Supplementary Material for Chemical Communications

Supplementary data

Redox-Robust Pentamethylamidoferrocenyl Metallodendrimers that Cleanly and Selectively Recognize the $H_2PO_4^-$ Anion.

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Experimental data

NEt_3 (2 mmol), CH_2Cl_2 (20 mL), then [FeCp*C_5H_4COCl)] (1.2 mmol) prepared according to ref 2b were added to the commercial DSM polyamine dend-DAB$(NH_2)_x$ (1 mmol). After stirring overnight at room temperature, this solution was washed with a saturated aq. K_2CO_3 solution, then with distilled water, and dried over Na_2SO_4, filtered and concentrated. Addition of ether led to the precipitation of the yellow-orange powdery metallodendrimer that was further purified by dissolution in CH_2Cl_2 and reprecipitation by addition of ether.

G_1 : ^{1}H NMR ($CDCl_3$, δ ppm.) 6.65 (t, 4H, NH), 4.24 (br, 8H, C_5H_4), 3.88 (br, 8H, C_5H_4), 3.43 (br, 8H, $NHCH_2$), 2.47 (br, 12H, CH_2N), 1.85 (s, 60H, C_5Me_5), 1.51 (br, 8H, CH_2), 1.48 (br, 4H, CH_2); ^{13}C NMR ($CDCl_3$, δ ppm.) 169.28 (CO), 82.07 (Cq, C_5H_4), 81.06 (Cq CCH_3), 76.05 and 70.21 (C_5H_4), 52.81 (CH_2), 38.92 (CH_2), 27.92 (CH_2), 10.67 (CH_3); IR (nujol, cm^{-1}) 1623 (ν CO), 1539 (ν, CN); MS (MALDI-TOF ; m/z) Calcd. for $C_{80}H_{112}N_6Fe_4O_4$: 1445.163, found : 1445.72; Anal. Calcd: C, 66.48, H, 7.81, found: C, 66.05, H, 7.36.

G_2 : ^{1}H NMR ($CDCl_3$, δ ppm.) 6.90 (br, 8H, NH), 4.31 (br, 16H, C_5H_4), 3.86 (br, 16H, C_5H_4), 3.43 (br, 16H, $NHCH_2$), 2.35 (br, 36H, CH_2N), 1.84 (s, 120H, C_5Me_5), 1.68 (br, 28H, CH_2), 1.48 (br, 4H, CH_2) ; ^{13}C NMR ($CDCl_3$, δ ppm.) 170.28 (CO), 81.16 (Cq CCH_3), 76.40 and 70.32 (C_5H_4), 53.21 (CH_2), 39.12 (CH_2), 28.45 (CH_2), 10.31 (CH_3); IR (nujol, cm^{-1}) 1620 (ν CO), 1539 (ν, CN); MS (MALDI-TOF ; m/z) Calcd. for $C_{168}H_{240}N_{14}Fe_8O_8$: 3028, found: 3029; Anal. Calcd. for $C_{168}H_{240}N_{14}Fe_8O_8$: C, 66.58, H, 7.98, found: C, 65.12, H, 7.28.

G_3 : ^{1}H NMR ($CDCl_3$, δ ppm.) 7.16 (br, 16H, NH), 4.31 (br, 32H, C_5H_4), 3.86 (br, 32H, C_5H_4), 3.43 (br, 32H, $NHCH_2$), 2.35 (br, 84H, CH_2N), 1.84 (s, 240H, C_5Me_5), 1.68 (br, 56H, CH_2), 1.48 (br, 4H, CH_2); ^{13}C NMR ($CDCl_3$, δ ppm.) 170.28 (CO), 80.98 (Cq CCH_3), 76.40 and 70.45 (C_5H_4), 53.21 (CH_2), 39.08 (CH_2), 28.36 (CH_2), 10.52 (CH_3); IR (nujol, cm^{-1}) 1620 (ν CO), 1540 (ν, CN); MS (MALDI-TOF ; m/z) Calcd. for $C_{344}H_{496}N_{30}Fe_{16}O_{16,}$ 6201.33, found : 6204.3; Anal. Calcd. for $C_{344}H_{496}N_{30}Fe_{16}O_{16}$: C, 66.62, H, 8.06, found: C, 65.32, H, 7.28.

G_4 : ^{1}H NMR ($CDCl_3$, δ ppm.) 7.21 (br, 32H, NH), 4.31 (br, 64H, C_5H_4), 3.86 (br, 64H, C_5H_4), 3.43 (br, 64H, $NHCH_2$), 2.35 (br, 180H, CH_2N), 1.84 (s, 480H, C5CH_3), 1.68 (br, 60H, CH_2), 1.48 (br, 4H, CH_2) ; ^{13}C NMR ($CDCl_3$, δ ppm.) 169.87 (CO), 80.97 (Cq CCH_3), 76.40 and 70.40 (C_5H_4), 53.21 (CH_2), 39.01 (CH_2), 28.42 (CH_2), 10.31 (CH_3); IR (nujol, cm^{-1}) 1622 (ν CO), 1540 (ν, CN); MS (MALDI-TOF; m/z) Calcd. for $C_{696}H_{1008}N_{62}Fe_{32}O_{32}$: 12542.89, found: 12544.9.; Anal. Calcd. for $C_{696}H_{1008}N_{62}Fe_{32}O_{32}$: C, 66.64, H, 8.10, found: C, 65.10, H, 7.78.

G_5 : ^{1}H NMR ($CDCl_3$, δ ppm.) 7.43 (br, 64H, NH), 4.41 (br, 128H, C_5H_4), 3.82 (br, 128H, C_5H_4), 3.43 (br, 128H, $NHCH_2$), 2.37 (br, 372H, CH_2N), 1.84 (s, 960H, C_5Me_5), 1.51 (br, 252H, CH_2) ; ^{13}C NMR ($CDCl_3$, δ ppm.) 170.15 (CO), 81.16 (Cq CCH_3), 76.47 and 70.46 (C_5H_4), 53.21 (CH_2), 39.23 (CH_2), 2838 (CH_2), 10.50 (CH_3); IR (nujol, cm^{-1}) 1622 (ν CO), 1540 (ν, CN); MS (MALDI-TOF ; m/z) Calcd. for $C_{1400}H_{2032}N_{126}Fe_{64}O_{64}$: 25226, found around 25000, broad.

The molecular peaks in the MALDI TOF mass spectra of the Fc* dendrimers are sharp except that of the G_5-64-Fc* dendrimer. The latter, as that of its parent analogue G_5-64-Fc,[6b] is broad around a mean value corresponding approximately to the molecular mass of the compound. Indeed, the mass-spectral

characterization showing the purity of the DSM polyamines has been reported by Meijer's group including the deviation in G_5 (23% purity only although the molecular peak corresponding to the perfect 64 branch- polyamine dendrimer is largely dominant). See reference 5b of the main text.

Titration graph of [*n*Bu_4N][H_2PO_4]by G_2-8Fc*

Variations of the intensities of the initial wave (circles) and new wave (triangles) during the titration of a 10^{-5} M solution of the G2 pentamethylamidoferrocenyl dendrimer (8 branches) by a 10^{-3} M solution of [nBu_4N][H_2PO_4] in CH_2Cl_2 in the presence of 0.1 M [nBu_4N] [PF_6], Pt anode, internal reference $FeCp^*_2$ (see text).