Redox-Robust Pentamethylamidoferrocenyl Metallodendrimers that Cleanly and Selectively Recognize the $\text{H}_2\text{PO}_4^-$ Anion.

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**Experimental data**

$\text{NEt}_3$ (2 mmol), $\text{CH}_2\text{Cl}_2$ (20 mL), then $[\text{FeCp*C}_5\text{H}_4\text{COCl}]$ (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. $\text{K}_2\text{CO}_3$ solution, then with distilled water, and dried over $\text{Na}_2\text{SO}_4$, filtered and concentrated. Addition of ether led to the precipitation of the yellow-orange powdery metallodendrimer that was further purified by dissolution in $\text{CH}_2\text{Cl}_2$ and reprecipitation by addition of ether.

$\text{G}_1$:

$^1\text{H}$ NMR (CDCl$_3$, $\delta$ ppm.) 6.65 (t, 4H, NH), 4.24 (br, 8H, C$_5$H$_4$), 3.88 (br, 8H, C$_5$H$_4$), 3.43 (br, 8H, NHCH$_2$), 2.47 (br, 12H, CH$_2$); $^{13}$C NMR (CDCl$_3$, $\delta$ ppm.) 169.28 (CO), 82.07 (C$_q$, C$_5$H$_4$), 81.06 (Cq CCH$_3$), 76.05 and 70.21 (C$_5$H$_4$), 52.81 (CH$_2$), 38.92 (CH$_2$), 27.92 (CH$_2$), 10.67 (CH$_3$); IR (nujol, cm$^{-1}$) 1623 ($\nu$ CO), 1539 ($\nu$, CN); MS (MALDI-TOF; m/z) Calcd. for $\text{C}_{80}\text{H}_{112}\text{N}_6\text{Fe}_4\text{O}_4$ : 1445.163, found : 1445.72; Anal. Calcd.: C, 66.48, H, 7.81, found: C, 66.05, H, 7.36.

$\text{G}_2$:

$^1\text{H}$ NMR (CDCl$_3$, $\delta$ ppm.) 6.90 (br, 8H, NH), 4.31 (br, 16H, C$_5$H$_4$), 3.86 (br, 16H, C$_5$H$_4$), 3.43 (br, 16H, NHCH$_2$), 2.35 (br, 36H, CH$_2$); $^{13}$C NMR (CDCl$_3$, $\delta$ ppm.) 170.28 (CO), 81.16 (Cq CCH$_3$), 76.40 and 70.32 (C$_5$H$_4$), 53.21 (CH$_2$), 39.12 (CH$_2$), 28.45 (CH$_2$), 10.31 (CH$_3$); IR (nujol, cm$^{-1}$) 1620 ($\nu$ CO), 1539 ($\nu$, CN); MS (MALDI-TOF; m/z) Calcd. for $\text{C}_{168}\text{H}_{240}\text{N}_{14}\text{Fe}_8\text{O}_8$: 3028, found: 3029; Anal. Calcd. for $\text{C}_{168}\text{H}_{240}\text{N}_{14}\text{Fe}_8\text{O}_8$: C, 66.58, H, 7.98, found: C, 65.12, H, 7.28.

$\text{G}_3$:

$^1\text{H}$ NMR (CDCl$_3$, $\delta$ ppm.) 7.16 (br, 16H, NH), 4.31 (br, 32H, C$_5$H$_4$), 3.86 (br, 32H, C$_5$H$_4$), 3.43 (br, 32H, NHCH$_2$), 2.35 (br, 84H, CH$_2$); $^{13}$C NMR (CDCl$_3$, $\delta$ ppm.) 170.28 (CO), 80.98 (Cq CCH$_3$), 76.40 and 70.45 (C$_5$H$_4$), 53.21 (CH$_2$), 39.08 (CH$_2$), 28.36 (CH$_2$), 10.52 (CH$_3$); IR (nujol, cm$^{-1}$) 1621 ($\nu$ CO), 1540 ($\nu$, CN); MS (MALDI-TOF; m/z) Calcd. for $\text{C}_{344}\text{H}_{496}\text{N}_{30}\text{Fe}_{16}\text{O}_{16}$: 6201.33, found : 6204.3; Anal. Calcd. for $\text{C}_{344}\text{H}_{496}\text{N}_{30}\text{Fe}_{16}\text{O}_{16}$: C, 66.62, H, 8.06, found: C, 65.32, H, 7.28.

$\text{G}_4$:

$^1\text{H}$ NMR (CDCl$_3$, $\delta$ ppm.) 7.21 (br, 32H, NH), 4.31 (br, 64H, C$_5$H$_4$), 3.86 (br, 64H, C$_5$H$_4$), 3.43 (br, 64H, NHCH$_2$), 2.35 (br, 180H, CH$_2$); $^{13}$C NMR (CDCl$_3$, $\delta$ ppm.) 170.38 (CO), 80.97 (Cq CCH$_3$), 76.40 and 70.47 (C$_5$H$_4$), 53.21 (CH$_2$), 39.01 (CH$_2$), 28.42 (CH$_2$), 10.31 (CH$_3$); IR (nujol, cm$^{-1}$) 1622 ($\nu$ CO), 1540 ($\nu$, CN); MS (MALDI-TOF; m/z) Calcd. for $\text{C}_{696}\text{H}_{1008}\text{N}_{62}\text{Fe}_{32}\text{O}_{32}$: 12542.89, found around 125000, broad.

The molecular peaks in the MALDI TOF mass spectra of the Fe* dendrimers are sharp except that of the G$_5$-64-Fe* dendrimer. The latter, as that of its parent analogue G$_5$-64-Fe*, 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 G5 (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 [nBu₄N][H₂PO₄] by G₂₈Fc***

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 [nBu₄N][H₂PO₄] in CH₂Cl₂ in the presence of 0.1 M [nBu₄N][PF₆], Pt anode, internal reference FeCp*₂ (see text).