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Ferrocenylsilylation of dendrons: a fast convergent route to redox-stable ferrocene dendrimers

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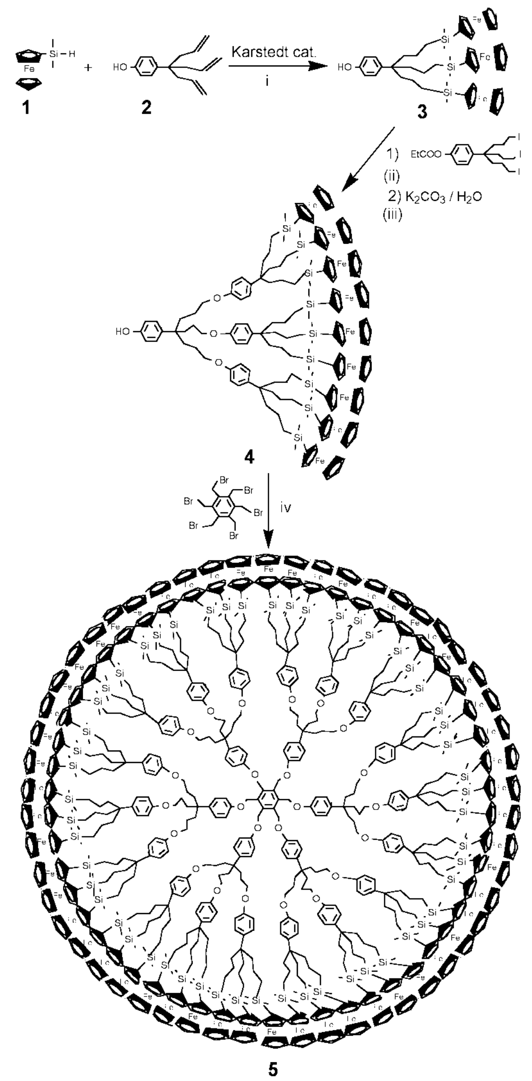
A 54-ferrocene dendrimer is synthesized by a convergent route and can be used to modify a Pt electrode in CH_2Cl_2; it can be reversibly oxidized in DMF in a single 54-electron wave (and with NO^+).

The redox activity of nanoscopic materials,[1,2] in particular that of dendrimers,[3] is of promise in considering applications as materials devices. Ferrocene dendrimers[4] illustrate the potential access to precise redox active nanoscopic molecules with original properties. We now report the ferrocenylsilylation of dendrons and a fast convergent route[5] to *redox stable* dendrimers using ferrocenyldimethylsilane **1**.[6] Hydrosilylation has already been used as an excellent synthetic route to dendrimers.[4e,7] and ferrocenylsilylation has been successfully carried out by Jutzi *et al*. with decaallylferrocene.[4e]

The ferrocenylsilylation of the phenoltriallyl dendron **2**[8] using **1** is achieved with Karstedt's catalyst[9] in the absence of air without protection of the phenol function (Scheme 1). After chromatographic separation, the triferrocenylsilane dendron **3**† is obtained in 90% yield. ^{1}H and ^{13}C NMR spectra indicate the absence of regioisomers, the analytical data are excellent, and the MALDI TOF mass spectrum shows the molecular peak at *m/z* 960.41 (calc. 960.91). A convergent route was developed for the synthesis of the nonaferrocene dendron. The protected dendron p-$EtO_2CC_6H_4C(CH_2CH_2I)_3$[8] reacts with **3** in DMF in the presence of K_2CO_3 to give **4**† in 60% yield after deprotection and chromatography. The MALDI TOF mass spectrum of **4** shows an excellent degree of purity, the molecular peak being largely dominant at *m/z* 3110.44 (calc. molecule 3111.09). Dendron **4** reacts with the core hexa(bromomethyl)benzene in EtOH in the presence of K_2CO_3 at 80 °C over two weeks to give the 54-ferrocene dendrimer **5**† in 20% yield after chromatographic separation (C analysis within 0.3%).

Cyclic voltammograms (CVs) of the ferrocenyl dendrons **3** and **4** and the ferrocenyl dendrimer **5** were recorded on a Pt anode in dichloromethane and dimethylformamide (DMF).[10] Dendrons **3** and **4** show a reversible oxidation wave in a diffusion process (no adsorption, as indicated by ΔE_p = 60 mV at 20 °C) in both solvents. The number of electrons involved in this ferrocene oxidation wave was determined using Bard's equation[11] and decamethylferrocene as the internal reference. The experimental number of electrons was found to be in full agreement within 5% with the actual number of dendritic branches. In DMF, the CV of **5** also gives a single reversible wave corresponding to the oxidation of the 54 ferrocene redox centers in a pure diffusion process as indicated by ΔE_p = 60 mV at 20 °C as for the decamethylferrocene reference. The number of redox centers determined experimentally as above is 54 ± 3. In dichloromethane, the CV of **5** shows a mixture of diffusion and adsorption as indicated by a value of ΔE_p = 30 mV at a scan rate of 0.1 V s^{-1}. Modified electrodes[12] with **5** could be prepared by cyclic scanning between the ferrocene and ferrocenium regions of potentials on a Pt electrode in dichloromethane solution, washing with dichloromethane and drying in air. Cycling about twenty times is necessary before observation of a constant curve. When such a derivatized electrode is used in a new dendrimer-free solution containing only the electrolyte, the cyclic voltammogram of the adsorbed dendrimers are obtained with ΔE_p = 0 and a linear relationship between the scan rate and the intensity, both features being characteristic of derivatized electrodes with ferrocene polymers[12] and dendrimers[4g] (Fig. 1). The orange–red dendrimer **5** can be instantaneously oxidized by $NOPF_6$ in dichloromethane, and the blue PF_6^- salt of the 54-ferrocenium dendrimer $\mathbf{5}^{54+}$ obtained as a precipitate can be reduced back to the 54-ferro-



Scheme 1 *Reagents and conditions*: i, toluene, 40 °C, 1 d; ii, DMF, room temp., 2 d; iii, 40 °C, 2 d; iv, EtOH, K_2CO_3, reflux, 14 d.

cene dendrimer **5** using the monoelectronic reducing agent decamethylferrocene. No decomposition of the dendrimer occurs during these redox processes as indicated by the indentity of the ^{1}H NMR spectra before and after the reactions.

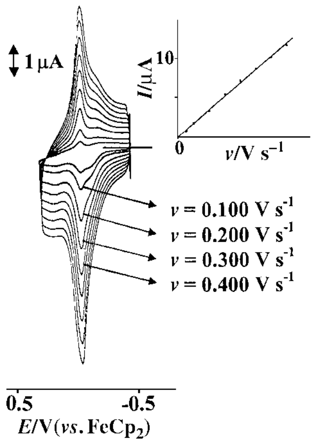


Fig. 1 Cyclic voltammogram of a Pt electrode modified with a film of the 54-ferrocene dendrimer **5**; CH_2Cl_2, 0.1 M $NBu^n{}_4PF_6$. Inset: plot of the peak intensity *vs.* sweep rate.

Whereas the mechanism of electron transfer in DNA is highly controversial,[13] that in multi-redox dendrimers is also of interest. The present study concerns a large dendrimer approaching a globular shape. The electrochemical reversibility observed for the oxidation of **5** indicates that the structural rearrangement between **5** and $\mathbf{5}^{54+}$ is small. Since the repulsion between the positively charged ferrocenium units in $\mathbf{5}^{54+}$ requires that they be at the periphery of the dendrimer with maximum space expansion, the shape of **5** is relatively closely related to that of $\mathbf{5}^{54+}$. The fact that a single reversible wave is observed is due to fast rotation of the dendrimer compared to the electrochemical timescale, so that all the redox centres come close to the electrode within this timescale.[14b] In addition, a kind of *relay*-mechanism from a ferrocene site to the next (hopping electron transfer or *via* π-stacking[14] of the ferrocene units or *via* the σ bonds between ferrocene units) may eventually occur. Otherwise, the heterogeneous electron transfer between the electrode and the most remote redox sites of the globular dendrimer would be slow, as it is when the redox site is isolated at the center of the dendrimer.[4l,m,15] This type of stable polyredox dendrimer in which the redox centers are all active and fully chemically and electrochemically reversible at about the same potential could find use in the future as molecular batteries and sensors.

Notes and references

† Satisfactory C and H elemental, and MALDI TOF mass spectral analyses were obtained for **3** and **4**. NMR: **3** δ_H($CDCl_3$, 250 MHz) 7.12 (d, 2H, C_6H_4), 6.75 (d, 2H, C_6H_4), 4.20 (t, 6H, C_5H_4), 4.09 (s, 15H, C_5H_5), 4.01 (t, 6H, C_5H_4), 1.59 (br s, 6H, CH_2Ar), 1.12 (br s, 6H, CH_2CH_2Ar), 0.61 (br s, 6H, CH_2Si), 0.17 (s, 18H, SiMe). δ_C($CDCl_3$, 62.9 MHz) 152.55 (C_q, ArOH), 139.88 (C_q, Ar), 127.66 (CH, Ar), 114.67 (CH, Ar), 72.95 (C_5H_4); 71.58 (C_q, C_5H_4), 70.52 (C_5H_4), 68.12 (C_5H_5), 43.12 (C_q-CH_2), 42.16 (CH_2), 18.08 ($\mathit{C}H_2CH_2Si$), 17.56 (CH_2Si), −1.93 (SiMe). **4**. δ_H($CDCl_3$, 250 MHz) 7.18 (m, 8H, C_6H_4), 7.04 (m, 8H, C_6H_4), 4.23 (br m, 18H, C_5H_4), 4.02 (s, 45H, C_5H_5), 3.94 (br m, 6H, C_5H_4), 3.89 (br s, 6H, CH_2O), 1.54 (br s, 24H, $CH_2\mathit{CH}_2$Ar); 1.18 (br s, 24H, CH_2CH_2Ar), 0.56 (br s, 18H, CH_2Si), 0.16 (s, 45H, SiMe); δ_C($CDCl_3$, 62.9 MHz) 156.11 (C_q, ArO), 152.39 (C_q, ArOH) 140.02 (C_q, Ar), 127.63 (CH, Ar), 127.60 (CH, Ar), 114.64 (CH, Ar), 113.69 (CH, Ar), 73.21 (C_5H_4), 71.83 (C_q, C_5H_4), 70.88 (C_5H_4), 68.38 (C_5H_5), 43.20 (C_q-$\mathit{C}H_2$), 42.16 (CH_2), 29.50 ($\mathit{C}H_2CH_2$Ar), 18.07 ($\mathit{C}H_2CH_2$Si), 17.56 (CH_2Si), −1.95 (SiMe). **5**, δ_H($CDCl_3$, 250 MHz) 7.12 (m, 60H, C_6H_4), 6.77 (m, 60H, C_6H_4), 5.21 (br s, 18H, Ph$\mathit{C}H_2$O), 4.29 (br m, 108H, C_5H_4), 4.09 (s, 270H, C_5H_5), 4.01 (br m, 108H, C_5H_4), 3.86 (br s, 36H, CH_2O), 1.54 (br s, 108H, $\mathit{C}H_2\mathit{C}H_2$Ar), 1.12 (br s, 108H, $\mathit{C}H_2\mathit{C}H_2$Ar), 0.60 (br s, 108H, CH_2Si), 0.16 (s, 324H, SiMe). δ_C($CDCl_3$, 62.9 MHz) 156.11 (C_q, ArO), 139.56 (C_q, Ar), 127.60 (CH, Ar), 127.3 (CH, Ar), 114.68 (CH, Ar), 113.72 (CH, Ar), 72.92 (C_5H_4), 70.62 (C_q, C_5H_4); 70.58 (C_5H_4); 68.08 (C_5H_5); 66.00 ($\mathit{C}H_2\mathit{C}H_2$O) 43.99 ($C_q$-$\mathit{C}H_2$) 41.36 ($CH_2$), 29.73 ($\mathit{C}H_2CH_2$Ar), 18.08 ($\mathit{C}H_2CH_2$Si), 17.67 ($CH_2$Si), −1.87 (SiMe).

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