Towards molecular batteries: coverage of small aminosilica nanoparticles with ferrocenyl and pentamethylferrocenyl groups and their redox properties†

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Small aminosilica nanoparticles (NPs, 12 nm SiO_2 core) were covered with ferrocenyl (Fc) and pentamethylferrocenyl (Fc*) groups by reactions with metallocenyl carbonyl chlorides. Cyclic voltammetry in methanol/acetonitrile showed a single fully chemically- and electrochemically-reversible wave with a diffusion-controlled current; colorimetric titrations with [FcCOMe][BF_4] of the Fc-SiO_2 and Fc*-SiO_2 NPs indicated a coverage of the aminosilica NPs of 335 ± 50 Fc or 240 ± 40 Fc* groups.

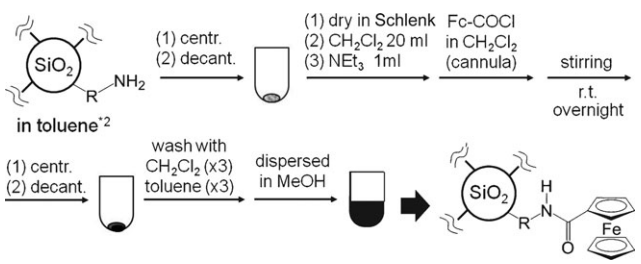
Hybrid inorganic–organic materials are a promising area of nanoscience with applications towards sensors, catalysis, medicine and other devices with specific physical properties.[1] For instance, ferrocenyl-containing polymers are a remarkable family of redox-active materials with unique electronic properties[2] that have been carefully studied from the point of view of their electrochemistry.[3] In particular, silica nanoparticles (NPs) with sizes between 60 and 800 nm have been covered with ferrocenyl groups. However, ferrocenyl coverage was often low, the electron transfer observed by cyclic voltammetry sluggish and/or the ferrocenyl groups found to be incompletely redox-active.[4] These electron-transfer properties are probably related to the relatively large sizes of the NPs. The studies involved the covalent attachment of ferrocene derivatives onto the surface of the silica NPs, but in another report, small silica NPs of 15 nm diameter were synthesized by embedding ferrocene itself during the polymerization process, and these ferrocene-doped silica NPs were used as an amperometric glucose sensor.[5] The cyclic voltammogram showed a 86 mV peak-to-peak separation between the potentials of the anodic and cathodic peaks at 100 mV s^{-1}, close to the theoretical value of 59 mV s^{-1}; the electron-transfer process was diffusion controlled.

Following our studies on highly loaded ferrocenyl-terminated gold NPs[6] and dendrimers,[7] we have been interested in the use of small silica NPs with covalently-attached ferrocenyl groups to achieve a high loading of robust redox centers onto the periphery of small silica NPs as models of molecular batteries.[8] In this respect, the advantages of small silica NPs are (i) a higher loading capacity per unit weight compared to large NPs, (ii) the possibility of obtaining molecule-like chemically- and electrochemically-reversible systems with a single wave for all the redox centers around the NP with diffusion-controlled electron transfer, and (iii) rapid synthesis of strongly anchored redox-robust systems onto NPs.

As a starting point, we used aminated silica NPs[4b,9] and their reactions with metallocenyl carbonyl chlorides. This reaction has not yet been used for the covalent coverage of silica NPs and turns out to be very efficient, yielding ferrocenylated and pentamethylferrocenylated silica NPs that show reversible cyclic voltammetry and diffusion-controlled electron transfer.

Following the amination of commercial 12 nm silica NPs according to the procedure of Budny *et al.*[4b] using (3-aminopropyl)trimethoxysilane, the reaction of known metallocenyl carbonyl chlorides FcCOCl [(Fc = ferrocenyl, {(η^5-C_5H_4)Fe(η^5-C_5H_5)}] and Fc*COCl [(Fc* = 1,2,3,4,5-pentamethylferrocenyl, {(η^5-C_5H_4-)Fe(η^5-C_5Me_5)}][6] yielded NPs as light orange powders subsequent to multiple washing–centrifugation sequences (Scheme 1).

The infrared spectrum of the ferrocenylated aminosilica NPs (Fc-SiO_2 NPs) showed a strong Si–O band at 1111 cm^{-1}, and amido bands at 1634 and 1539 cm^{-1}, respectively. Cyclic voltammograms (CVs) were recorded using Pt electrodes and 10 mM [*n*-Bu_4N][PF_6] as the supporting electrolyte in methanol/acetonitrile. In addition, some CVs were recorded with decamethylferrocene ($FeCp^*_2$) as an internal reference.[10] In this medium, the NPs appeared as a suspension, and prolonged stirring followed by slow decantation allowed the suspension to deposit at the bottom of the electrochemical cell, whereas the upper layer appeared colorless. If the NPs were not completely dried from methanol before the electrochemical experiments, the stirred NPs in this medium appeared as a



Scheme 1

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† Electronic supplementary information (ESI) available: Instruments, details of the calculations of the numbers of Fc and Fc* groups per SiO_2 NP, CV in the presence of $FeCp^*_2$ and infrared spectra. See DOI: 10.1039/b9nj00481e

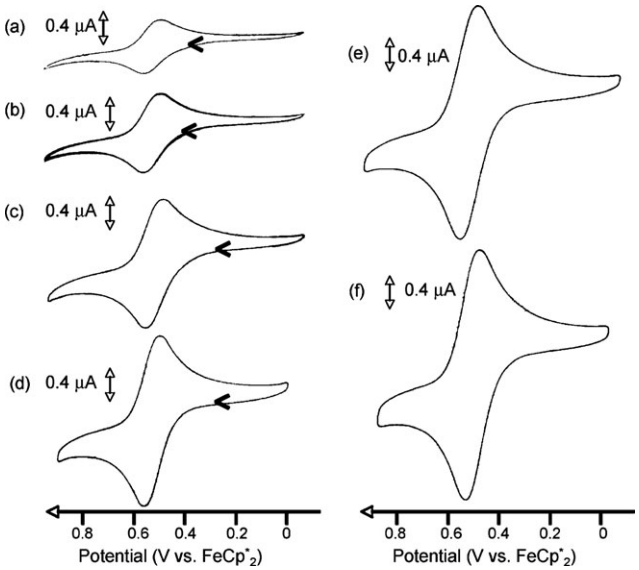

Fig. 1 CVs of Fc-SiO_2 NPs at scan rates of (a) 50, (b) 100, (c) 250, (d) 500, (e) 750 and (f) 1000 mV s^{-1}. Conditions: MeOH (4 mL) + 3 drops of CH_3CN, working electrode Pt, counter-electrode Pt, reference Ag, 50 mg of sample, 10 mM [*n*-Bu_4N][PF_6].

slurry, which turned to a suspension after one day. The CV of the silica-bound amidoferrocene showed a single, fully chemically reversible, wave (i_a/i_c = 1) at $E_{\frac{1}{2}}$ = 0.55 V *vs.* $FeCp^*_2$ with a peak-to-peak separation of ΔE_p = 65 mV at 25 °C between the potentials of the anodic and cathodic peaks, essentially independent of the scan rate and very close to the theoretical value of 59 mV at 25 °C (Fig. 1, Fig. 2 and Fig. 3).

The intensity of the anodic peak is proportional to the square root of the scan rate between 0.05 and 1 V s^{-1} with a zero intercept, indicating a diffusion-controlled current. Thus, it can be concluded that the NPs in suspension are (partly) soluble enough to show a CV wave without much adsorption. The single reversible wave is due to the fact that all the amidoferrocenyl groups around the NPs are identical and independent.[11–13] Thus, the electrostatic factor distinguishing the various redox potentials of the NP redox sites as a function of NP charge is extremely weak (although not zero). This does not mean that the potential of all of these redox sites is the same, because, as indicated in the seminal article of Bard *et al.*,[14] they are statistically distributed around the mean

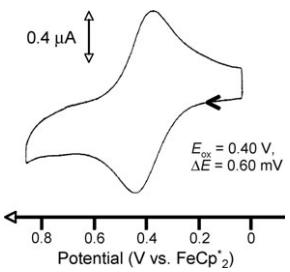

Fig. 2 The CV of Fc*-SiO_2 NPs. Conditions: methanol 2 mL + CH_3CN 2 mL; working electrode Pt, counter-electrode Pt, reference electrode Ag, 32 mg of sample, 10 mM [*n*-Bu_4N][PF_6], 100 mV s^{-1}. $E_{\frac{1}{2}}$ = 0.45 V *vs.* $FeCp^*_2$ (see CV in the SI).

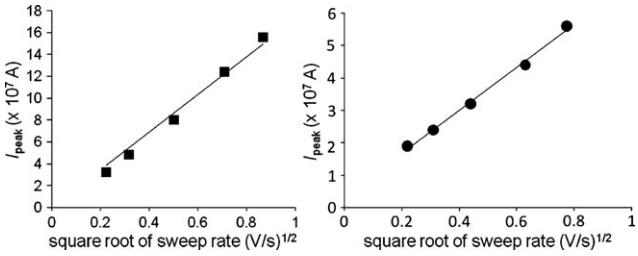

Fig. 3 A plot of oxidation peak current *vs.* the square root of the sweep rate for amidoferrocenyl (left) and pentamethylamidoferrocenyl (right) silica NPs. Conditions: methanol 4 mL + 3 drops of CH_3CN, working electrode Pt, counter-electrode Pt, reference electrode Ag, 10 mM [*n*-Bu_4N][PF_6]. Sample: 50 mg (Fc-SiO_2 NPs) *vs.* 20 mg (Fc*-SiO_2 NPs).

E^0 value all along the CV wave (these numerous standard potentials are those of multiple mixed-valence systems[7b,15]). The mechanism of the fast heterogeneous electron transfer between all of the redox sites can be electron hopping,[16a–c] resulting from fast rotation[16d] of the NPs, or both.

Fc*-SiO_2 NPs were investigated and synthesized analogously, especially because Cp permethylation renders the 17-electron ferricinium species more kinetically and thermodynamically robust. Infrared bands were observed at 1108 cm^{-1} (Si–O), and 1626 and 1537 cm^{-1} (amide). They showed CVs analogous to those of Fc-SiO_2 NPs, *i.e.* a single, reversible wave at $E_{\frac{1}{2}}$ = 0.45 V *vs.* $FeCp^*_2$ with a peak-to-peak separation of ΔE_p = 60 mV at 25 °C between the potentials of the anodic and cathodic peaks, essentially independent of the scan rate. The intensity of the anodic peak was proportional to the square root of the scan rate between 0.05 and 1 V s^{-1}, indicating a diffusion-controlled current (Fig. 2 and Fig. 3).

Redox titration of the amidoferrocenyl NP sites was achieved using acetylferricinium tetrafluoroborate ([FcCOMe][BF_4])[17] as the oxidant in order to determine the approximate number, *n*, of aminoferrocenyl sites on the SiO_2-NPs. The standard potential of the redox system $[FcCOMe]^{+/0}$ was 0.75 V *vs.* $[FeCp^*_2]^{+/0}$,[17] and the color change from the orange 18-electron form to the dark green 17-electron form was strong enough for colorimetric titration. The redox potential of $[FcCOMe]^{+/0}$ was 0.2 V more positive than that of $[(FcCONHR)_nSiO_2]^{+/0}$ (R = *n*-C_3H_6Si); thus the redox equilibrium was largely shifted towards the redox reaction products:[14b]

$$n[FcCOMe][BF_4] + [(FcCONHR)_nSiO_2] \rightarrow n[FcCOMe] + [(FcCONHR)_nSiO_2][BF_4]_n$$

Commercial silica NPs have a diameter of 12 nm, and, using the 2.2 g cm^{-3} value for their density, the mass (including the organometallic groups and linkers) and number of NPs can be determined. This lead to our titration experiments converging to a value of $n = 335 \pm 50$ for the amidoferrocenyl silica NPs, which can be formulated as $(FcCONHR)_{335}SiO_2$. It is probable that most amino groups of these aminosilica NPs are carbonylated because excess ferrocenyl carbonyl chloride was used.

Likewise, titration of $[(Fc^*CONHR)_nSiO_2]$ NPs converged to a value of $n = 240 \pm 40$, which could be formulated more

precisely as $(Fc^*CONHR)_{240}SiO_2$. The significantly reduced number of Fc* groups attached to the amino silica NPs compared to parent $(FcCONHR)_{335}SiO_2$ NPs probably results from the much larger steric bulk of the Fc* moiety compared to its parent Fc moiety.

In conclusion, although numerous examples are known of ferrocenyl coverage of silica NPs, ours are a rare example of adsorption-free electrochemically-reversible silica NPs with a diffusion-controlled current and high coverage. In addition, after gold NPs and metallocenyl dendrimers, these small Fc- and Fc*-SiO_2 NPs are a third family of molecular NPs terminated by a large number of redox-robust systems featuring models of molecular batteries with a high level of charge loading. Extension to electron reservoir complexes with very negative redox potentials[17,18] is a promising further step.

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Experimental section

For general data, see ref. 7*b*, the captions to Figs. 1–3 and the ESI.† Silica NPs with a 12 nm diameter were purchased from Nissan Chemical. Aminosilica NPs were prepared according to ref. 4*b*. The resulting NPs were washed with toluene (four times) and methanol (four times) by successive centrifugation, decantation and redispersion (by sonication). The existence of amino moieties on the surface of the SiO_2 NPs was confirmed by a Kaiser test.[9] The obtained NH_2-terminated SiO_2 NPs were kept as a methanol dispersion.

The syntheses and reactions of FcCOCl and Fc*COCl with other primary amine-terminated nanoparticles were described in ref. 6*b* and adapted as follows. Toluene was added to a methanol dispersion of NH_2-terminated SiO_2 NPs followed by decantation and centrifugation. The precipitates were washed with toluene (3 times) by successive centrifugation, decantation and redispersion (by sonication). After the final decantation of toluene, 0.51 g of the resulting precipitate was transferred to a Schlenk flask with the minimum amount of Et_2O. After the solvents had been removed *in vacuo*, CH_2Cl_2 (10 mL) and NEt_3 (0.30 mL) were added, and the reaction mixture cooled down to 0 °C. Excess (0.5 g) FcCOCl (*vs.* Fc*COCl) in CH_2Cl_2 was added to the suspension through a cannula, and the mixture stirred for 5 min at 0 °C and additional 19 h at r.t. The resulting suspension was centrifuged and the solution decanted. The remaining dark brown precipitate was washed with CH_2Cl_2 (three times), toluene (three times) and methanol–CH_2Cl_2 (1 : 5), with successive centrifugation, decantation and redispersion (sonication). After the precipitate had been dried *in vacuo*, yellow-orange Fc-SiO_2 NPs (220 mg) (*vs.* Fc*-SiO_2 NPs, 250 mg) were obtained.

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