Supporting Information

Dendron-Stabilized Palladium Nanoparticles: Effect of Generation and Peripheral Groups on Particle Size and Hydrogenation Activity

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Syntheses of G n Py-COOMe (n = 1, 2, 3) dendrons

Methyl acrylate (12.9 g, 150 mmol) was added to a methanol solution of 4-picolyamine (5.4 g, 50 mmol). The mixture was stirred for 120 h, then concentrated under reduced pressure. The residue was purified by dialysis (Spectra/Por® CE MWCO: 100) in MeOH, and dried under vacuum at 40 °C for 24 h to give 13.2 g (94 %) of G 1 Py-COOMe dendron as light orange oil. G 2 and G 3 Py-COOMe dendrons were also synthesized from G 1 and G 2 Py-NH 2 dendrons according the above procedures, respectively.

Syntheses of G n Py-C m (n = 1, 2, 3, m = 6, 12) and Py-NH 2 (n = 1, 2) dendrons

To a methanol solution of G 1 Py-COOMe (2.8 g, 10 mmol) was added n-hexylamine (15.2 g, 150 mmol) slowly at -75 °C and the mixture was stirred at room temperature for 72 h. The combined solution was concentrated under reduced pressure, and the residue was purified by dialysis.
(Spectra/Por® CE MWCO: 100) in MeOH, then dried under vacuum at 40 °C for 24 h to give 4.19 g (95 %) of G₁ Py-C₆ dendron as light orange oil. According to the above procedure, G₂ and G₃ Py-C₆ dendrons were also synthesized from G₂ and G₃ Py-COOMe, respectively. Use of n-dodecylamine in place of n-hexylamine or ethylene diamine could afford Gn Py-C₁₂ or Gn Py-NH₂ dendrons, respectively.

**Selected data for G₂ Py-C₆ and G₂ Py-C₁₂:**

**G₂ Py-C₆:** $^1$H NMR (270 MHz, $d_6$-DMSO, TMS, 30 °C): $\delta$8.47 (2H, d, aromatic CH of 4-picolyamine), 7.82 (6H, br, NH), 7.30 (2H, d, aromatic CH of 4-picolyamine), 3.58 (2H, s, CH₂ of 4-picolyamine), 3.20 (4H, br, NHCH₂CH₂N), 3.10 (8H, m, CH₂(CH₂)₄CH₃), 2.66 (12H, br, NCH₂CH₂CO), 2.54 (4H, m, NHCH₂CH₂N), 2.31 (12H, br, NCH₂CH₂CO), 1.36 (8H, m, CH₂(CH₂)₃CH₃), 1.23 (24H, m, (CH₂)₃CH₃), 0.87 (12H, m, (CH₂)₃CH₃). $^{13}$C($^1$H) NMR (68 MHz, $d_6$-DMSO, TMS, 30 °C): $\delta$170.6 (CONH), 148.9 (aromatic carbon of 4-picolyamine), 128.3 (aromatic carbon of 4-picolyamine), 123.1 (aromatic carbon of 4-picolyamine), 56.0 (CH₂ of 4-picolyamine), 51.9 (NHCH₂CH₂N), 49.5 (NHCH₂CH₂CO), 41.5 (CH₂(CH₂)₄CH₃), 36.8 (NHCH₂CH₂N), 33.2 (NHCH₂CH₂CO), 31.1 (CH₂(CH₂)₃CH₃), 28.9 (CH₂(CH₂)₂CH₃), 26.0 (CH₂CH₂CH₃), 21.9 (CH₂CH₃), 13.7 ((CH₂)₃CH₃). IR (KBr): 3079 ($\nu$N-H), 2956, 2929, 2857 ($\nu$C-H), 1645 ($\nu$C=O, amide), 1552 ($\delta$N-H, amide). MS m/z (ESI) 968.1 (M-H⁻).

**G₂ Py-C₁₂:** $^1$H NMR (270 MHz, $d_6$-DMSO, TMS, 30 °C): $\delta$8.46 (2H, d, aromatic CH of 4-picolyamine), 7.80 (6H, br, NH), 7.28 (2H, d, aromatic CH of 4-picolyamine), 3.57 (2H, s, CH₂ of 4-picolyamine), 3.18 (4H, br, NHCH₂CH₂N), 3.01 (8H, m, CH₂(CH₂)₄CH₃), 2.63 (12H, br, NCH₂CH₂CO), 2.52 (4H, m, NHCH₂CH₂N), 2.25 (12H, br, NCH₂CH₂CO), 1.36 (8H, m, CH₂(CH₂)₃CH₃), 1.22 (72H, m, (CH₂)₃CH₃), 0.85 (12H, m, (CH₂)₃CH₃). $^{13}$C($^1$H) NMR (68 MHz,
$d_6$-DMSO, TMS, 30 °C): δ170.9 (CONH), 149.0 (aromatic carbon of 4-picolylamine), 130.0 (aromatic carbon of 4-picolylamine), 123.2 (aromatic carbon of 4-picolylamine), 56.4 (CH$_2$ of 4-picolylamine), 51.8 (NHCH$_2$CH$_2$N), 49.6 (NCH$_2$CH$_2$CO), 38.3 (CH$_2$(CH$_2$)$_{10}$CH$_3$), 36.7 (NHCH$_2$CH$_2$N), 33.3 (NCH$_2$CH$_2$CO), 32.2 (CH$_2$(CH$_2$)$_3$CH$_3$), 31.3 (CH$_2$CH$_2$CH$_3$), 29.0 (CH$_2$(CH$_2$)$_3$CH$_3$), 28.9 (CH$_2$(CH$_2$)$_2$CH$_3$), 28.8 (CH$_2$(CH$_2$)$_2$CH$_3$), 26.4 (CH$_2$(CH)$_3$CH$_3$), 22.1 (CH$_2$CH$_3$), 13.9 (CH$_2$(CH$_2$)$_3$CH$_3$).

IR (KBr): 3055 ($\nu$N-H), 2924, 2853 ($\nu$C-H), 1644 ($\nu$C=O, amide), 1556 ($\delta$N-H, amide). MS m/z (ESI) 1294.5 (M-H$^+$).

**General procedure for preparation of the dendritic Pd(0) nanoparticles:** Typical procedures for the preparation of the dendritic Pd nanoparticles [Gn Py-C$_6$ Pd(0) (n = 1, 2, 3)] are as follows. To a CH$_2$Cl$_2$ solution (6 mL) of G$_n$ Py-C$_6$ (0.164 mmol) was added [PdCl(C$_3$H$_5$)$_2$] (0.010 mmol), and stirred vigorously at room temperature for 1 h. The solution was treated with LiB(C$_3$H$_5$)$_2$H (0.020 mmol) and stirred at room temperature for 1 h.

**Hydrogenation of olefins and acetylenes catalysed by the dendritic Pd nanoparticles:** A side-armed flask attached to a gas burette and a manometer was evacuated and filled with molecular hydrogen, followed by addition of 3 mL of Pd solutions (Pd: 5.0 μmol) and stirred for half an hour at 25 °C. Hydrogen uptake was measured just after the addition of substrates. The products were determined by GC and GC-MS using an internal standard method.

**Competitive hydrogenation of acetylenes catalysed by the dendritic Pd nanoparticles:**

G$_2$ Py-C$_6$ Pd(0) (Pd: 10 μmol) in CH$_2$Cl$_2$ (3 mL) was stirred at -25 °C for 0.5 h under hydrogen atmosphere. To this Pd solution added a CH$_2$Cl$_2$ solution (1 mL) of an equimolar mixture of 3-phenyl-2-propyn-1-ol (0.5 mmol) and 1-phenyl-1-propyne (0.5 mmol). The products were determined by GC-MS using an internal standard method.
Timecourse of the Hydrogenation in Scheme 1

Hydrogenation of 1-Phenyl-1-propyne

a) Catalyst 3a

b) Lindlar catalyst

Hydrogenation of 3-Phenyl-2-propyn-1-ol

a) Catalyst 3a

b) Lindlar catalyst