

# Colloids as redox sensors: recognition of $\text{H}_2\text{PO}_4^-$ and $\text{HSO}_4^-$ by amidoferrocenylalkylthiol–gold nanoparticles

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**Gold colloids containing a mixture of alkylthiol and amidoferrocenylalkylthiol (AFAT) ligands are new redox sensors for  $\text{H}_2\text{PO}_4^-$  and  $\text{HSO}_4^-$ .**

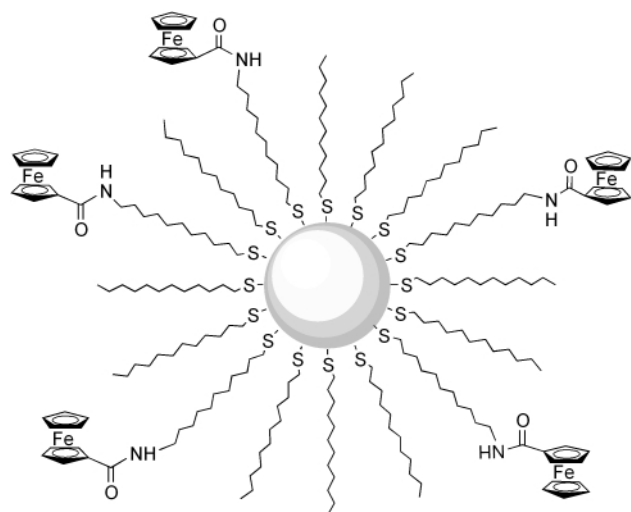
A promising approach towards nanoscopic materials is the investigation of their supramolecular properties which may lead to new sensors, catalysts and nanoscale electronic devices.<sup>1</sup> Only a few molecular recognition studies have been reported with colloids, however.<sup>3</sup> We wished to combine the effect of the topology in alkylthiol–gold nanoparticles and the supramolecular properties of their redox-active termini for their use as exo-receptors.<sup>4</sup> In order to attain this goal, we have synthesized functional alkylthiol–gold nanoparticles containing a mixture of alkylthiol ligands and amidoferrocenylalkylthiol (AFAT) ligands (Fig. 1). We then monitored the titration of  $\text{NBu}^n_4^+$  salts of  $\text{H}_2\text{PO}_4^-$  and  $\text{HSO}_4^-$  by these nanoparticles using cyclic voltammetry (CV). These ligands have been introduced and studied by Creager on gold surfaces,<sup>5</sup> and ferrocenylalkylthiol colloids are known,<sup>6</sup> but the introduction of an amido group close to the ferrocene center now adds the supramolecular aspect to these colloids.

Recognition of anions is an important topic because a number of anions are found in biological systems.<sup>7</sup> In particular, Beer showed that amidoferrocenyl groups linked to endo-receptors are able to sense anions.<sup>4a–c</sup> We now find that the redox potential of the amidoferrocenyl group is sufficiently perturbed by the synergy between the hydrogen-bonding, electrostatic interaction and topology in alkylthiol–gold nanoparticles containing AFAT ligands (unlike in alkylamidoferrocene monomers) to recognize  $\text{H}_2\text{PO}_4^-$  and  $\text{HSO}_4^-$ .

The AFAT-containing colloids were synthesized by ligand substitution using Brust's colloids, leaving the gold core unchanged.<sup>2</sup> We have applied this technique with a variable proportion of amidoferrocenylalkylthiol ligands of variable

lengths (11 and 6 C atoms)<sup>11</sup> and verified using TEM that the core size is not modified upon ligand substitution. Indeed, the combination of elemental analysis,  $^1\text{H}$  NMR spectroscopy and TEM leads, for instance, to an average number of 269 gold atoms per core of 2 nm diameter and 80–106 dodecanethiolate chains.<sup>8</sup> Table 1 shows the proportion of AFAT ligands (determined by  $^1\text{H}$  NMR) which is introduced onto the nanoparticles as a function of the amount engaged in the ligand-substitution reactions. Saturation is reached for 38 AFAT ligands per particle. These thermally stable nanoparticles are unaffected by air and are soluble in  $\text{CH}_2\text{Cl}_2$ .

The CVs of these colloids containing a variable amount of AFAT ligands always show a reversible ferrocene/ferrocenium wave (Pt,  $\text{CH}_2\text{Cl}_2$ , 0.1 M  $[\text{NBu}^n_4][\text{PF}_6]$ ) at  $E_{1/2} = 0.220$  V vs.  $\text{FeCp}_2^{0/+}$  in  $\text{CH}_2\text{Cl}_2$ <sup>12</sup> with some adsorption indicated by the  $E_{\text{pa}}-E_{\text{pc}}$  values (typically 20 mV) lower than the 58 mV value expected at 20 °C for classic mono-electronic waves. The observation of a single wave is due to the fact that all the redox centers of a particle appear identical and independent of the electrochemical time scale, indicating that the rotation of the particles and H-bonding formation and cleavage are faster than this time scale. Mediation of electron transfer among the ferrocenyl sites may also occur.<sup>9</sup> Addition of  $[\text{NBu}^n_4][\text{H}_2\text{PO}_4]$  to a  $\text{CH}_2\text{Cl}_2$  solution of these nanoparticles leads to the appearance of a new, cathodically shifted, wave the intensity of which increases at the expense of the initial wave. The replacement of the initial wave by the new one is complete after addition of 1 equivalent  $[\text{NBu}^n_4][\text{H}_2\text{PO}_4]$  per AFAT branch (Fig. 2), indicating a 1:1 interaction between the anion and the amidoferrocenium group. It is remarkable that the potential shift upon addition of the anion is large ( $\Delta E^\circ = 220$  mV) and constant whatever the proportion of AFAT ligand in the nanoparticles (from 7 to 38%) and its length (6 or 11  $\text{CH}_2$  units). This shift is much larger not only than that obtained for the alkylamidoferrocene monomer  $\text{FcCONHCH}_2\text{CH}_2\text{OPh}$  (45 mV) but also for the tripod  $\text{PhC}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCOfc})_3$  (110 mV), and is analogous to the value observed with a nona-branched amidoferrocene dendrimer.<sup>9</sup> Thus, it is probable that the channels defined between the parallel ligands create sufficient steric strain to provide a favorable particle effect comparable to

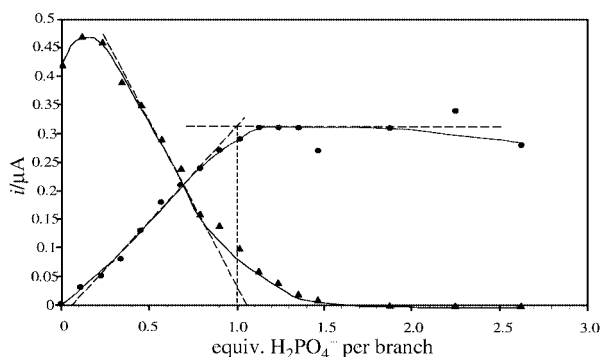


**Fig. 1** Gold nanoparticles containing, on average, 29% of AFAT ligands (29-Fc).

**Table 1** Results of ligand-exchange reactions between AFAT- and dodecanethiol (DT)-gold nanoparticles

AFAT chain length	AFAT/DT ratio		AFAT/DT members in product <sup>c</sup>	%AFAT in product <sup>d</sup>
	Reaction <sup>a</sup>	Product <sup>b</sup>		
C <sub>11</sub>	1:4	1:13	8/97	7
C <sub>11</sub>	1:1	1:8	10/70	13
C <sub>11</sub>	1.5:1	1:5	21/85	20
C <sub>11</sub>	1.75:1	1:3.5	31/75	29
C <sub>11</sub>	2:1	1:2.6	39/64	38
C <sub>6</sub>	2:1	1:5.5	16/70	18

<sup>a</sup> Mole ratio of AFAT ligand to nanoparticle-bound DT ligands in ligand-exchange reactions. <sup>b</sup> Average mole ratio of AFAT/DT ligands in the nanoparticles. <sup>c</sup> Average numbers of AFAT/DT ligands in the particles. <sup>d</sup> Average percentage of AFAT ligands in the nanoparticles.



**Fig. 2** Titration of the 20-Fc (AFAT) nanoparticles with  $[\text{NBu}^n_4][\text{H}_2\text{PO}_4^-]$  monitored by CV. Decrease of the intensity of the initial ferrocene CV wave and increase of the intensity of the new wave vs. the number of equivalents of  $[\text{NBu}^n_4][\text{H}_2\text{PO}_4^-]$  added per Fc (AFAT) branch; nanoparticles:  $5 \times 10^{-6}$  M in  $\text{CH}_2\text{Cl}_2$ ;  $[\text{NBu}^n_4][\text{H}_2\text{PO}_4^-]$ :  $10^{-2}$  M in  $\text{CH}_2\text{Cl}_2$ ,  $[\text{NBu}^n_4][\text{PF}_6^-]$ : 0.1 M, 20 °C, reference electrodes: SCE and  $\text{FeCp}_2$ ; auxiliary and working electrodes: Pt, scan rate:  $200 \text{ mV s}^{-1}$ . Plots of these intensities with particles containing various numbers of Fc (AFAT) branches (see text) gave analogous results: ( $\blacktriangle$ ) initial wave, ( $\bullet$ ) new wave.

the dendritic effect observed with metallodendrimers. This  $\Delta E^\circ$  value means that the apparent association constant  $K_{(+)}$  between  $\text{H}_2\text{PO}_4^-$  and the polyferrocenium form of the particle is  $5350 \pm 550$  times larger than that,  $K_{(0)}$ , related to the neutral polyferrocene form (electrostatic effect).<sup>10</sup>

Gratifyingly, this technique also allows confirmation of the number of AFAT ligands in the particles determined by  $^1\text{H}$  NMR, viz. 10–30% AFAT ligands on the particles (Table 2). It is also possible to titrate  $[\text{NBu}^n_4][\text{H}_2\text{PO}_4^-]$  in the presence of both  $[\text{NBu}^n_4][\text{HSO}_4^-]$  and  $\text{NBu}^n_4\text{Cl}$  (in addition to the electrolyte  $[\text{NBu}^n_4][\text{PF}_6^-]$  in large excess), but the initial wave is now progressively shifted cathodically instead of being progressively replaced by another wave. This dramatic change of behavior may be understood in terms of a dynamic equilibrium among various anion complexes and by the fact that the kinetics of complexation can be different in the presence of a single anion or a mixture of anions.<sup>11</sup>

Finally, it is possible to titrate  $[\text{NBu}^n_4][\text{HSO}_4^-]$  alone since the initial wave of those particles which have a low content of AFAT ligands (10–20%) is progressively shifted cathodically by addition of this anion up to 40 mV after addition of 1 equivalent of  $[\text{NBu}^n_4][\text{HSO}_4^-]$ , which again corresponds to a 1 : 1 interaction, with an apparent association constant  $K_{(+)} = 480 \pm 120 \text{ mol}^{-1} \text{ L}$  at a concentration of  $10^{-2} \text{ M}$ .<sup>10</sup> It is noteworthy that the  $\Delta E^\circ$  value is much smaller for  $\text{HSO}_4^-$  than for  $\text{H}_2\text{PO}_4^-$ , which shows the selectivity of the recognition by these nanoparticles. When the AFAT ligand content of the particles is larger (29–38% AFAT) or the chain shorter ( $\text{C}_6$ ), this 1 : 1

**Table 2** Determination of the average number of AFAT ligands in the nanoparticles

	Total number of AFAT ligands			
	H NMR	Titration by CV		
		$\text{H}_2\text{PO}_4^-$	$\text{H}_2\text{PO}_4^{-a}$	$\text{HSO}_4^-$
7-Fc ( $\text{C}_{11}$ )	8	8.3	—	—
13-Fc ( $\text{C}_{11}$ )	10	9.5	9	10.25
20-Fc ( $\text{C}_{11}$ )	21	22	19	18
29-Fc ( $\text{C}_{11}$ )	31	29	25	17 <sup>b</sup>
38-Fc ( $\text{C}_{11}$ )	39	32	29.5	13 <sup>b</sup>
18-Fc ( $\text{C}_6$ )	16	14	—	9 <sup>b</sup>

<sup>a</sup> Titration carried out in the presence of excess  $[\text{NBu}^n_4][\text{HSO}_4^-]$  ( $5 \times 10^{-6}$  mol) and  $\text{NBu}^n_4\text{Cl}$  ( $2.5 \times 10^{-6}$  mol). <sup>b</sup> Low value due to intramolecular H-bonding at high content of the AFAT ligand (see text).

interaction is no longer found, and equivalence points are reached with a lower quantity of added  $[\text{NBu}^n_4][\text{HSO}_4^-]$ . This distortion might best be accounted for by intramolecular amide–amide double hydrogen-bonding of two neighboring AFAT ligands at high AFAT ligand content. This effect is also more pronounced for  $\text{HSO}_4^-$  than for  $\text{H}_2\text{PO}_4^-$ . The moderate adsorption as monitored by the  $E_a - E_p$  values along these titration studies changes slightly during the titration, but does not disturb the titrations. These particles do not recognize chloride, bromide and nitrate anions and thus there is a selectivity for the above oxo-anions. We are now continuing our research with other particles of similar and different types to extend the scope of the present results and investigate solvation and pH effects.

In conclusion, these particles are used as exo-receptors which can sense  $\text{H}_2\text{PO}_4^-$  and  $\text{HSO}_4^-$  owing to their hydrogen-bonding capacity with these oxo-anions, and excellent selectivity between the two oxo-anions has been found. They can be compared to dendrimers, but they show effects which are different, although the particles are as efficient as non-amydiferrocene dendrimers to sense  $\text{HPO}_4^-$  (some of our polyamidiferrocene dendrimers<sup>9b</sup> do not recognize  $\text{HPO}_4^-$ ). The particles also present a great advantage in that they are synthesized in one step whereas dendritic syntheses require a large number of steps.

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