

## A divergent approach to the precise synthesis of giant organometallic dendrimers using platinum–acetylides as building blocks

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Giant platinum–acetylides dendrimers were precisely synthesized by a divergent method; the sixth generation dendrimer, the diameter of which is larger than 10 nm, has 189 Pt atoms per molecule, and its molecular weight is as high as 139750.

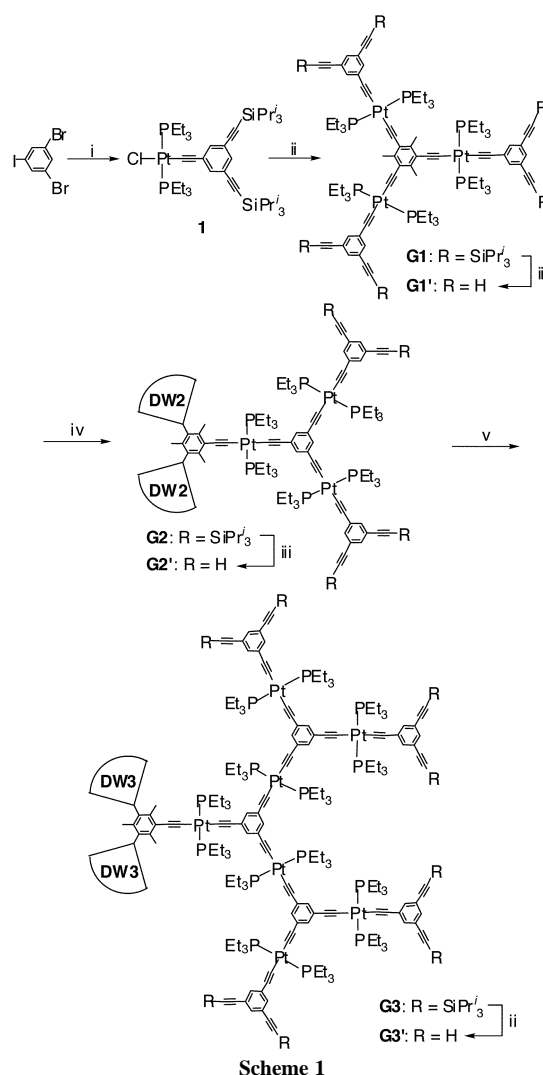
To develop novel functionalized nano-size materials, the incorporation of metallic species into dendrimers has attracted much attention, since transition metal complexes have characteristic magnetic, electronic, and photo-optical properties as well as distinctive reactivity.<sup>1</sup> In particular, organometallic dendrimers offer the advantage of making it possible to tailor dendritic molecules with desirable functionalities due to not only the availability of a wide variety of organic compounds that coordinate to many kinds of metal atoms but also the flexibility of the coordination modes of organic ligands to the metal.<sup>2</sup> Although many organometallic dendrimers have been prepared so far, most of them contain metallic species at specific positions in the molecule; *i.e.*, at the core or at the periphery. Dendrimers composed of organometallic complexes in each generation are current challenging targets. Some examples of such dendrimers have been reported using an appropriate choice of organometallic complexes for the core and building blocks.<sup>3–7</sup> However, large dendrimers greater than fourth-generation have not yet been prepared.

Platinum–acetylide complexes are thermally robust and stable, even when exposed to air and moisture, and can be obtained in high yields by a well-established synthetic methodology.<sup>8</sup> Since some platinum–acetylide complexes show unique properties,<sup>9</sup> platinum–acetylide dendrimers are of special interest due to their potential to provide new nano-size organometallic materials. Recently, we developed a convergent route to the synthesis of platinum–acetylide dendrimers up to the third-generation.<sup>10</sup> We present here a divergent approach to platinum–acetylide dendrimers up to the sixth-generation, which is much larger organometallic dendrimers than those have been reported previously.

The synthetic route up to the third-generation dendrimer is shown in Scheme 1. The building block for divergent synthesis is the mononuclear platinum–acetylide complex (**1**), which was prepared from 1-bromo-3,5-diiodobenzene using the trimethylsilyl and triisopropylsilyl groups to protect the terminal acetylene.<sup>10,11</sup> We used 2,4,6-triethynylmesitylene (**2**), the methyl groups of which are very important for characterization of the resulting dendrimers, as the core. The treatment of **1** with **2** in a molar ratio of 3:1 using a CuCl catalyst in diethylamine at room temperature for 24 h resulted in the quantitative formation of the first-generation dendrimer (**G1**), which was fully characterized by spectral analyses. The reaction of the deprotected first-generation dendrimer (**G1'**), which was generated by reacting **G1** with Bu<sub>4</sub>NF, with 6 equiv. of **1** gave the second-generation dendrimer (**G2**), which was subsequently grown to the third-generation dendrimer (**G3**) in a similar manner. In these reactions, the building block **1** was completely consumed and the desired dendrimers were obtained as the sole product.

On the other hand, when we tried to prepare the fourth-generation dendrimer by reacting **G3'** with 24 equiv of **1**, small

amounts of **1** remained after 48 h, and a structural defect in the product was detected by <sup>1</sup>H NMR (Fig. 1(a)). Two signals assignable to the protons of terminal acetylenes were observed at  $\delta$  3.00 and 3.05. The former is attributed to a diethynyl–monoplatinum group and the latter to a monoethynyl–diplatinum group. The integral ratio of these signals relative to that of the methyl groups at the core suggests that 25% of the product has on average one unreacted terminal acetylene, even though 75% of the product has the expected structure. This problem was resolved by using a 25 mol% excess of the building block **1** in the reaction. Disappearance of the signal assignable to the terminal acetylenes in the <sup>1</sup>H NMR spectrum clearly showed that the reaction proceeded completely to give the desired fourth-generation dendrimer **G4** (Fig. 1(b)). Although the reaction mixture contained not only **G4** but also considerable amounts of **1**, these were easily separated by reprecipitation.



Although molecular ions of these dendrimers, except for **G1** and **G1'**, were not detected even by MALDI-TOF mass spectrometry, the number of unreacted terminal acetylenes can be sensitively estimated by  $^1\text{H NMR}$  in each generation because all of the dendrimers have three methyl groups at the core regardless of the generation number. Successive reactions led to the formation of up to the sixth-generation dendrimer (**G6**). In the  $^1\text{H NMR}$  spectra of **G5** and **G6**, no signal due to the terminal acetylenes was observed, indicating no significant amounts of structural defects. The sixth-generation dendrimer **G6** has 189 Pt atoms per molecule, and its molecular weight is as high as 139750 (Scheme 2).

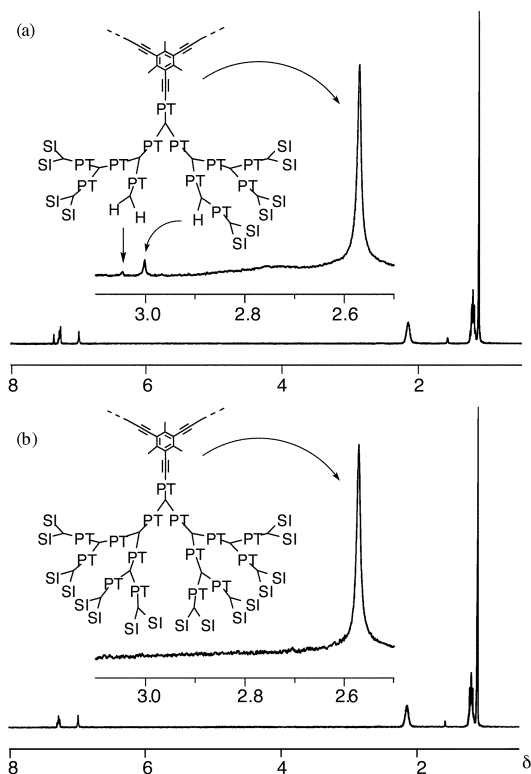
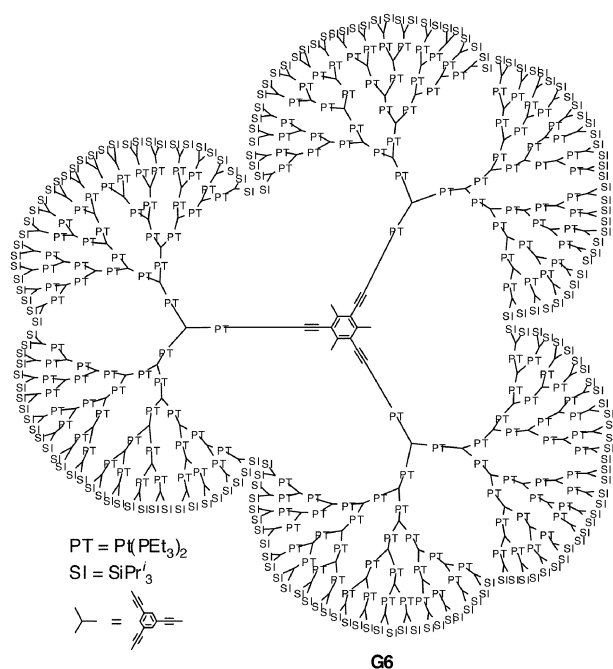


Fig. 1



Scheme 2

Table 1 GPC data for dendrimers **G1**–**G6**

Dendrimer	$M_n^a$	FW	$M_n/\text{FW}$
<b>G1</b>	2800	2869	0.98
<b>G2</b>	6700	7285	0.92
<b>G3</b>	11900	16116	0.74
<b>G4</b>	19100	33778	0.57
<b>G5</b>	29100	69102	0.42
<b>G6</b>	40200	139750	0.29

<sup>a</sup> Determined by using polystyrene standards.

The relative molecular size of these dendrimers was investigated by gel permeation chromatography (Table 1). The number averaged molecular weight ( $M_n$ ) of **G1** is coincidentally consistent with the formula weight (FW). Whereas the FW grows exponentially with an increase in the number of the generation, the  $M_n$  value increases proportionally, so that **G6** has an  $M_n$  value of less than one-third of the formula weight. The molecular size of **G6** was measured by small angle neutron scattering (SANS), which showed that the radius was  $56.8 \pm 0.2$  Å. This result is in very good agreement with the diameter of **G6** (12 nm) calculated by molecular modeling.

In summary, we have precisely synthesized a large organometallic dendrimer, the diameter of which is larger than 10 nm, by using platinum–acetylide as a repeating unit. With the facile chemistry described here, nanoscale organometallic objects may be realized. Further studies focused on the properties of these nano-size organometallic dendrimers are now in progress.

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