¹ (C≡C); elemental analysis calcd (%) for C₁₄₄H₂₁₈O₈P₁₂Pt₆ (3555.48): C 48.65, H 6.18, P 10.45; found: C 48.63, H 6.04, P 10.19.

Synthesis of second-generation dendrimer (3G2): Second-generation dendron **DW2** (533 mg, 150 μmol) and core **7** (79.5 mg, 50 μmol) were reacted in a similar manner to that of the preparation of the first-generation dendrimer **3G1**. The crude product that was obtained by alumina column chromatography was dissolved in dichloromethane and precipitated with methanol to give a pale-yellow solid (230 mg, 38%). M.p. 195–210 °C (decomp); ¹H NMR: δ = 1.21 (dt, $J_{\text{H-P}} = 16$, $J_{\text{H-H}} = 8$ Hz, 378H; PCH₂CH₃), 2.15–2.19 (m, 252H; PCH₂CH₃), 2.57 (s, 9H; C₆H₄), 3.77 (s, 36H; OCH₃), 6.76 (d, $J = 9$ Hz, 24H; C₆H₄OMe), 6.99 (s, 27H; Ar), 7.21 ppm (d, $J = 9$ Hz, 24H; C₆H₄OMe); ¹³C NMR: δ = 8.4 (s, PCH₂CH₃), 16.3 (vt, $N = 17$ Hz; PCH₂CH₃), 20.7 (s, C₆H₄), 55.2 (s, OCH₃), 104.9 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 106.2 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 108.7 (s, PtC≡C), 109.4 (s, PtC≡C), 109.5 (s, PtC≡C), 113.5 (s, C₆H₄OMe), 121.5 (s, Ar C_{ipso}-C≡), 125.4 (s, Ar C_{ipso}-C≡), 128.0 (s, Ar C_{ipso}-C≡), 130.5 (s, Ar), 131.9 (s, C₆H₄OMe), 135.7 (s, Ar C_{ipso}-CH₃), 157.3 ppm (s, Ar C_{ipso}-OMe); ³¹P NMR: δ = 10.9 (s, $J_{\text{P-Pt}} = 2381$ Hz, 36P), 11.1 ppm (s, $J_{\text{P-Pt}} = 2394$ Hz, 6P); IR (KBr): $\bar{\nu}$ = 2093 cm⁻¹ (C≡C); elemental analysis calcd (%) for C₄₈₃H₇₅₀O₁₂P₄₈Pt₂₄ (12146.84): C 47.76, H 6.22, P 10.71; found: C 47.94, H 6.12, P 10.66.

Synthesis of protected third-generation dendron (10): Second-generation dendron **DW2** (8.26 g, 2.32 mmol) and building block **8** (1.40 g, 1.13 mmol) were reacted in a similar manner to that of the preparation of the protected first-generation dendron **6**. Alumina column chromatography was performed with dichloromethane as eluent, and recrystallization from toluene/ethanol gave a pale-yellow solid (7.47 g, 80%). M.p. 200 °C (decomp); ¹H NMR: δ = 1.12 (s, 21H; SiC₃H₇), 1.21 (dt, $J_{\text{H-P}} = 16$, $J_{\text{H-H}} = 8$ Hz, 252H; PCH₂CH₃), 2.15–2.19 (m, 168H; PCH₂CH₃), 3.78 (s, 24H; OCH₃), 6.76 (d, $J = 9$ Hz, 16H; C₆H₄OMe), 6.99 (s, 18H; Ar), 7.12 (s, 3H; Ar), 7.21 ppm (d, $J = 9$ Hz, 16H; C₆H₄OMe); ¹³C NMR: δ = 8.4 (s, PCH₂CH₃), 11.4 (s, SiCH), 16.3 (vt, $N = 17$ Hz; PCH₂CH₃), 18.7 (s, SiCH(CH₃)₂), 55.2 (s, OCH₃), 89.5 (s, SiC≡), 104.9 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 106.3 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 107.6 (s, SiC≡C), 108.7 (s, PtC≡C), 109.4 (s, PtC≡C), 109.5 (s, PtC≡C), 113.5 (s, C₆H₄OMe), 121.5 (s, Ar C_{ipso}-C≡), 122.8 (s, Ar C_{ipso}-C≡), 128.0 (s, Ar C_{ipso}-C≡), 128.6 (s, Ar C_{ipso}-C≡), 130.5 (s, Ar), 131.0 (s, Ar), 131.9 (s, C₆H₄OMe), 133.5 (s, Ar), 157.3 ppm (s, Ar C_{ipso}-OMe); ³¹P NMR: δ = 10.8 (s, $J_{\text{P-Pt}} = 2382$ Hz, 24P), 11.0 ppm (s, 4P); IR (KBr): $\bar{\nu}$ = 2094 cm⁻¹ (C≡C); elemental analysis calcd (%) for C₃₃₃H₅₁₈O₈Si₃P₂₈Pt₁₄ (8276.24): C 48.33, H 6.31, P 10.48; found: C 48.10, H 6.27, P 10.60.

Synthesis of third-generation dendron (DW3): Protected third-generation dendron **10** (2.56 g, 0.31 mmol) was treated with a solution of Bu₄NF (0.37 mL, 0.37 mmol) in THF (1.0 M) in a similar manner to that of the preparation of the first-generation dendron **DW1**. The crude product was purified by alumina column chromatography with dichloromethane containing 0.25% of ethyl acetate as eluent, and recrystallization from toluene/ethanol gave a yellow solid (2.31 g, 92%). M.p. 185 °C (decomp); ¹H NMR: δ = 1.21 (dt, $J_{\text{H-P}} = 16$, $J_{\text{H-H}} = 8$ Hz, 252H; PCH₂CH₃), 2.15–2.19 (m, 168H; PCH₂CH₃), 3.00 (s, 1H; ≡CH), 3.78 (s, 24H; OCH₃), 6.76 (d, $J = 9$ Hz, 16H; C₆H₄OMe), 6.99 (s, 18H; Ar), 7.15 (s, 2H; Ar), 7.17 (s, 1H; Ar), 7.21 ppm (d, $J = 9$ Hz, 16H; C₆H₄OMe); ¹³C NMR: δ = 8.4 (s, PCH₂CH₃), 16.3 (vt, $N = 17$ Hz; PCH₂CH₃), 55.2 (s, OCH₃), 76.2 (s, ≡CH), 84.0 (s, C≡CH), 104.9 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 105.9 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 106.3 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 106.4 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 108.5 (s, PtC≡C), 108.7 (s, PtC≡C), 108.7 (t, $J_{\text{C-P}} = 15$ Hz; PtC≡), 109.4 (s, PtC≡C), 109.5 (s, PtC≡C), 109.7 (s, PtC≡C), 113.5 (s, C₆H₄OMe), 121.3 (s, Ar

$C_{\text{ipso}}-\text{C}\equiv$, 121.5 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 127.9 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 128.0 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 128.7 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 130.5 (s, Ar), 131.1 (s, Ar), 131.9 (s, $C_6H_4\text{OMe}$), 134.0 (s, Ar), 157.3 ppm (s, Ar $C_{\text{ipso}}-\text{OMe}$); ^{31}P NMR: $\delta = 10.8$ (s, $J_{\text{P-Pt}} = 2381$ Hz, 24P), 11.0 ppm (s, 4P); IR (KBr): $\tilde{\nu} = 2095$ cm^{-1} ($\text{C}\equiv\text{C}$); elemental analysis calcd (%) for $C_{324}H_{498}O_8P_{28}Pt_{14}$ (8119.90): C 47.93, H 6.18, P 10.68; found: C 48.04, H 6.24, P 10.60.

Synthesis of third-generation dendrimer (3G3): Third-generation dendron **DW3** (536 mg, 66 μmol) and core **7** (35 mg, 22 μmol) were reacted in a similar manner to that of the preparation of the first-generation dendrimer **3G1**. Purification of the product was performed by a method similar to that of the second-generation dendrimer **3G2** to give a yellow solid (290 mg, 51%). M.p. 220–225 °C (decomp); ^1H NMR: $\delta = 1.21$ (dt, $J_{\text{H-P}} = 16$, $J_{\text{H-H}} = 8$ Hz, 810H; PCH_2CH_3), 2.15–2.18 (m, 540H; PCH_2CH_3), 2.57 (s, 9H; $C_6\text{H}_5$), 3.77 (s, 72H; OCH_3), 6.75 (d, $J = 9$ Hz, 48H; $C_6H_4\text{OMe}$), 6.99 (s, 63H; Ar), 7.21 ppm (d, $J = 9$ Hz, 48H; $C_6H_4\text{OMe}$); ^{13}C NMR: $\delta = 8.4$ (s, PCH_2CH_3), 16.3 (vt, $N = 17$ Hz; PCH_2CH_3), 20.6 (s, $C_6\text{H}_5$), 55.2 (s, OCH_3), 104.9 (t, $J_{\text{C-P}} = 15$ Hz; $\text{Pt}\equiv$), 106.2 (s, $\text{Pt}\equiv$), 108.7 (s, $\text{Pt}\equiv\text{C}$), 109.4 (s, $\text{Pt}\equiv\text{C}$), 109.5 (s, $\text{Pt}\equiv\text{C}$), 113.5 (s, $C_6H_4\text{OMe}$), 121.5 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 125.4 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 128.0 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 130.5 (s, Ar), 131.9 (s, $C_6H_4\text{OMe}$), 135.7 (s, Ar $C_{\text{ipso}}-\text{CH}_3$), 157.3 ppm (s, Ar $C_{\text{ipso}}-\text{OMe}$); ^{31}P NMR: $\delta = 10.8$ (s, $J_{\text{P-Pt}} = 2381$ Hz, 84P), 11.0 ppm (s, 6P); IR (KBr): $\tilde{\nu} = 2094$ cm^{-1} ($\text{C}\equiv\text{C}$); elemental analysis calcd (%) for $C_{483}H_{750}O_{12}P_{42}Pt_{21}$ (25840.10): C 47.55, H 6.20, P 10.79; found: C 47.76, H 6.30, P 11.02.

Synthesis of protected fourth-generation dendron (11): Third-generation dendron **DW3** (2.44 g, 0.300 mmol) and building block **8** (0.186 g, 0.150 mmol) were reacted in a similar manner to that of the preparation of the protected first-generation dendron **6**. Alumina column chromatography was performed with dichloromethane containing 1% ethyl acetate as eluent, and recrystallization from toluene/ethanol gave a pale-yellow solid (2.02 g, 77%). M.p. 220–230 °C (decomp); ^1H NMR: $\delta = 1.12$ (s, 21H; SiC_3H_7), 1.21 (dt, $J_{\text{H-P}} = 15$ Hz, $J_{\text{H-H}} = 8$ Hz, 540H; PCH_2CH_3), 2.15–2.19 (m, 360H; PCH_2CH_3), 3.77 (s, 48H; OCH_3), 6.76 (d, $J = 9$ Hz, 32H; $C_6H_4\text{OMe}$), 6.99 (s, 42H; Ar), 7.13 (s, 3H; Ar), 7.21 ppm (d, $J = 9$ Hz, 32H; $C_6H_4\text{OMe}$); ^{13}C NMR: $\delta = 8.4$ (s, PCH_2CH_3), 11.4 (s, SiCH), 16.3 (vt, $N = 17$ Hz; PCH_2CH_3), 18.7 (s, $\text{SiCH}(\text{CH}_3)_2$), 55.2 (s, OCH_3), 89.5 (s, $\text{Si}\equiv$), 104.9 (t, $J_{\text{C-P}} = 15$ Hz; $\text{Pt}\equiv$), 106.2 (t, $J_{\text{C-P}} = 15$ Hz; $\text{Pt}\equiv$), 108.7 (s, $\text{Pt}\equiv\text{C}$), 109.4 (s, $\text{Pt}\equiv\text{C}$), 109.5 (s, $\text{Pt}\equiv\text{C}$), 113.5 (s, $C_6H_4\text{OMe}$), 121.5 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 122.8 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 127.9 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 128.5 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 130.5 (s, Ar), 131.9 (s, $C_6H_4\text{OMe}$), 157.3 ppm (s, Ar $C_{\text{ipso}}-\text{OMe}$); ^{31}P NMR: $\delta = 10.8$ (s, $J_{\text{P-Pt}} = 2380$ Hz, 56P), 10.9 ppm (s, 4P); IR (KBr): $\tilde{\nu} = 2094$ cm^{-1} ($\text{C}\equiv\text{C}$); elemental analysis calcd (%) for $C_{693}H_{1078}O_{16}SiP_{60}Pt_{30}$ (17405.08): C 47.82, H 6.24, P 10.68; found: C 48.18, H 6.01, P 10.41.

Synthesis of fourth-generation dendron (DW4): Protected fourth-generation dendron **11** (1.96 g, 0.11 mmol) was treated with a solution of Bu_4NF (0.13 mL, 0.13 mmol) in THF (1.0 M) in a similar manner to that of the preparation of first-generation dendron **DW1**. The crude product was purified by alumina column chromatography with dichloromethane containing 1% of ethyl acetate as eluent, and recrystallization from toluene/ethanol gave a yellow solid (1.74 g, 92%). M.p. 230–240 °C (decomp); IR (KBr): $\tilde{\nu} = 2093$ cm^{-1} ($\text{C}\equiv\text{C}$); ^1H NMR: $\delta = 1.21$ (dt, $J_{\text{H-P}} = 16$, $J_{\text{H-H}} = 8$ Hz, 540H; PCH_2CH_3), 2.15–2.19 (m, 360H; PCH_2CH_3), 3.00 (s, 1H; $\equiv\text{CH}$), 3.77 (s, 48H; OCH_3), 6.76 (d, $J = 9$ Hz, 32H; $C_6H_4\text{OMe}$), 6.99 (s, 42H; Ar), 7.15 (s, 3H; Ar), 7.21 ppm (d, $J = 9$ Hz, 32H; $C_6H_4\text{OMe}$); ^{13}C NMR: $\delta = 8.4$ (s, PCH_2CH_3), 16.3 (vt, $N = 18$ Hz; PCH_2CH_3), 55.2 (s, OCH_3), 104.9 (t, $J_{\text{C-P}} = 15$ Hz; $\text{Pt}\equiv$), 106.2 (t, $J_{\text{C-P}} = 15$ Hz; $\text{Pt}\equiv$), 108.7 (s, $\text{Pt}\equiv\text{C}$), 109.40 (s, $\text{Pt}\equiv\text{C}$), 109.5 (s, $\text{Pt}\equiv\text{C}$), 113.5 (s, $C_6H_4\text{OMe}$), 121.5 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 128.0 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 130.5 (s, Ar), 131.9 (s, $C_6H_4\text{OMe}$), 157.3 ppm (s, Ar $C_{\text{ipso}}-\text{OMe}$); the signals due to the carbons of the terminal acetylene could not be detected; ^{31}P NMR: $\delta = 10.82$ (s, 24P), 10.84 (s, $J_{\text{P-Pt}} = 2381$ Hz, 32P), 11.0 ppm (s, 4P); elemental analysis calcd (%) for $C_{684}H_{1058}O_{16}P_{60}Pt_{30}$ (17248.74): C 47.63, H 6.18, P 10.77; found: C 47.63, H 6.00, P 10.56.

Synthesis of 1-bromo-4-(triisopropylsilylethynyl)benzene (13): To a solution of 1-bromo-4-iodobenzene (9.82 g, 34.7 mmol) and (triisopropylsilyl)acetylene (6.65 g, 36.5 mmol) in diethylamine (200 mL), catalytic amounts (ca. 5 mol%) of $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI were added, and the reaction mixture was stirred for two days at room temperature. After removal of the solvent, the residue was extracted with diethyl ether and the extract was dried over Na_2SO_4 . The solvent was removed again, the

residue was dissolved in hexane and the solution was passed through a short alumina column with hexane to give a colorless oil (10.76 g, 92%). ^1H NMR: $\delta = 1.12$ (s, 21H; SiC_3H_7), 7.33 (d, $J = 9$ Hz, 2H; Ar), 7.43 ppm (d, $J = 9$ Hz, 2H; Ar). This compound was used for the next reaction without further purification.

Synthesis of 1-(triisopropylsilylethynyl)-4-(trimethylsilylethynyl)benzene (14): A mixture of 1-bromo-4-(triisopropylsilylethynyl)benzene **13** (10.76 g, 31.9 mmol) and (trimethylsilyl)acetylene (12.53 g, 127.6 mmol) in triethylamine (250 mL) and benzene (100 mL) was left under reflux overnight in the presence of catalytic amounts (ca. 5 mol%) of $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI. Similar workup to that of the preparation of 1-bromo-4-(trimethylsilylethynyl)benzene gave a yellow oil (9.80 g, 87%). ^1H NMR: $\delta = 0.25$ (s, 9H; SiCH_3), 1.12 (s, 21H; SiC_3H_7), 7.39 ppm (s, 4H; Ar); IR (neat): $\tilde{\nu} = 2159$ cm^{-1} ($\text{C}\equiv\text{C}$). This compound was also used for the next reaction without further purification.

Synthesis of 1-ethynyl-4-(triisopropylsilylethynyl)benzene (15): To a solution of 1-(triisopropylsilylethynyl)-4-(trimethylsilylethynyl)benzene **14** (9.80 g, 27.6 mmol) in acetone (250 mL) an aqueous K_2CO_3 solution (30 mL; 1.38 g, 10 mmol) was added, and the reaction mixture was stirred overnight at room temperature. Extraction with diethyl ether followed by silica-gel column chromatography with hexane as eluent gave a yellow oil (6.99 g, 90%). ^1H NMR: $\delta = 1.13$ (s, 21H; SiC_3H_7), 3.16 (s, 1H; $\equiv\text{CH}$), 7.42 ppm (s, 4H; Ar); IR (neat): $\tilde{\nu} = 2155$ ($\text{C}\equiv\text{C}$), 3303 cm^{-1} ($\equiv\text{C-H}$). This compound was also used for the next reaction without further purification.

Synthesis of 2,4,6-tris[4-(trimethylsilylethynyl)phenyl]ethynylmesitylene (16): A mixture of 2,4,6-triiodomesitylene (3.16 g, 6.34 mmol) and 1-ethynyl-4-(triisopropylsilylethynyl)benzene **15** (6.98 g, 24.7 mmol) in diethylamine (200 mL) and THF (100 mL) was reacted under reflux for one week in the presence of catalytic amounts (ca. 5 mol%) of $[\text{PdCl}_2(\text{PPh}_3)_2]$ and CuI. After extraction with diethyl ether, the crude product was purified by silica-gel column chromatography (the eluent was gradually changed from hexane/benzene 1:1 to benzene, and then dichloromethane). Recrystallization from dichloromethane/ethanol gave colorless micro-needles (1.59 g, 26%). M.p. 156 °C; ^1H NMR: $\delta = 1.14$ (s, 63H; SiC_3H_7), 2.73 (s, 9H; $C_6\text{H}_5$), 7.47 ppm (s, 12H; Ar); ^{13}C NMR: $\delta = 11.3$ (s, SiCH), 18.7 (s, $\text{SiCH}(\text{CH}_3)_2$), 20.4 (s, $C_6\text{H}_5$), 88.6 (s, $\text{C}\equiv$), 92.9 (s, $\text{C}\equiv$), 97.2 (s, $\text{C}\equiv$), 106.7 (s, $\text{C}\equiv$), 121.2 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 123.3 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 123.4 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 131.2 (s, Ar), 132.0 (s, Ar), 142.4 ppm (s, Ar $C_{\text{ipso}}-\text{CH}_3$); IR (neat): $\tilde{\nu} = 2154$ cm^{-1} ($\text{C}\equiv\text{C}$); elemental analysis calcd (%) for $C_{66}H_{84}Si_3$ (961.65): C 82.43, H 8.80; found: C 82.15, H 8.91.

Synthesis of 2,4,6-tris[4-(4-ethynylphenyl)ethynyl]mesitylene (17): To a solution of 2,4,6-tris[4-(trimethylsilylethynyl)phenyl]ethynylmesitylene **16** (1.56 g, 1.62 mmol) in THF (100 mL), a solution of Bu_4NF (5.8 mL, 5.8 mmol) in THF (1.0 M) was added in a similar manner to that of the preparation of the first-generation dendron **DW1**. The crude product was purified by alumina column chromatography with benzene as eluent followed by recrystallization from dichloromethane/hexane to give colorless micro-needles (0.68 g, 85%). M.p. 175 °C (decomp); ^1H NMR: $\delta = 2.73$ (s, 9H; $C_6\text{H}_5$), 3.19 (s, 3H; $\equiv\text{CH}$), 7.50 ppm (s, 12H; Ar); ^{13}C NMR: $\delta = 20.4$ (s, $C_6\text{H}_5$), 79.0 (s, $\text{C}\equiv$), 83.3 (s, $\text{C}\equiv$), 88.7 (s, $\text{C}\equiv$), 97.0 (s, $\text{C}\equiv$), 121.2 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 122.0 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 123.9 (s, Ar $C_{\text{ipso}}-\text{C}\equiv$), 131.3 (s, Ar), 132.2 (s, Ar), 142.5 ppm (s, Ar $C_{\text{ipso}}-\text{CH}_3$); IR (KBr): $\tilde{\nu} = 2106$, 2202 ($\text{C}\equiv\text{C}$), 3290 cm^{-1} ($\equiv\text{C-H}$); elemental analysis calcd (%) for $C_{39}H_{24}$ (492.62): C 95.09, H 4.91; found: C 94.85, H 4.86.

Synthesis of trinuclear core that has extended arms (18): A mixture of $[\text{PtCl}_2(\text{PEt}_3)_2]$ (2.26 g, 4.50 mmol) and 2,4,6-tris[4-(4-ethynylphenyl)ethynyl]mesitylene **17** (0.67 g, 1.36 mmol) in piperidine (150 mL) and toluene (150 mL) was stirred under reflux for one week in the presence of a catalytic amount (ca. 5 mol%) of CuI. After removal of the solvent, the residue was extracted with dichloromethane and the extract was dried over Na_2SO_4 . The solution was concentrated, and the solution was passed through a short alumina column with dichloromethane as eluent. The solvent was evaporated again, and the crude product was purified by alumina column chromatography (the eluent was gradually changed from hexane/benzene 1:1 to benzene, and then dichloromethane). Recrystallization from dichloromethane/hexane gave yellow plates (0.52 g, 20%). M.p. 195–205 °C (decomp); ^1H NMR: $\delta = 1.21$ (dt, $J_{\text{H-P}} = 16$, $J_{\text{H-H}} = 8$ Hz, 54H; PCH_2CH_3), 2.03–2.11 (m, 36H; PCH_2), 2.71 (s, 9H; $C_6\text{H}_5$), 7.23 (d, $J = 8$ Hz, 6H; Ar), 7.40 ppm (d, $J = 8$ Hz, 6H; Ar); ^{13}C NMR: $\delta = 8.1$

(s, PCH₂CH₃), 14.6 (vt, $N=17$ Hz; PCH₂), 20.3 (s, C₆H₅), 86.1 (t, $J_{C-P}=15$ Hz; PtC≡), 87.6 (s, C≡), 97.8 (s, C≡), 101.9 (s, C≡), 120.1 (s, Ar C_{ipso}-C≡), 121.5 (s, Ar C_{ipso}-C≡), 128.8 (s, Ar C_{ipso}-C≡), 130.8 (s, Ar), 131.1 (s, Ar), 141.62 ppm (s, Ar C_{ipso}-CH₃); ³¹P NMR: $\delta=14.9$ ppm (s, $J_{P-Pt}=2382$ Hz); IR (neat): $\tilde{\nu}=2116$ cm⁻¹ (C≡C); elemental analysis calcd (%) for C₇₂H₁₁₁Cl₃P₈Pt₃C₆H₁₄ (1940.29): C 48.28, H 6.49; found: C 48.71, H 6.29.

Synthesis of tetranuclear core (22): The reaction of [PtCl₂(PEt₃)₂] (1.56 g, 3.10 mmol) with tetra(4-ethynylphenyl)methane (0.26 g, 0.62 mmol) by a similar method to that of the preparation of trinuclear core **18** gave yellow needles (0.75 g, 53%). M.p. 285–295 °C (decomp); ¹H NMR: $\delta=1.19$ (dt, $J_{H-P}=16$, $J_{H-H}=8$ Hz, 72H; PCH₂CH₃), 2.02–2.09 (m, 48H; PCH₂CH₃), 7.04 (d, $J=9$ Hz, 8H; Ar), 7.09 ppm (d, $J=9$ Hz, 8H; Ar); ¹³C NMR: $\delta=8.0$ (s, PCH₂CH₃), 14.5 (vt, $N=17$ Hz; PCH₂CH₃), 64.3 (s, CAr₄), 82.0 (t, $J_{C-P}=15$ Hz; PtC≡), 101.2 (s, PtC≡C), 126.0 (s, Ar C_{ipso}-C≡), 129.9 (s, Ar), 130.6 (s, Ar), 143.8 ppm (s, Ar C_{ipso}-CAr₃); ³¹P NMR: $\delta=14.8$ ppm (s, $J_{P-Pt}=2393$ Hz); IR (KBr): $\tilde{\nu}=2117$ cm⁻¹ (C≡C); elemental analysis calcd (%) for C₈₁H₁₃₆P₈Cl₄Pt₄ (2279.89): C 42.67, H 6.01, P 10.87, Cl 6.22; found: C 42.91, H 5.82, P 10.64, Cl 6.00.

Synthesis of first-generation dendrimer (4G1): First-generation dendron **DW1** (447 mg, 351 μ mol) was reacted with core **22** (200 mg, 87.7 μ mol) in a similar manner to that of the preparation of protected first-generation dendrimer **6**. The crude product was purified by recrystallization from ethanol to give a yellow solid (280 mg, 44%). M.p. 210–215 °C (decomp); ¹H NMR: $\delta=1.21$ (dt, $J_{H-P}=16$, $J_{H-H}=8$ Hz, 216H; PCH₂CH₃), 2.15–2.19 (m, 144H; PCH₂CH₃), 3.77 (s, 24H; OCH₃), 6.76 (d, $J=9$ Hz, 16H; C₆H₄OMe), 6.99 (s, 12H; Ar), 7.04 (d, $J=8$ Hz, 8H; C(C₆H₄)₄), 7.12 (d, $J=8$ Hz, 8H; C(C₆H₄)₄), 7.21 ppm (d, $J=9$ Hz, 12H; C₆H₄OMe); ¹³C NMR: $\delta=8.4$ (s, PCH₂CH₃), 16.3 (vt, $N=17$ Hz; PCH₂CH₃), 55.2 (s, OCH₃), 64.3 (s, CAr₄), 104.9 (t, $J_{C-P}=15$ Hz; PtC≡), 106.2 (t, $J_{C-P}=15$ Hz; PtC≡), 107.5 (t, $J_{C-P}=15$ Hz; PtC≡), 108.7 (s, PtC≡C), 109.0 (s, PtC≡C), 109.4 (s, PtC≡C), 109.6 (s, PtC≡C), 113.5 (s, C₆H₄OMe), 121.5 (s, Ar C_{ipso}-C≡), 126.0 (s, Ar C_{ipso}-C≡), 127.9 (s, Ar C_{ipso}-C≡), 129.9 (s, C(C₆H₄)₄), 130.5 (s, Ar), 130.7 (s, C(C₆H₄)₄), 131.9 (s, C₆H₄OMe), 143.7 (s, Ar C_{ipso}-CAr₃), 157.2 ppm (s, Ar C_{ipso}-OMe); ³¹P NMR: $\delta=10.8$ (s, $J_{P-Pt}=2380$ Hz, 16P), 10.9 ppm (s, $J_{P-Pt}=2381$ Hz, 8P); IR (KBr): $\tilde{\nu}=2095$ cm⁻¹ (C≡C); elemental analysis calcd (%) for C₂₉₇H₄₄₄O₈P₂₄Pt₁₂ (7227.12): C 49.36, H 6.19, P 10.29; found: C 49.39, H 6.11, P 10.37.

Synthesis of second-generation dendrimer (4G2): Second-generation dendron **DW2** (312 mg, 87.7 μ mol) was reacted with core **22** (50 mg, 21.9 μ mol) in a similar manner to that of the preparation of the protected first-generation dendrimer **6**. Reprecipitation of a dichloromethane solution of the crude product with methanol gave a pale-yellow solid (226 mg, 63%). M.p. 225–235 °C (decomp); ¹H NMR: $\delta=1.22$ (dt, $J_{H-P}=16$, $J_{H-H}=8$ Hz, 504H; PCH₂CH₃), 2.15–2.19 (m, 336H; PCH₂CH₃), 3.77 (s, 48H; OCH₃), 6.76 (d, $J=9$ Hz, 32H; C₆H₄OMe), 7.00 (s, 36H; Ar), 7.03 (d, $J=8$ Hz, 8H; C(C₆H₄)₄), 7.12 (d, $J=8$ Hz, 8H; C(C₆H₄)₄), 7.21 ppm (d, $J=9$ Hz, 32H; C₆H₄OMe); ¹³C NMR: $\delta=8.4$ (s, PCH₂CH₃), 16.3 (vt, $N=17$ Hz; PCH₂CH₃), 55.2 (s, OCH₃), 64.3 (s, CAr₄), 104.9 (t, $J_{C-P}=15$ Hz; PtC≡), 106.2 (s, PtC≡), 108.7 (s, PtC≡C), 109.4 (s, PtC≡C), 109.5 (s, PtC≡C), 113.5 (s, C₆H₄OMe), 121.5 (s, Ar C_{ipso}-C≡), 126.0 (s, Ar C_{ipso}-C≡), 127.9 (s, Ar C_{ipso}-C≡), 129.9 (s, C(C₆H₄)₄), 130.5 (s, Ar), 130.7 (s, C(C₆H₄)₄), 131.9 (s, C₆H₄OMe), 143.7 (s, Ar C_{ipso}-CAr₃), 157.3 ppm (s, Ar C_{ipso}-OMe); ³¹P NMR: $\delta=10.8$ (s, $J_{P-Pt}=2381$ Hz, 48P), 10.9 ppm (s, 8P); IR (KBr): $\tilde{\nu}=2094$ cm⁻¹ (C≡C); elemental analysis calcd (%) for C₆₅₇H₁₀₀₄O₁₆P₅₆Pt₂₈ (16355.96): C 48.25, H 6.19, P 10.60; found: C 48.01, H 6.09, P 10.33.

Synthesis of third-generation dendrimer (4G3): Third-generation dendron **DW3** (325 mg, 40 μ mol) was reacted with core **22** (23 mg, 10 μ mol) in a similar manner to that of the preparation of the protected first-generation dendrimer **6**. Reprecipitation of a dichloromethane solution of the crude product with methanol gave a pale-yellow solid (223 mg, 64%). M.p. 225–235 °C (decomp); ¹H NMR: $\delta=1.21$ (dt, $J_{H-P}=16$, $J_{H-H}=8$ Hz, 1080H; PCH₂CH₃), 2.14–2.19 (m, 720H; PCH₂CH₃), 3.77 (s, 96H; OCH₃), 6.76 (d, $J=9$ Hz, 64H; C₆H₄OMe), 6.99 (s, 84H; Ar), 7.03 (d, $J=7$ Hz, 8H; C(C₆H₄)₄), 7.12 (d, $J=7$ Hz, 8H; C(C₆H₄)₄), 7.21 ppm (d, $J=9$ Hz, 64H; C₆H₄OMe); ¹³C NMR: $\delta=8.4$ (s, PCH₂CH₃), 16.3 (vt, $N=17$ Hz; PCH₂CH₃), 55.2 (s, OCH₃), 104.9 (t, $J_{C-P}=15$ Hz; PtC≡), 106.3 (s, PtC≡), 108.7 (s, PtC≡C), 109.4 (s, PtC≡C), 109.5 (s, PtC≡C), 113.5 (s, C₆H₄OMe), 121.5 (s, Ar C_{ipso}-C≡), 128.0 (s, Ar C_{ipso}-C≡), 129.9 (s, C(C₆H₄)₄), 130.5 (s, Ar), 130.7 (s, C(C₆H₄)₄), 131.94 (s, C₆H₄OMe),

157.3 ppm (s, Ar C_{ipso}-OMe); ³¹P NMR: $\delta=10.84$ ppm (s, $J_{P-Pt}=2381$ Hz); IR (KBr): $\tilde{\nu}=2094$ cm⁻¹ (C≡C); elemental analysis calcd (%) for C₁₃₇₇H₂₁₂₄O₃₂P₁₂₀Pt₆₀ (34613.64): C 47.78, H 6.19, P 10.74; found: C 47.71, H 5.98, P 10.60.

X-ray diffraction study of complex 22: A crystal suitable for X-ray diffraction was obtained by recrystallization from a dichloromethane/hexane solution and was mounted on a glass fiber with epoxy resin. All measurements were performed on a MacScience DIPLabo imaging plate detector using Mo_{K α} radiation ($\lambda=0.71069$ Å). The structure was solved by a direct method and all non-hydrogen atoms were refined anisotropically using a full-matrix least-squares refinement procedure. The hydrogen atoms were placed at geometrically estimated positions. All calculations were performed by using the SHELXL-97 program.^[23]

Crystallographic data for 22: C₈₁H₁₃₆Cl₄P₈Pt₄ ($M_w=2279.94$ g mol⁻¹), monoclinic, space group $P2_1/c$ (No. 14), $a=38.9970(5)$ Å, $b=16.1730(1)$ Å, $c=33.2380(3)$ Å, $\beta=114.74^\circ$, $V=19039.8(3)$ Å³, $Z=8$, $\rho_{\text{calcd}}=1.591$ g cm⁻³, $\mu(\text{MoK}\alpha)=6.129$ cm⁻¹, 200 K, $2\theta_{\text{max}}=56.04^\circ$, $R1=0.0955$ ($wR2$ (all data)=0.2515) for 1743 parameters against 27920 reflections with $I>2.0\sigma(I)$ out of 43131 unique reflections, GOF=1.053. CCDC-238415 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

This work was partly supported by a Grant-in-Aid from the Ministry of Education, Culture, Sports, Science, and Technology. We thank the members of the Material Analysis Center, ISIR, Osaka University, for spectral measurements and microanalyses.

- [1] a) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendrimers and Dendrons*, Wiley-VCH, Weinheim, **2001**; b) J. M. Fréchet, D. A. Tomalia, *Dendrimers and Other Dendritic Polymers*, Wiley, Chichester, **2001**.
- [2] For reviews, see: a) C. Gorman, *Adv. Mater.* **1998**, *10*, 295; b) I. Cuadrado, M. Moran, C. M. Casado, B. Alonso, J. Losada, *Coord. Chem. Rev.* **1999**, *193–195*, 395; c) M. A. Hearshaw, J. R. Moss, *Chem. Commun.* **1999**, 1; d) G. R. Newkome, E. He, C. N. Moorefield, *Chem. Rev.* **1999**, *99*, 1689; e) D. Astruc, J.-C. Blais, E. Cloutier, L. Djakovitch, S. Rigaut, J. Ruiz, V. Sartor, C. Valerio, *Top. Curr. Chem.* **2000**, *210*, 229; f) D. Astruc, F. Chardac, *Chem. Rev.* **2001**, *101*, 2991; g) H.-J. van Manen, F. C. J. M. van Veggel, D. N. Reinhoudt, *Top. Curr. Chem.* **2001**, *217*, 121; h) R. Kreiter, A. W. Kleij, R. J. M. Klein Gebbink, G. van Koten, *Top. Curr. Chem.* **2001**, *217*, 163; i) G. E. Oosterom, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Angew. Chem.* **2001**, *113*, 1878; *Angew. Chem. Int. Ed.* **2001**, *40*, 1828; j) R. van Heerbeek, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Chem. Rev.* **2002**, *102*, 3717; k) K. Onitsuka, S. Takahashi, *Top. Curr. Chem.* **2003**, *228*, 39.
- [3] a) S. Achar, R. J. Puddephatt, *J. Chem. Soc. Chem. Commun.* **1994**, 1895; b) S. Achar, R. J. Puddephatt, *Angew. Chem.* **1994**, *106*, 895; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 847; c) S. Achar, J. J. Vittal, R. J. Puddephatt, *Organometallics* **1996**, *15*, 43; d) G.-X. Liu, R. J. Puddephatt, *Organometallics* **1996**, *15*, 5257.
- [4] a) W. T. S. Huck, F. C. J. M. van Veggel, B. L. Kropman, D. H. A. Blank, E. G. Keim, M. M. A. Smithers, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1995**, *117*, 8293; b) W. T. S. Huck, F. C. J. M. van Veggel, D. N. Reinhoudt, *Angew. Chem.* **1996**, *108*, 1304; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1213; c) W. T. S. Huck, B. Snellink-Rueel, F. C. J. M. van Veggel, D. N. Reinhoudt, *Organometallics* **1997**, *16*, 4287; d) W. T. S. Huck, L. J. Prins, R. H. Fokkens, N. M. M. Nibbering, F. C. J. M. van Veggel, D. N. Reinhoudt, *J. Am. Chem. Soc.* **1998**, *120*, 6240; e) H.-J. van Manen, R. H. Fokkens, N. M. M. Nibbering, F. C. J. M. van Veggel, D. N. Reinhoudt, *J. Org. Chem.* **2001**, *66*, 4643.

- [5] S. Leininger, P. J. Stang, S. Huang, *Organometallics* **1998**, *17*, 3981.
- [6] a) A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, *Organometallics* **1999**, *18*, 5195; b) S. K. Hurst, M. P. Cifuentes, M. G. Humphrey, *Organometallics* **2002**, *21*, 2353; c) A. M. McDonagh, C. E. Powell, J. P. Morrall, M. P. Cifuentes, M. G. Humphrey, *Organometallics* **2003**, *22*, 1402.
- [7] N. Hagihara, K. Sonogashira, S. Takahashi, *Adv. Polym. Sci.* **1981**, *41*, 149.
- [8] N. J. Long, C. K. Williams, *Angew. Chem.* **2003**, *115*, 2690; *Angew. Chem. Int. Ed.* **2003**, *42*, 2586.
- [9] a) S. Takahashi, E. Murata, M. Kariya, K. Sonogashira, N. Hagihara, *Macromolecules* **1979**, *12*, 1016; b) S. Takahashi, Y. Takai, H. Morimoto, K. Sonogashira, *J. Chem. Soc. Chem. Commun.* **1984**, *3*; c) T. Kaharu, H. Matsubara, S. Takahashi, *J. Mater. Chem.* **1992**, *2*, 43.
- [10] a) M. Younus, A. Kohler, S. Cron, N. Chawdhury, M. R. A. Al-Mandhary, M. S. Khan, J. Lewis, N. J. Long, R. H. Friend, P. R. Raithby, *Angew. Chem.* **1998**, *110*, 3180; *Angew. Chem. Int. Ed.* **1998**, *37*, 3036; b) J. S. Wilson, A. S. Dhoot, A. J. A. B. Seeley, M. S. Khan, A. Kohler, *Nature* **2001**, *413*, 828; c) W.-Y. Wong, K.-H. Choi, G.-L. Lu, J.-X. Shi, *Makromol. Rapid Commun.* **2001**, *22*, 461; e) W.-Y. Wong, G.-L. Lu, K.-H. Choi, J.-X. Shi, *Macromolecules* **2002**, *35*, 3506.
- [11] a) M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte, R. Eisenberg, *Inorg. Chem.* **2000**, *39*, 447; b) S.-C. Chan, M. C. W. Chan, Y. Wang, C.-M. Che, K.-K. Cheung, N. Zhu, *Chem. Eur. J.* **2001**, *7*, 4180; c) V. W.-W. Yam, R. P.-L. Tang, K. M.-C. Wong, K.-K. Cheung, *Organometallics* **2001**, *20*, 4476; d) Q.-Z. Yang, L.-Z. Wu, Z.-X. Wu, L.-P. Zhang, C.-H. Tung, *Inorg. Chem.* **2002**, *41*, 5653; e) T. J. Wadas, R. J. Lachicotte, R. Eisenberg, *Inorg. Chem.* **2003**, *42*, 3772; f) J. E. McGarrah, R. Eisenberg, *Inorg. Chem.* **2003**, *42*, 4355; g) W. Lu, B.-X. Mi, M. C. W. Chan, Z. Hui, C.-M. Che, N. Zhu, S.-T. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 4958.
- [12] a) I. R. Whittall, M. G. Humphrey, A. Persoons, S. Houbrechts, *Organometallics* **1996**, *15*, 1935; b) I.-Y. Wu, J. T. Lin, J. Luo, C.-S. Li, C. Tsai, Y. S. Wen, C.-C. Hsu, F.-F. Yeh, S. Liou, *Organometallics* **1998**, *17*, 2188; c) A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, *Organometallics* **1999**, *18*, 5195; d) A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, S. Houbrechts, T. Wada, H. Sasabe, A. Persoons, *J. Am. Chem. Soc.* **1999**, *121*, 1405; e) M. H. Garcia, M. P. Robalo, A. R. Dias, M. T. Duarte, W. Wenselers, G. Aerts, E. Goovaerts, M. P. Cifuentes, S. Hurst, M. G. Humphrey, M. Samoc, B. Luther-Davies, *Organometallics* **2002**, *21*, 2107.
- [13] a) N. Ohshiro, F. Takei, K. Onitsuka, S. Takahashi, *Chem. Lett.* **1996**, 871; b) N. Ohshiro, F. Takei, K. Onitsuka, S. Takahashi, *J. Organomet. Chem.* **1998**, *569*, 195.
- [14] K. Onitsuka, M. Fujimoto, N. Ohshiro, S. Takahashi, *Angew. Chem.* **1999**, *111*, 751; *Angew. Chem. Int. Ed.* **1999**, *38*, 689.
- [15] a) Y.-F. Lu, C. W. Harwig, A. G. Fallis, *J. Org. Chem.* **1993**, *58*, 4202; b) O. Lavastre, L. Ollivier, P. H. Dixneuf, S. Sibandhit, *Tetrahedron* **1996**, *52*, 5495; c) M. M. Haley, M. L. Bell, J. J. English, C. A. Johnson, T. J. R. Weakley, *J. Am. Chem. Soc.* **1997**, *119*, 2956.
- [16] a) S. Takahashi, E. Murata, K. Sonogashira, N. Hagihara, *J. Polym. Sci. Polym. Chem. Ed.* **1980**, *18*, 661; b) K. Onitsuka, T. Joh, S. Takahashi, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1179.
- [17] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, *Synthesis* **1980**, 627.
- [18] a) K. Sonogashira, T. Yatake, Y. Tohda, S. Takahashi, N. Hagihara, *J. Chem. Soc. Chem. Commun.* **1977**, 291; b) K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi, N. Hagihara, *J. Organomet. Chem.* **1978**, *145*, 101.
- [19] a) M. Simard, D. Su, J. D. Wuest, *J. Am. Chem. Soc.* **1991**, *113*, 4696; b) U.-M. Wiesler, A. J. Berresheim, F. Morgenroth, G. Lieser, K. Müllen, *Macromolecules* **2001**, *34*, 187.
- [20] a) D.-L. Jiang, T. Aida, *J. Am. Chem. Soc.* **1998**, *120*, 10895; b) S. Hecht, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1999**, *121*, 4084; c) M. Higuchi, S. Shiki, K. Ariga, K. Yamamoto, *J. Am. Chem. Soc.* **2001**, *123*, 4414.
- [21] a) Y. Fujikura, K. Sonogashira, N. Hagihara, *Chem. Lett.* **1975**, 1067; b) Y. Liu, S. Jiang, K. Glusac, D. H. Powell, D. F. Anderson, K. S. Schanze, *J. Am. Chem. Soc.* **2002**, *124*, 12412.
- [22] K. Onitsuka, H. Kitajima, M. Fujimoto, A. Tuchi, F. Takei, S. Takahashi, *Chem. Commun.* **2002**, 2576.
- [23] G. M. Sheldrick, SHELXL-97, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

Received: June 1, 2004

Published online: November 10, 2004