Supplementary Material (ESI) for Chemical Communications

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-picolylamine (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 ^{o}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 form 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 ^{o}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 ^{o}C for 24 h to give 4.19 g (95 %) of G_1 Py-C6 dendron as light orange oil. According to the above procedure, G_2 and G_3 Py-C6 dendrons were also synthesize from G_2 and G_3 Py-COOMe, respectively. Use of *n*-docecylamine in place of *n*-hexylamine or ethylene diamine could afford Gn Py-C_{12} or Gn Py-NH_2 dendrons, respectively.

Selected data for G_2 Py-C_6 and G_2 Py-C_{12}:

G_2 Py-C_6: ^{1}H NMR (270 MHz, d_6-DMSO, TMS, 30 ^{o}C): δ8.47 (2H, d, aromatic CH of 4-picolylamine), 7.82 (6H, br, NH), 7.30 (2H, d, aromatic CH of 4-picolylamine), 3.58 (2H, s, CH_2 of 4-picolylamine), 3.20 (4H, br, NHC$H_2$$CH_2$N), 3.10 (8H, m, C$H_2$$(CH_2)_4CH_3$), 2.66 (12H, br, NC$H_2$$CH_2$CO), 2.54 (4H, m, $NHCH_2CH_2$N), 2.31 (12H, br, NCH_2CH_2CO), 1.36 (8H, m, C$H_2$$(CH_2)_3CH_3$), 1.23 (24H, m, (C$H_2$$)_3CH_3$), 0.87 (12H, m, $(CH_2)_5CH_3$). ^{13}C{^{1}H} NMR (68 MHz, d_6-DMSO, TMS, 30 ^{o}C): δ170.6 (CONH), 148.9 (aromatic carbon of 4-picolylamine), 128.3 (aromatic carbon of 4-picolylamine), 123.1 (aromatic carbon of 4-picolylamine), 56.0 (CH_2 of 4-picolylamine), 51.9 ($NHCH_2CH_2$N), 49.5 (NCH_2CH_2CO), 41.5 ($CH_2(CH_2)_4CH_3$), 36.8 (NHCH_2CH_2N), 33.2 (NCH_2CH_2CO), 31.1 ($CH_2(CH_2)_3CH_3$), 28.9 ($CH_2(CH_2)_2CH_3$), 26.0 ($CH_2CH_2CH_3$), 21.9 (CH_2CH_3), 13.7 ($(CH_2)_5CH_3$). IR (KBr): 3079 (ν_{N-H}), 2956, 2929, 2857 (ν_{C-H}), 1645 ($\nu_{C=O,}$ amide), 1552 ($\delta_{N-H,}$ amide). MS m/z (ESI) 968.1 ($M-H^{+}$).

G_2 Py-C12: ^{1}H NMR (270 MHz, d_6-DMSO, TMS, 30 ^{o}C): δ8.46 (2H, d, aromatic CH of 4-picolylamine), 7.80 (6H, br, NH), 7.28 (2H, d, aromatic CH of 4-picolylamine), 3.57 (2H, s, CH_2 of 4-picolylamine), 3.18 (4H, br, NHC$H_2$$CH_2$N), 3.01 (8H, m, C$H_2$$(CH_2)_4CH_3$), 2.63 (12H, br, NC$H_2$$CH_2$CO), 2.52 (4H, m, $NHCH_2CH_2$N), 2.25 (12H, br, NCH_2CH_2CO), 1.36 (8H, m, C$H_2$$(CH_2)_3CH_3$), 1.22 (72H, m, (C$H_2$$)_3CH_3$), 0.85 (12H, m, $(CH_2)_5CH_3$). ^{13}C{^{1}H} NMR (68 MHz,

d_6-DMSO, TMS, 30 ^{o}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 ($NHCH_2CH_2N$), 49.6 (NCH_2CH_2CO), 38.3 ($CH_2(CH_2)_{10}CH_3$), 36.7 ($NHCH_2CH_2N$), 33.3 (NCH_2CH_2CO), 32.2 ($CH_2(CH_2)_9CH_3$), 31.3 ($CH_2CH_2CH_3$), 29.0 ($(CH_2)_4(CH_2)_3CH_3$), 28.9 ($CH_2(CH_2)_7CH_3$), 28.8 ($CH_2(CH_2)_2CH_3$), 26.4 ($CH_2(CH_2)_8CH_3$), 22.1 (CH_2CH_3), 13.9 ($(CH_2)_{11}CH_3$). IR (KBr): 3055 (ν_{N-H}), 2924, 2853 (ν_{C-H}), 1644 ($\nu_{C=O,}$ amide), 1556 (δ_{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_2Cl_2 solution (6 mL) of G_n Py-C_6 (0.164 mmol) was added $[PdCl(C_3H_5)]_2$ (0.010 mmol), and stirred vigorously at room temperature for 1 h. The solution was treated with $LiB(C_3H_5)_3H$ (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 ^{o}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.

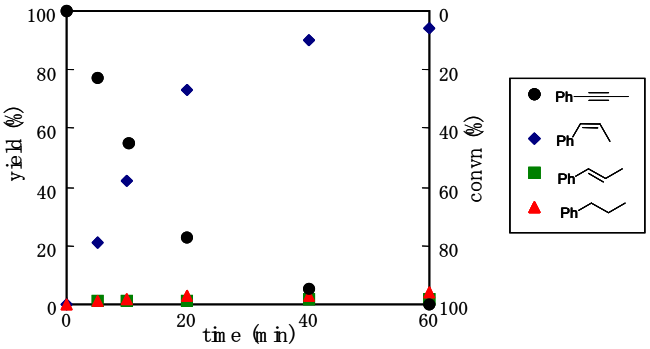
Competitive hydrogenation of acetylenes catalysed by the dendritic Pd nanoparticles:

G_2 Py-C_6 Pd(0) (Pd : 10 μmol) in CH_2Cl_2 (3 mL) was stirred at -25 ^{o}C for 0.5 h under hydrogen atmosphere. To this Pd solution added a CH_2Cl_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.

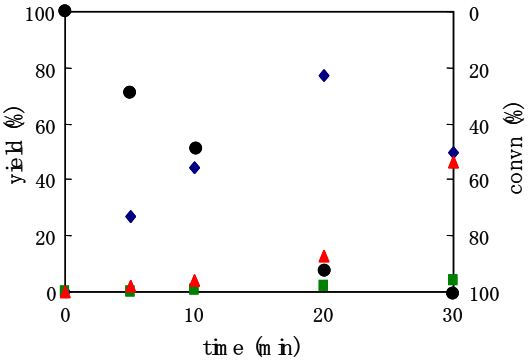
Timecourse of the Hydrogenation in Scheme 1

Hydrogenation of 1-Phenyl-1-propyne

a) Catalyst 3a

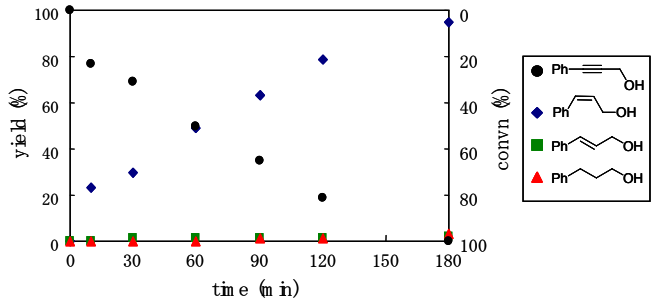


b) Lindlar catalyst



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

a) Catalyst 3a



b) Lindlar catalyst