ChemComm
www.rsc.org/chemcomm

Redox-robust pentamethylamidoferrocenyl metallodendrimers that cleanly and selectively recognize the $H_2PO_4^-$ anion†

Jaime Ruiz,[a] Maria Jesus Ruiz Medel,[a] Marie-Christine Daniel,[a] Jean-Claude Blais[b] and Didier Astruc*[a]

[a] *LCOO, UMR CNRS N° 5802, Université Bordeaux I, 33405 Talence Cedex, France*
[b] *LCSOB, UMR CNRS N° 7613, Université Paris VI, 75252 Paris, France*

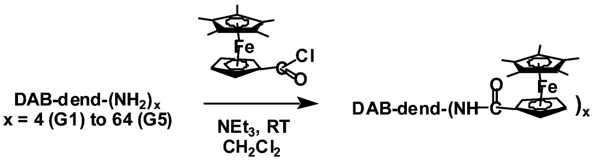
Received (in Cambridge, UK) 26th November 2002, Accepted 10th January 2003
First published as an Advance Article on the web 27th January 2003

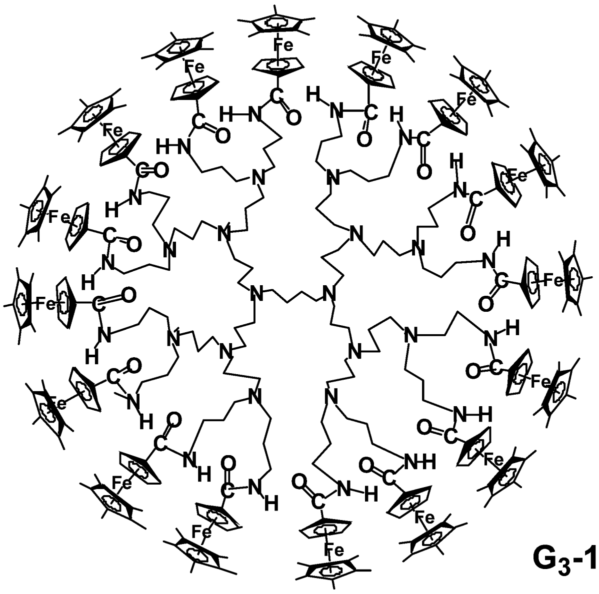
The first pentamethylferrocenyl (Fc*) dendrimers are synthesized from DSM polyamine dendrimers (generations 1 to 5) and cleanly and selectively recognize the $H_2PO_4^-$ anion.

Nanoreceptors for anion recognition should have practical applications but are so far much less common than the model molecular systems.[1] Nanoscopic exoreceptors have recently been designed with dendrimers[2a] and gold nanoparticles[2b] terminated with amidoferrocenyl groups that bring the supramolecular basis for the recognition of $H_2PO_4^-$ anion. A key drawback is that these systems are marred by adsorption peaks in the cyclovoltammograms and by chemical irreversibility due to instability upon oxidation. The stabilizing C_5Me_5 (Cp*) ligand has already been introduced in pentamethylferrocenyl (Fc*) termini on thiol ligands of nanoparticles in order to study the electronic consequence of Cp permethylation on the recognition parameters.[2b] Metallodendrimers[3] are especially attractive, and positive dendritic effects enhance the recognition of this anion for high generations.[2a] Whereas there are numerous ferrocenyl (Fc) dendrimer families,[4] we are reporting here the first examples of Fc* dendrimer and their excellent and selective sensing properties.

The new compounds are derived from DSM's polyamine dendrimers DAB-dend-$(NH_2)_x$ (x = 4, 8, 16, 32, 64).[5] These five generations G_1 (x = 4) to G_5 (x = 64) of metallodendrimers are easily available by reactions between these polyamines and Fc*COCl[2b] in CH_2Cl_2 at RT overnight in the presence of triethylamine. The parent amidoferrocenyl dendrimers (Fc series) are known from the work of Cuadrado's group who has also reported their electrochemistry in order to examine their deposition on platinum surfaces.[6] Since no molecular recognition studies have been published with these compounds, we have undertaken anion recognition studies with both Fc* and Fc series for comparison. We now report that both families can recognize $H_2PO_4^-$ using the variation of Fe^{II}/Fe^{III} redox potentials of these metallodendrimers, and that this new Fc* series shows much less adsorption and no chemical irreversibility that prevent a clean recognition in the Fc series. The dramatic advantage of the Fc* series over the parent one for redox recognition is due to both the stabilization of the 17-electron form and the lipophilicity brought about by the numerous methyl groups located at the dendrimer periphery.

These new dendrimers were suitably characterized by the standard analytical and spectroscopic techniques (including molecular peaks that are prominent in the MALDI TOF mass spectra and sharp for G_1 to G_4†) and by cyclic voltammetry (CV, Table 1). The fact that there is only one CV wave is attributable to the rotation of the dendrimers that is much more rapid than the electrochemical time scale, as for other Fc dendrimers.[7] Their $E_{1/2}$ value is 0.405 ± 0.005 V *vs.* [$FeCp^*_2$] in CH_2Cl_2, and thus does not significantly vary from G_1 to G_5. This value is compared to that of the parent series that is 0.690 ± 0.010 V *vs.* [$FeCp^*_2$].[6] [$FeCp^*_2$] is a much better reference than ferrocene[8] (because ferrocenium is sensitive to the medium) for the investigation of possible small dendritic effects, and we conclude here to their absence using [$FeCp^*_2$] as the reference ($E_{1/2}$ *vs.* $FeCp_2$ = $E_{1/2}$ *vs.* $FeCp^*_2$ + 0.545 V in CH_2Cl_2, or + 0.595 V in DMF[8]).





G_3-16Fc*

The comparison of these CV with those of the parent series shows that the permethylated Fc* dendrimers behave in a much better fashion than the parent Fc series. One of the dramatic differences between the CV of the dendritic Fc* and parent Fc series is that the Fc* series shows almost no adsorption in CH_2Cl_2, the i_{pc}/i_{pa} values being 1.00 ± 0.03 for G_1, G_2 and G_3, 1.1 for G_4 and 1.2 for G_5. On the contrary, the parent Fc series shows i_{pc}/i_{pa} values between 2 and 3.4 under the same conditions (0.2 V s^{-1}, 20 °C, Pt anode, CH_2Cl_2, 0.1 M $n$$Bu_4NPF_6$) indicating strong adsorption (Fig. 1). This difference of behavior towards adsorption is confirmed by the $E_{pc} - E_{pa}$ values which are 0.06 V for G_1, G_2 and G_3, 0.05 V for G_4 and 0.035 V for G_5 for the Fc* series and only 0.03 V for G_1 to G_5 in the parent Fc series. In DMF, the i_{pc}/i_{pa} value is 1.05 ± 0.05 for the Fc* series, but it decreases from 0.9 for G_1 to 0.4 for G_2, G_3 and G_4 in the parent Fc series under these conditions. This shows chemical irreversibility in the Fc series, *i.e.* decomposition of the parent ferrocenium dendrimers is all the more rapid in this solvent as the generation number increases, even on the short CV time scales (Fig. 1). The measured values of the number n of electrons correspond to the theoretical numbers[9] within 10% in either CH_2Cl_2 or DMF for the generations G_1 to G_4 (Table 1).

---

† Electronic supplementary information (ESI) available: experimental procedures, spectroscopic and analytical data of the Fc* dendrimers, and titration graph of [$n$$Bu_4N$][$H_2PO_4$] by G_2-8Fc* using the variations of current intensities of the initial and new waves by cyclic voltammetry. See http://www.rsc.org/suppdata/cc/b2/b211772j/

DOI: 10.1039/b211772j

Table 1 Cyclovoltammetry data for G_1–G_5 (both Fc and Fc* series) before and after titration of $[n\text{Bu}_4\text{N}][\text{H}_2\text{PO}_4]$

	$E_{1/2}{}^a$ ($E\text{p}_a$-$E\text{p}_c$)		ip_c/ip_a		n^b		$\Delta E_{1/2}(\text{H}_2\text{PO}_4^-)^a$ ($E\text{p}_a - E\text{p}_c$)		$K_{(+)}/K_{(o)}{}^c$ $K_{(+)}{}^d$	
	CH_2Cl_2	DMF	CH_2Cl_2	DMF	CH_2Cl_2	DMF	CH_2Cl_2	DMF	CH_2Cl_2	DMF
G_0-1Fc	0.700 (0.06)	0.615 (0.06)	1.1	0.92	1.1	1.1	0.155 (0.15)	0.65 (0.09)	470	
G_1-4Fc	0.695 (0.03)	0.645 (0.07)	3.2	0.75	3.5		0.310 (0.09)	0.265 (0.16)	$2.2.10^5$	
G_2-8Fc	0.675 (0.03)	0.650 (0.08)	2.2	0.46	7.2		0.250 (0.11)	**	$2.0.10^4$	
G_3-16Fc	0.690 (0.03)	0.650 (0.08)	3.5	0.42	16.0		0.170 (0.15)	**	850	
G_4-32Fc	0.690 (0.04)	0.650 (0.08)	1.9	0.40	32	31.5	**	**		
G_5-64Fc	0.680 (0.03)	0.670 (0.10)	3.4	0.62		53	**	**		
G_1-4Fc*	0.406 (0.06)	0.360 (0.07)	1.05	1.07	3.8	4.2	0.155 (0.16)	0.115 (0.06)	470	$9.6.10^3$
G_2-8Fc*	0.395 (0.06)	0.370 (0.08)	1.02	1.1	7.9	8.0	0.160 (0.11)	0.125 (0.07)	570	14.10^3
G_3-16Fc*	0.410 (0.06)	0.370 (0.07)	1.01	1.12	15.1		0.130 (0.13)	0.145 (0.08)	170	32.10^3
G_4-32Fc*	0.400 (0.05)	0.390 (0.07)	1.1	1.05	32		0.140 (0.17)	0.165 (0.06)	260	70.10^3
G_5-64Fc*	0.410 (0.035)	0.375 (0.03)	1.2	1.06	55		0.160 (0.17)	0.140 (0.03)	570	26.10^3

[a] $E_{1/2} = (E\text{p}_a + E\text{p}_c)/2$ *vs.* $\text{FeCp}_2{}^*$, in Volts. Electrolyte: $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ 0.1 M; working and counter electrodes: Pt; reference electrode: Ag; (internal reference: FeCp*_2); scan rate: 0.200 V s^{-1}; 20 °C; [b] Values of the number of electrons involved calculated from the Anson–Bard equation[9] using anodic intensities; [c] Error = 10%; $\Delta E_{1/2} = 0.058 \log (K_{(+)}/K_{(o)})$[11] at 20 °C; [d] Error = 10%; progressive shift of the wave: $K_{(o)} << 1$, $\Delta E_{1/2} = 0.058 \log [\text{c. } K_{(+)}]$;[11] **no cathodic wave (no accessible $\Delta E_{1/2}$ value).

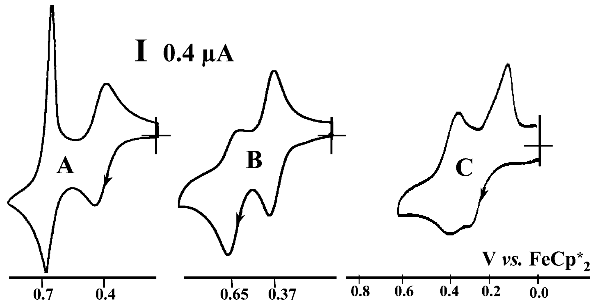


Fig. 1 Cyclovoltammograms of a mixture of G_3-16Fc and G_3-16Fc* (10^{-4} M, Pt anode; 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$, 20 °C). **A**: in CH_2Cl_2 showing the extensive adsorption only for G_3-16Fc; **B**: in DMF showing the chemical irreversibility only for G_3-16Fc that perturbs access to $E_{1/2}$ and K; **C**: CV of G_3-16Fc* in CH_2Cl_2 with 0.5 eq. $[n\text{Bu}_4\text{N}][\text{H}_2\text{PO}_4]$.

The addition of $[n\text{Bu}_4\text{N}][\text{H}_2\text{PO}_4]$ to the electrochemical cell containing the CH_2Cl_2 solution of the dendrimer (Fig. 1C) provokes the apparition of a new wave at a potential less positive than the initial one whose intensity decreases along with the intensity increase of the new wave. The equivalence point is reached as indicated by the complete replacement of the initial wave by the new one.[2] In the case of the parent Fc dendrimer series, however, this phenomenon is marred by both the chemical and electrochemical irreversibilities[10] of the new wave. Gratifyingly, there is no chemical irreversibility with the Fc* dendrimers and the new wave is electrochemically quasi-reversible (Fig. 1C, and Table 1). The use of the parent Fc dendrimer series is difficult again in DMF, because of the complete chemical irreversibility except with the first generation. On the contrary, all the Fc* dendrimer show CV waves that are fully chemically reversible and progressively shifted upon addition of $[n\text{Bu}_4\text{N}][\text{H}_2\text{PO}_4]$. This shift of $E_{1/2}$ values is the subject of a small dendritic effect: 115 mV (G_1), 125 mV (G_2), 145 mV (G_3), 165 mV (G_4) (all values ± 10 mV) and 140 mV (G_5 with more adsorption). The largest shift is that observed in the parent Fc series between FcCONHPr (65 mV) and G_1 (265 mV). These shifts provide direct access to the apparent association constants $K_{(+)}$ in DMF (±20%) for the whole Fc* series only: 9600 (G_1), 14000 (G_2), 32000 (G_3), 70000 (G_4) according to the Echegoyen–Kaifer model.[11]

The addition of $n\text{-Bu}_4\text{N}^+$ salts of chloride or hydrogensulfate only has a minute influence, provoking a shift of the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ wave by 40 mV for Cl^- and 80 mV for HSO_4^- after addition of one equiv. of each anion to G_2-8Fc*. Indeed, the recognition of dihydrogenphosphate can be carried out in the presence of these anions. Instead of provoking the appearance of a new $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ wave as when Cl^- and HSO_4^- are not in the solution, the addition of H_2PO_4^-, when Cl^- and HSO_4^- are both present, induces a shift of this wave by $\Delta E_{1/2}$ = 180 mV for H_2PO_4^-.

In conclusion, these new Fc* dendrimers are redox robust and selectively recognize H_2PO_4^- much more cleanly (no chemical irreversibility, much less adsorption) than the compared Fc series due to enhanced stability of the 17-electron form and lipophilicity provided by permethylation of the Cp ligands. A modest positive dendritic effect (*i.e.* larger shift of potential provoked by the addition of the anion when the generation is higher) is found in DMF whereas no dendritic effect is noted in CH_2Cl_2. This situation contrasts with the large dendritic effect found for the redox recognition of H_2PO_4^- with other Fc dendrimers[2a] showing that these effects are dependent on the dendritic structure.

Notes and references

1 (*a*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 486; (*b*) P. D. Beer, J. Davis, D. A. Drillsma-Millgrom and F. Szemes, *Chem. Commun.*, 2002, 1716.

2 (*a*) C. Valério, J.-L. Fillaut, J. Ruiz, J. Guittard., J.-C. Blais and D. Astruc, *J. Am. Chem. Soc.*, 1997, **119**, 2588; (*b*) A. Labande, J. Ruiz and D. Astruc, *J. Am. Chem. Soc.*, 2002, **124**, 1782.

3 G. R. Newkome, C. N. Moorefield and F. Vögtle, *Dendrimers and Dendrons. Concepts, Synthesis and Applications*, Wiley, Weinheim, 2001; H. M. Janssen and E. W. Meijer, *Chem. Rev.*, 1999, **99**, 1665.

4 (*a*) C. M. Casado, M. Cuadrado, M. Morán, B. Alonso, B. Garcia, J. Gonzales and J. Losada, *Coord. Chem. Rev.*, 1999, **185/186**, 53; (*b*) A. E. Kaifer and M. Gomez-Kaifer, *Supramolecular Electrochemistry*, Wiley-VCH, Weinheim, 1999, ch. 16, p. 207.

5 (*a*) E. M. M. de Brabander-van den Berg and E. W. Meijer, *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 1308; (*b*) J. C. Hummelen, J. L. J. van Dongen and E. W. Meijer, *Chem. Eur. J.*, 1997, **3**, 1489.

6 K. Takada, D. J. Diaz, H. Abruña, I. Cuadrado, C. M. Casado, B. Alonso, M. Morán and J. Losada, *J. Am. Chem. Soc.*, 1997, **119**, 10763.

7 C. B. Gorman, J. C. Smith, B. L. Parkhurst, H. Sierzputowska-Gracz and C. A. Haney, *J. Am. Chem. Soc.*, 1999, **121**, 9958.

8 D. Astruc, in *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley-VCH, New York, 2001, vol. 2, section 2, Chapter 4, p. 728.

9 J. B. Flanagan, S. Margel, A. J. Bard and F. C. Anson, *J. Am. Chem. Soc.*, 1978, **100**, 4248.

10 (*a*) D. Astruc, *Electron Transfer and Radical Processes in Transition-Metal Chemistry*, VCH, New York, 1995, ch. 2; (*b*) E_{pc} and E_{pa} are the cathodic and anodic peak potentials respectively. If $E_{\text{pa}} - E_{\text{pc}} > 58$ mV at 20 °C, the heterogeneous electron transfer is slow (signifying structural reorganization upon electron transfer). If $E_{\text{pa}} - E_{\text{pc}} < 58$ mV, it means that some adsorption occurs.

11 Seminal report: S. R. Miller, D. A. Gustowski, Z.-H. Chen, G. W. Gokel, L. Echegoyen and A. E. Kaifer, *Anal. Chem.*, 1988, **60**, 2021. When a new wave appears, $K_o > 1$ and only the ratio K_+/K_o is determined whereas, when the initial wave is only shifted, $K_0 << 1$, and access to K_+ is provided (see text and Table 1).