

PAMAM dendron-stabilised palladium nanoparticles: effect of generation and peripheral groups on particle size and hydrogenation activity†

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Dendron stabilised Pd nanoparticles were prepared using the self-assembly of dendrons, which could catalyze a highly selective hydrogenation of dienes and acetylenes to monoenes.

Dendrons, wedge-like molecules composed of a core, divergent branching units, and, end groups, have generated interest because of their great potential in tailoring highly ordered structures and functions.^{1,2} Self-assembly of dendrons can afford spherically shaped architectures similar to micelles and vesicles.³ A variety of subunits have been reported to create well-defined and finely tuned capsule structures, which are expected to provide integrated functional nano-materials in combination with metal species such as metal complexes and particles.^{4,5} The dendritic shell can act as a stabilizer for active metal species in organic syntheses, where the internal branch units function as solvents or additives to facilitate catalytic reactions.

Metal nanoparticles have an extremely large surface area to volume ratio, which can be highly tunable to create various nanoscale objects. Applications of these metal nanoparticles are widely expanding in areas such as catalysis, sensor devices, and nanoelectronics.⁶ Since their function strongly depends on the metal particle size, preparation of size-regulated nanoparticles is a crucial yet challenging problem.⁷ In particular, the precise control of particle sizes in the single nanometer (<10 nm) range is of current interest in developing high performance catalysts for organic synthesis. Although there have been many reports on the stabilization of metal nanoparticles such as Pd, Pt and Au using dendrimers⁵ and dendrons,⁸ the range of particle size has been limited to between 1–3 nm. In the present paper, we describe poly(amidoamine) (PAMAM) dendrons having a pyridine core and alkyl end groups assembled into spherical micelle-like structures. The size of Pd nanoparticles prepared *in situ* by these dendrons can be controlled by chemical reduction. To our knowledge, this is the first example of the controlled synthesis of Pd nanoparticles with a wide size range between 3 to 10 nm using dendron assemblies. The obtained dendritic Pd nanocomposites catalyse selective hydrogenation of dienes and acetylenes, where

the dendron units provide multiple functionalities for the Pd nanoparticles, *e.g.*, templates for Pd nanoparticle formation, ligands for active intermediates, and specific interactions with substrates.

PAMAM dendrons with a pyridine core unit were synthesized using a divergent method from the reaction of 4-picolylamine with methyl acrylate and ethylenediamine,^{8b} and their terminal ester moieties were alkylated by *n*-hexylamine [G_n Py- C_6 ($n = 1-3$), Fig. 1]. Similarly, using dodecylamine instead of hexylamine gave G_n Py- C_{12} . Their structures were characterized using ¹H NMR spectroscopy, dynamic light scattering (DLS) measurements and TEM imaging. After complexation of $[PdCl(C_2H_5)_2]$ with the above dendrons in dichloromethane, reduction of the palladium complex with addition of 2 equivalents of $LiB(Et)_3H$ gave a homogeneous dark solution. Notably, the obtained palladium nanoparticles [**1a** G_1 Py- C_6 Pd(0), **2a** G_2 Py- C_6 Pd(0), and **3a** G_3 Py- C_6 Pd(0)] were stable for several months due to the encapsulation effect of the globular assemblies of the dendrons.

¹H NMR spectra of G_n Py- C_6 and G_n Py- C_{12} exhibited broad signals due to the internal methylenes at around δ 3.2 ppm and the pyridyl core at δ 8.4 and 7.3 ppm, suggesting a reversed micelle-like assembly for the dendrons.⁹ DLS and TEM imaging provided information about the size of the dendritic Pd nanoparticles as

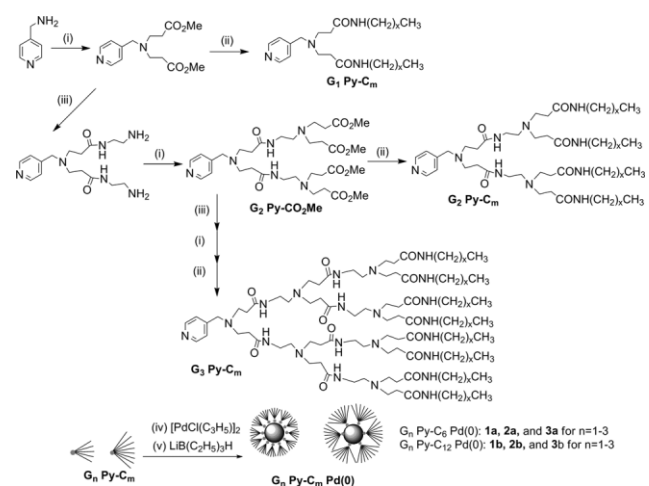


Fig. 1 Synthesis of G_1 to G_3 amidoamine dendrons (G_n Py- C_m ; $n = 1-3$, $m = 6, 12$) and the dendron-assembly encapsulated Pd nanoparticles G_n Py- C_m Pd(0). (i) excess methyl acrylate, (ii) excess alkyl amine ($x = 5, 11$), (iii) excess ethylenediamine, (iv) $[PdCl(C_2H_5)_2]$ in CH_2Cl_2 , (v) $LiB(Et)_3H$ in THF.

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shown in Table 1 and Fig. 2. DLS measurement of the dendrons revealed the formation of globular assemblies in CH_2Cl_2 with average diameters of 10.8 ± 1.7 , 10.9 ± 2.0 , and 11.8 ± 1.7 nm for G_1 , G_2 , and G_3 Py- C_6 (entries 1–3), respectively. Adding the Pd complex to the dendrons did not alter their size distributions, and even after reduction of the Pd complex, the size distributions for **1a**, **2a** and **3a** were similar to those of the parent dendron assemblies (entries 4–6). From TEM images, the average Pd nanoparticle sizes for G_1 , G_2 , and G_3 Py- C_6 dendrons were 6.8 ± 2.0 (**1a**), 5.3 ± 1.7 (**2a**), and 5.1 ± 1.9 nm(**3a**), respectively. By changing the C_6 alkyl chain to a C_{12} chain, G_1 , G_2 , and G_3 Py- C_{12} dendrons gave smaller Pd nanoparticles of 4.6 ± 1.9 (**1b**), 3.6 ± 1.3 (**2b**) and 3.5 ± 1.3 (**3b**), respectively (entries 10–12). Furthermore, the G_2 Py- CO_2Me dendron without an alkyl chain forms a large spherical assembly with an average diameter of 15.6 ± 2.0 nm, where the Pd nanoparticles of 10.6 ± 2.8 nm were accommodated within the dendron assembly (entries 13 and 14). From these results, it is clear that the end group of the dendron strongly influences and controls the size of Pd nanoparticles. Also, increasing the generation of the dendron decreases the size of the Pd nanoparticles. According to the results by DLS and TEM measurements, the size distribution of the dendron assemblies agreed well with the distribution derived from the combination of the Pd nanoparticle and dendron sizes. ‡ *These self-assembled dendrons can thus form monolayer capsules with polar voids to act as controllable templates for Pd nanoparticles with the wide size range from 3 to 10 nm.*^{8b} *This is the first example of the size regulation of Pd nanoparticles by dendron assemblies.*

In order to examine the catalytic activity of the dendron Pd nanoparticles, the hydrogenation of olefins and acetylenes was carried out. The dendron Pd catalysts show high selectivity for hydrogenation of conjugated dienes to the corresponding monoenes. For example, using **1a–3a**, 1,3-cyclooctadiene exclusively gave cyclooctene (Table 2). The reactivity toward the monoene was much lower than that toward the diene; cyclohexene was barely hydrogenated compared to 1,3-cyclohexadiene. The initial hydrogenation rates increased with increasing generation of the dendrons: the G_3 dendron catalyst (**3a**) showed the highest catalytic activity among G_1 , G_2 , and G_3 . These findings are interpreted in terms of accessibility of the substrate to the

Table 1 Average diameter of dendron assemblies and Pd nanoparticles by DLS and TEM measurements

Entry	Dendron	Average diameter/nm	
		DLS ^a	Pd ^b
1	G_1 Py- C_6	10.8 ± 1.7	—
2	G_2 Py- C_6	10.9 ± 2.0	—
3	G_3 Py- C_6	11.8 ± 1.7	—
4	G_1 Py- C_6 Pd(0) 1a	10.5 ± 1.6	6.8 ± 2.0
5	G_2 Py- C_6 Pd(0) 2a	11.0 ± 1.7	5.3 ± 1.7
6	G_3 Py- C_6 Pd(0) 3a	12.5 ± 2.6	5.1 ± 1.9
7	G_1 Py- C_{12}	9.4 ± 1.4	—
8	G_2 Py- C_{12}	10.1 ± 1.6	—
9	G_3 Py- C_{12}	11.2 ± 1.7	—
10	G_1 Py- C_{12} Pd(0) 1b	9.5 ± 1.6	4.6 ± 1.9
11	G_2 Py- C_{12} Pd(0) 2b	10.0 ± 1.5	3.6 ± 1.3
12	G_3 Py- C_{12} Pd(0) 3b	11.4 ± 1.8	3.5 ± 1.3
13	G_2 Py-COOMe	15.6 ± 2.0	—
14	G_2 Py-COOMe Pd(0)	15.7 ± 3.3	10.6 ± 2.8

^a Measured in CH_2Cl_2 at 25 °C. ^b Measured by TEM images.

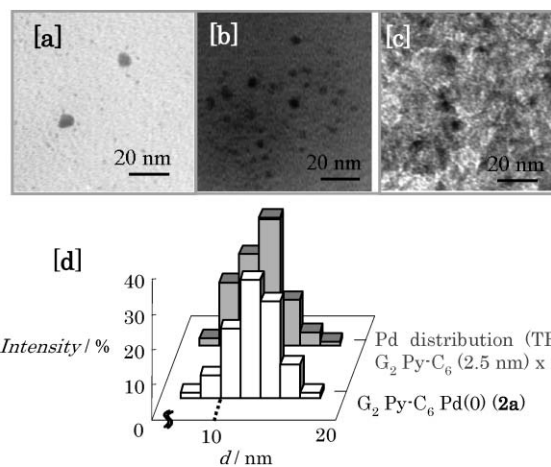


Fig. 2 TEM images of Pd nanoparticles encapsulated within the G_2 dendrons; (a) G_2 Py- CO_2Me Pd(0), (b) G_2 Py- C_6 Pd(0) (**2a**), (c) G_2 Py- C_{12} Pd(0) (**2b**), and (d) the size distributions of **2a**.

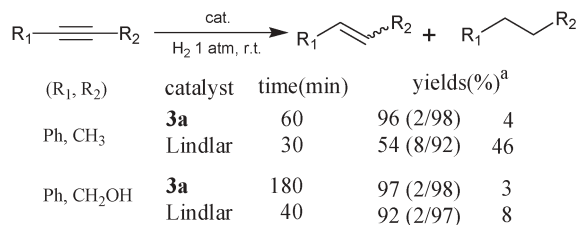
Table 2 Hydrogenation of conjugated dienes catalysed by dendron-encapsulated Pd nanoparticle^a

Substrate	Dendron	TOF (mol H_2 /mol Pd min)		
		G_1	G_2	G_3
$n = 1$	G_n - C_6	5.2	6.4	12.5
$n = 3$	G_n - C_6	4.3	5.5	12.3
$n = 3$	G_n - C_{12}	6.0	9.6	20.3

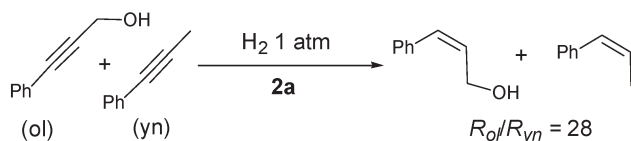
^a Reaction conditions: substrate 1.0 mmol, Pd 5.0 μmol , dendron 82 μmol , CH_2Cl_2 3 mL.

palladium active site; the increasing dendron generation provides a less congested particle surface.^{8e} In the case of unimolecular dendrimer encapsulated Pd nanoparticles, the surface active sites were passivated by the highly congested surface and branching units in the higher generation dendrimers.^{5f} The above generation effect of the dendrons was also observed with dendrons having C_{12} alkyl groups. The C_{12} dendron Pd nanoparticles of **1b–3b** showed higher catalytic activities than **1a–3a** having C_6 alkyl groups, as shown in Table 2, which might be due to the smaller Pd nanoparticles. The above high monoene selectivities in the hydrogenation of conjugated dienes were similar to the results by PPI dendrimer-encapsulated Pd nanoparticle catalysts.^{5f}

In the hydrogenation of 1-phenyl-1-propyne, catalyst **3a** gave a 96% yield of 1-phenyl-1-propene ($E/Z = 2/98$) together with 4% of 1-phenylpropane at 100% conversion of the substrate (Scheme 1). The monoene selectivity is much superior to that of the Lindlar catalyst under the same reaction conditions: 54% yield of 1-phenyl-1-propene ($E/Z = 8/92$) and 46% of propylbenzene were obtained when the conversion of 1-phenyl-1-propyne reached 100% as shown in Scheme 1. Also, cinnamyl alcohol ($E/Z = 2/98$) was obtained in 97% yield together with 3% of 3-phenyl-1-propanol in the hydrogenation of 3-phenyl-1-propyne-1-ol.¹⁰ *The above high selectivity for monoenes using the dendron stabilised Pd nanoparticle is due to the ligand effect of the pyridine core of the dendrons.*^{11,12g}



Scheme 1 Hydrogenation of alkynes using **3a** and Lindlar catalyst. Reaction conditions are in similar to those in Table 2. ^a Figures in parentheses are the selectivity of the (*E*)- and (*Z*)-olefins.



Scheme 2 Intermolecular competitive hydrogenation of 3-phenyl-2-propyn-1-ol (ol) and 1-phenyl-1-propyne (yn) catalysed by **2a**. R_{ol} and R_{yn} are the initial hydrogenation rates of ol and yn, respectively.

Furthermore, the effect of the surrounding dendron branches was emphasized in the intermolecular competitive hydrogenation between 3-phenyl-2-propyn-1-ol and 1-phenyl-1-propyne using **2a** as shown in Scheme 2. The initial hydrogenation rate for 3-phenyl-2-propyn-1-ol (R_{ol}) was greater than that for 1-phenyl-1-propyne (R_{yn}) by a factor of 28, although the hydrogenation rate ratio for individual hydrogenations of 3-phenyl-2-propyn-1-ol and 1-phenyl-1-propyne was 2.1. Clearly, the hydrogenation of an acetylenic compound is accelerated by the hydroxyl group of the substrate through hydrogen bonding with the amide groups within the dendron.¹³

In conclusion, we demonstrated the preparation of supramolecular dendritic Pd(0) nanoparticles utilizing self-assembly of dendrons. Fine tuning of the Pd nanoparticle size ranging from 3 nm to 10 nm was achieved by adjusting the alkyl chain length and the generation of the dendrons. The dendron units provide multiple functionalities to the Pd nanoparticles: (1) templates and stabilizing agents for the palladium nanoparticles, (2) ligands of active sites adjusting the catalytic activity and selectivity, and (3) binding hosts by hydrogen bonding between the amido group of the dendron and the oxygen group of the substrate. Further investigations on the size controllability of these dendrons for high performance metal nanoparticle catalysts are underway.

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Notes and references

‡ The molecular sizes of G₁, G₂, and G₃ Py-Cn dendrons calculated by Chem 3D are 1.8, 2.5, and 3.2 nm for C₆ and 2.4, 3.1, and 3.8 nm for C₁₂, respectively.

§ The Lindlar catalyst was obtained from N. E. ChemCat.

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- The dendron catalyst is stable and no precipitation was observed after complete conversion of the alkynes.
- Dendrimer-encapsulated Pd nanoparticles showed similar selectivity through an attractive hydrogen bonding interaction between the dendrimers and the functional group of the substrate. See ref. 5f.