

single crystals consist of solid solutions of the monomer and the polymer (Figure 1b). A typical crystal after 30 Mrads of γ radiation maintained its $P\bar{1}$ space group symmetry with $a = 7.201(2)$, $b = 10.751(3)$, $c = 11.1421(3)$ Å, $\alpha = 76.94(2)$, $\beta = 87.67(2)$, $\gamma = 80.18(2)^\circ$. $R_w = 5.7$, $R = 6.3$ for 208 variables and 1211 unique observations with $I > 3\sigma$. The occupancy of the three independent central atoms of the triacetylene polymer refined to 0.58 for this particular crystal. The experiment was repeated for many different crystals all of which gave similar, but not identical parameters. The a axis of the triclinic unit cell corresponds to the critical polymerization direction. In a fresh crystal this axis has length of 7.143(2) Å. As the polymerization proceeds, the a axis lengthens in proportion, but only slightly. The highest observed value of 7.210(6) Å was for a crystal polymerized to an extent of 70%. Since this value is still considerably shorter than the 7.4 Å repeat distance predicted for the polymer, it is likely that strain may build up in the crystals as the polymerization proceeds. As the degree of polymerization exceeds 70%, this accumulated strain in the crystals may be the driving force of the change to an amorphous state. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-138504–135509. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

The host compounds **3** and **5** were prepared by refluxing 1,3-cyclohexanedione with one equivalent of the appropriate amine in benzene, and the water produced during the reaction was removed with a Dean–Stark trap. Glycine and 4-aminomethylpyridine gave 71% and 91% yields of the vinylous amides **3** (m.p. 215 °C) and **5** (m.p. 138 °C), respectively.

The triacetylenes were prepared by two successive Cadiot–Chodkiewicz reactions (CuCl (0.1 equiv), $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.3 equiv), and propylamine (3 equiv) in methanol). Triacetylene **6** was prepared by treating 4-pentynoic acid with 1-bromo-2-triethylsilylacetylene under the above Cadiot–Chodkiewicz reaction conditions to give the triethylsilyl-protected diacetylene (59%). The protecting group was removed (95%) using 1 M tetrabutylammonium fluoride (TBAF) in THF and the diacetylene was coupled with 5-bromo-4-pentynoic acid under the above Cadiot–Chodkiewicz reaction conditions^[14] to give the triacetylene **6** (95%).

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Mixed Ferrocene–Cobaltocenium Dendrimers: The Most Stable Organometallic Redox Systems Combined in a Dendritic Molecule**

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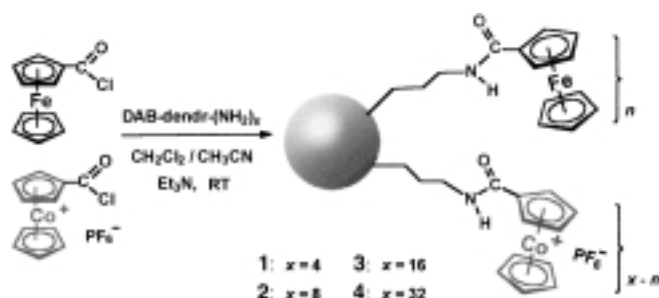
Exciting advances continue to be made in dendrimer chemistry.^[1] The incorporation of metals in dendritic structures has attracted growing interest as it generates new metallodendrimers^[2] with interesting redox, magnetic, catalytic, and photo-optical properties. At the same time, new synthetic methods have been used for the introduction of functionally diverse terminal groups in the same molecule,^[3] which give access to dendritic macromolecules having special properties and a variety of functions.

In the last few years, we reported the synthesis of several families of silicon- and nitrogen-based dendritic molecules containing organometallic moieties as surface functional groups.^[4] In particular, poly(propylene imine) dendrimers functionalized with ferrocene or cobaltocenium moieties were shown to act as multisite redox-active guests for inclusion complexation by β -cyclodextrins, which yielded soluble supramolecular assemblies of high molecular weight.^[5] Here we report on the synthesis and redox properties of novel metallodendrimers containing both ferrocene and cobaltocenium units. To our knowledge, this is the first time that multiple neutral and cationic redox-active organometallic moieties are present in a dendritic structure.^[6, 7] These peripherally heterogeneous dendrimers combine the advantages of both metallocenes, in particular, their stability and redox reversibility on oxidation and reduction, respectively. Electrode surfaces modified with these metallodendrimers were successfully used as a novel type of glucose sensor.

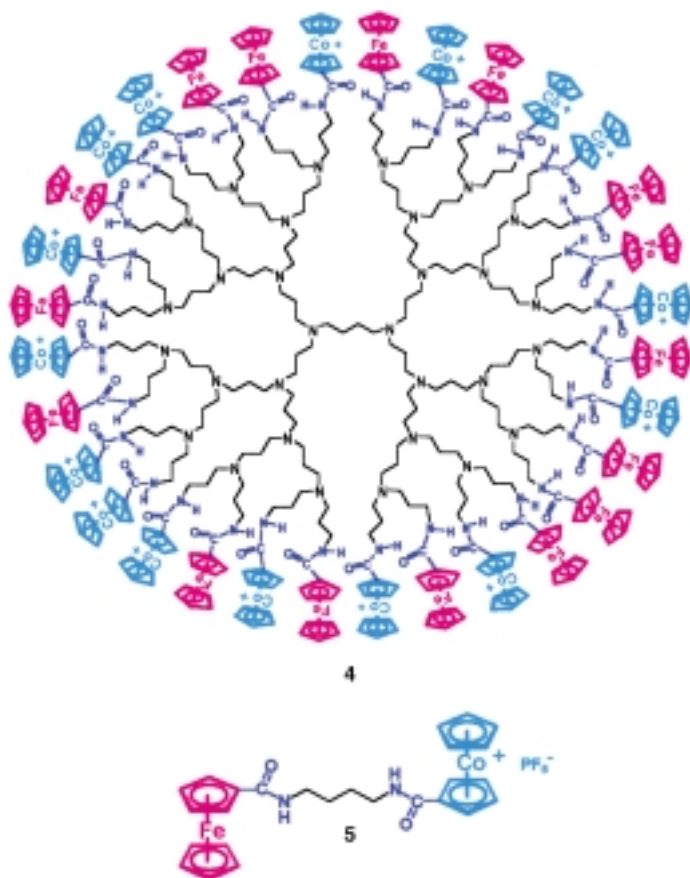
The new mixed-metal dendrimers **1–4** were obtained by treatment of the first four generations of poly(propylene imine) dendrimers DAB-dendr-(NH₂)_x ($x = 4, 8, 16, 32$) with an equimolar mixture of freshly prepared chlorocarbonylferrocene and the PF₆⁻ salt of chlorocarbonylcobaltocenium in CH₂Cl₂/CH₃CN (1/1) (Scheme 1). They were isolated as air-stable orange-brown shiny solids. Ideally, each metallodendritic molecule should have the same number of ferrocene and cobaltocenium units on the surface (see the schematic representation of **4**). However, the experimental results

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Scheme 1. Synthesis of heteromultimetallic dendrimers **1–4**.

showed that, as expected, the formation of a single defined product is unlikely. In fact, after treatment of the reaction products with CH_2Cl_2 and CH_3CN , several fractions with different ratios of the organometallic end groups on the dendritic surface were isolated. Reaction of 1,4-diaminobutane with a mixture of $[(\text{C}_5\text{H}_4\text{COCl})\text{Fe}(\text{C}_5\text{H}_5)]$ and $[(\text{C}_5\text{H}_4\text{COCl})\text{Co}(\text{C}_5\text{H}_5)]\text{PF}_6$ (one equivalent each) afforded the heterodinuclear compound **5**, which is a valuable model for the characterization of the mixed-metal dendrimers of higher nuclearity.



The presence of neutral ferrocene and cationic cobaltocenium units imparts an interesting solubility behavior to the heteromultimetallic dendrimers, which can be modified by varying the ratio of the organometallic moieties at the periphery. Dendrimers with a higher loading of cobaltocenium moieties are soluble in H_2O and insoluble in CH_2Cl_2 ,

and they become increasingly soluble in CH_2Cl_2 as the loading of ferrocene units increases.

The new heterometallic dendrimers were characterized by ^1H and ^{13}C NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and total X-ray fluorescence (TXRF).^[8] The NMR spectra show the same signals as the corresponding homogeneous ferrocene and cobaltocenium dendrimers,^[5a,c] as well as those of **5**. The signals of the two peripheral organometallic moieties are observed in the range $\delta = 4.3\text{--}5.9$ for the ferrocene units and $\delta = 5.8\text{--}6.4$ for the cobaltocenium fragments. On the basis of these signals, the ratio of the two peripheral organometallic units can be estimated. For dendrimers that are insoluble in CH_2Cl_2 , the loading of the NH_2 end groups with cobaltocenium is significantly higher than with ferrocene. This was further confirmed by TXRF analyses, which showed a ratio of cobaltocenium to ferrocene units of 3:1 for **1**, 6.5:1.5 for **2**, 13:3 for **3**, and 19:13 for **4**. The ESI mass spectra of the heterometallic dendrimers show different peaks corresponding to species with different states of charge, which result from successive loss of counteranions.

The electrochemical behavior of the novel heterometallic dendrimers **1–4** and the model compound **5** was investigated by cyclic voltammetry (CV) in CH_3CN and aqueous solutions. All four dendrimers show only one reversible oxidation process at about $+0.60\text{ V}$, which was clearly assigned to the simultaneous one-electron oxidation of the multiple peripheral noninteracting ferrocene units (see Figure 1a). Likewise,

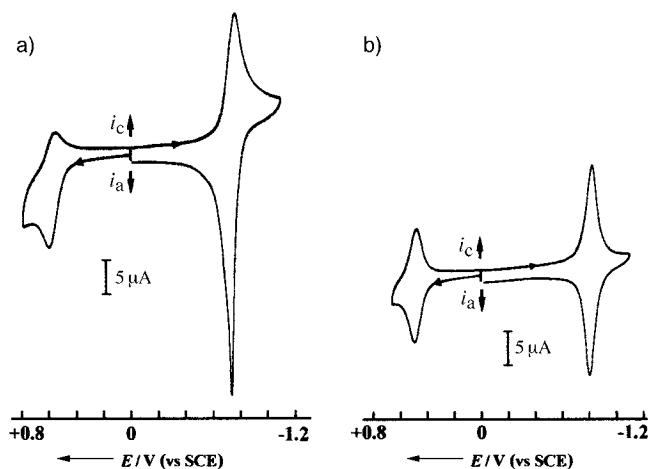


Figure 1. a) Cyclic voltammogram of **3** measured in $\text{CH}_3\text{CN}/0.1\text{M Bu}_4\text{NPF}_6$. b) Cyclic voltammetric response of a glassy carbon disk electrode modified with a film of **3** in $\text{H}_2\text{O}/0.1\text{M LiClO}_4$. Scan rate 100 mV s^{-1} .

the appearance of a single reduction wave near -0.70 V confirms the presence of multiple noninteracting terminal cobaltocenium moieties. In this case, a change in solubility of the dendrimers accompanied the change in oxidation state. Reduction of the dendrimers appeared to result in the precipitation of the reduced neutral dendrimers onto the electrode surfaces, and on the reverse scan the dendrimer redissolved as it was oxidized. The ferrocene/cobaltocenium ratio calculated from the CV is in close agreement with that estimated from the NMR spectrum.

One remarkable feature of these heterogeneous organo-metallic dendrimers is their ability to modify electrode surfaces.^[8] Figure 1 b shows the voltammetric response of an electrodeposited film of the heteromultinuclear dendrimer **3** in aqueous solution as a representative example. Two well-defined, reversible systems are observed, with formal potential values of +0.47 and –0.83 V, which correspond to the ferrocene/ferrocenium and cobaltocenium/cobaltocene systems, respectively, whose voltammetric features unequivocally indicate the surface-confined nature of the electroactive dendrimer film. These modified electrodes are extremely durable and reproducible. Cyclic voltammetric scans can be carried out hundreds of times, with no loss of electroactivity. To our knowledge, this is the first example of electrode surfaces modified with films of electroactive molecules that incorporate both ferrocene and cobaltocenium sites.

The surface-confined heterometallic dendrimers were shown to exhibit a double function: While the ferrocene units act as mediators in enzymatic processes under anaerobic conditions, the cobaltocenium moieties take part in an electrocatalytic process in reactions conducted in the presence of oxygen. We immobilized glucose oxidase (GOx) by depositing the enzyme into conducting films of **3**.^[9] Initial experiments to test these modified electrodes as glucose sensors were successful. A major advantage of these electrodes is the large amount of enzyme due to electrostatic interactions between the positive ferrocenium and cobaltocenium moieties and the negatively charged enzyme. Furthermore, the presence of cobaltocenium units prevents loss of GOx due to the reduction of ferrocenium groups, and this increases the long-term stability of the sensor. Glucose was detected by measuring the amperometric response due to the mediation of the enzymatic reaction by the electrochemical oxidation of ferrocene (Figure 2a)^[10] and, alternatively, by

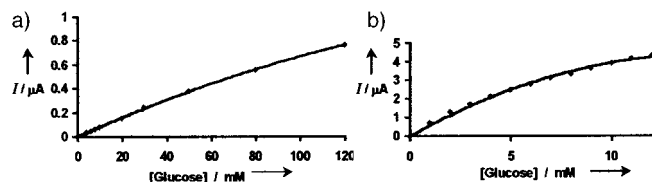


Figure 2. Variations of the steady-state current with glucose concentration, measured with a **3**/enzyme-modified electrode in 0.1 M phosphate buffer, pH = 7.3, containing 0.1 M NaClO₄, compared to a solution without glucose. a) Increases observed at +0.5 V in a N₂-saturated solution. b) Decreases observed at –0.65 V in an O₂-saturated solution.

monitoring the reduction of dissolved oxygen in the presence of the substrate (Figure 2b).^[10] At potentials where the ferrocene moieties act as mediators, the enzyme electrodes respond rapidly to glucose, and steady-state currents are achieved in less than 10 s after each addition. Likewise, significant sensitivity and linearity to clinically relevant glucose concentrations were obtained. On the other hand, the catalytic activity of the cobaltocenium centers was proved by CV.^[11] The application of these modified dendrimer/GOx electrodes allows the reduction of oxygen to occur at a less negative potential (thus diminishing interference) and with higher intensity than with bare glassy carbon electrodes. By

holding the potential at –0.65 V a decrease in the current due to oxygen reduction is detected as the concentration of glucose increases. Such intense currents are not obtained for a glucose-oxidase-coated bare electrode held at the same potential.

Experimental Section

All dendrimers were prepared by the same procedure.

3: To a solution of 1-chlorocarbonylferrocene (0.60 g, 2.42 mmol) and 1-chlorocarbonylcobaltocenium hexafluorophosphate (0.96 g, 2.42 mmol) in CH₂Cl₂/CH₃CN (1/1) (100 mL) was added dropwise a solution of DAB-dend-(NH₂)₁₆ (commercially available from DSM; 0.51 g, 0.30 mmol) and 3 mL of Et₃N in CH₂Cl₂/CH₃CN (1/1) (40 mL). The reaction mixture was stirred for about 12 h under argon at room temperature. After removal of the solvent in vacuum, the resulting brown residue was washed several times with CH₂Cl₂, then dissolved in acetonitrile and precipitated into dichloromethane. The precipitate was dried in vacuum and an orange-brown shiny solid was obtained (0.55 g). Removal of the solvent from the dichloromethane solution afforded a reddish-orange solid (0.31 g).

Selected data for **3** as a representative example: ¹H NMR (300 MHz, [D₆]DMSO, 25 °C): δ = 9.25 (CONH_[Cb]), 8.06 (CONH_[Fc]), 6.39, 5.91 (C₅H₄[Cb]), 5.85 (C₅H₅[Cb]), 4.82, 4.31 (C₅H₄[Fc]), 4.13 (C₅H₅[Fc]), 2.68, 2.95, 1.83 (CH₂); ¹³C NMR (500 MHz, [D₆]DMSO, 25 °C): δ = 170.3 (CO_[Fc]), 162.3 (CO_[Cb]), 94.6 (C₅H₄[Cb]), 86.8 (C₅H₅[Cb]), 86.5, 85.0 (C₅H₄[Fc]), 77.4, 70.9 (C₅H₅[Fc]), 70.3 (C₅H₅[Fc]), 69.2 (C₅H₄[Fc]), 51.4, 38.2, 37.5, 25.2, 21.9 (CH₂); ESI-MS (*m/z*) of the CH₂Cl₂-insoluble fraction: 856.0 [*M*_(3Fc, 13Cb) – 7PF₆]⁷⁺, 730.7 [*M*_(3Fc, 13Cb) – 8PF₆]⁸⁺, 633.4 [*M*_(3Fc, 13Cb) – 9PF₆]⁹⁺, 555.5 [*M*_(3Fc, 13Cb) – 10PF₆]¹⁰⁺, 492.4 [*M*_(3Fc, 13Cb) – 11PF₆]¹¹⁺, 834.2 [*M*_(4Fc, 12Cb) – 7PF₆]⁷⁺, 712.2 [*M*_(4Fc, 12Cb) – 8PF₆]⁸⁺, 616.7 [*M*_(4Fc, 12Cb) – 9PF₆]⁹⁺, 540.5 [*M*_(4Fc, 12Cb) – 10PF₆]¹⁰⁺, 478.1 [*M*_(4Fc, 12Cb) – 11PF₆]¹¹⁺, 813.3 [*M*_(5Fc, 11Cb) – 7PF₆]⁷⁺, 693.2 [*M*_(5Fc, 11Cb) – 8PF₆]⁸⁺, 600.2 [*M*_(5Fc, 11Cb) – 9PF₆]⁹⁺, 525.7 [*M*_(5Fc, 11Cb) – 10PF₆]¹⁰⁺, 465.0 [*M*_(5Fc, 11Cb) – 11PF₆]¹¹⁺. Fc = C₅H₄FeC₅H₅, Cb = C₅H₄CoC₅H₅.

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- [9] The dendrimer-modified electrodes were immersed in an electrochemical cell containing an enzyme solution (0.1 % of GOx in acetate buffer, pH = 6.3, and NaClO_4 0.1M). A potential of +0.6 V versus SCE was applied to the dendrimer-coated electrodes for 30 min with stirring, and the electrodes were subsequently rinsed in deionized water and air-dried before use.
- [10] The electrode enzymatic reactions are $\text{S} + \text{enzyme}_{\text{ox}} \rightarrow \text{P} + \text{enzyme}_{\text{red}}$ and $\text{enzyme}_{\text{red}} + \text{M}_{\text{ox}} \rightarrow \text{enzyme}_{\text{ox}} + \text{M}_{\text{red}}$, where M = mediator, $\text{M}_{\text{ox}} = \text{O}_2$ or ferrocenium, S = substrate (glucose), P = product (gluconolactone).
- [11] E_p of the O_2 reduction -0.83 V versus SCE at a bare carbon glassy electrode, and -0.70 V at the dendrimer modified electrode.

Structure of Homoleptic $\text{Cu}^I(\text{CO})_3$ Cations in Cu^I -Exchanged ZSM-5 Zeolite: An X-ray Absorption Study**

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Copper is a transition metal that plays a remarkable role in redox catalysis by several selective, three-dimensionally organized, inorganic, organic, and biological systems.^[1–3] In

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all these catalysts the structure of the active sites is rather complex, and often the interplay between two adjacent copper centers is required for their operation.

Copper(I)-exchanged zeolites can be considered the best known type of inorganic three-dimensionally organized catalysts, because of their crystalline structure and the controlled dispersion of the metal centers, which impart a good structural definition to the adsorbing sites.^[4] Copper-exchanged zeolites are usually prepared by standard exchange procedures with aqueous solutions of Cu^{II} salts. Depending on the preparation and pretreatment conditions, they contain variable mixtures of copper species in different oxidation and aggregation states.^[1, 5] Products containing exclusively isolated Cu^{I} ions can be prepared by reaction of H-zeolites with CuCl in the gas phase.^[6] Structural and spectroscopic studies have shown that the Cu-ZSM-5 thus obtained contains solely isolated Cu^{I} ions,^[7] located in structurally and energetically well defined positions.^[8] Hence, these materials have model character and are suitable for theoretical investigations.^[9, 10]

In addition, Cu complexes of well-defined structure can be synthesized in zeolitic materials, and the zeolitic framework can often stabilize complexes that would otherwise be unstable.^[11, 12] Although binary compounds of the type $\text{Cu}^I(\text{CO})_n$ were observed in strongly acidic media such as H_2SO_4 , $\text{CF}_3\text{SO}_3\text{H}$, FSO_3H , $\text{BF}_3 \cdot \text{H}_2\text{O}$, and HF ,^[3] none of these complexes could be isolated as solids. Only recently did Rack et al.^[13] report the formation and the structural and spectroscopic characterization of $[\text{Cu}^I(\text{CO})_n]^+ \text{AsF}_6^-$ ($n = 1-3$).^[14]

Infrared spectroscopy (Figure 1) has been very informative on the structure of intrazeolitic $[\text{Cu}^I(\text{CO})_n]^+$ species ($n = 1-3$), and the main results can be summarized as follows:^[6b, 8] 1) at low CO equilibrium pressures p_{CO} linear $\text{Cu}^I(\text{CO})$ complexes are formed;^[15] 2) on increasing p_{CO} the formation of C_{2v} -symmetric $\text{Cu}^I(\text{CO})_2$ adducts is observed;^[16] 3) on decreasing the temperature, $\text{Cu}^I(\text{CO})_3$ complexes of C_{3v}

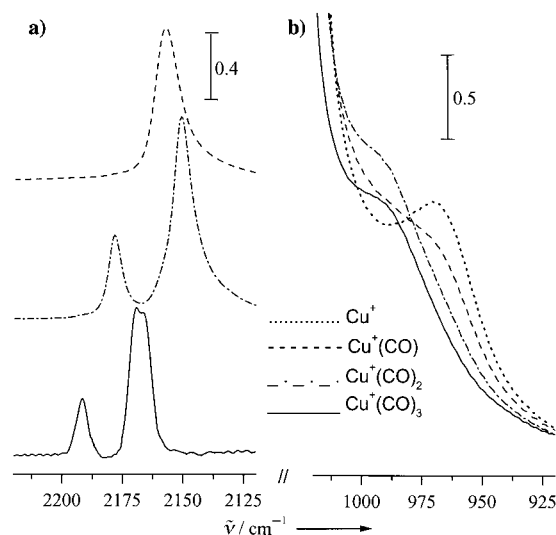


Figure 1. IR spectra of $[\text{Cu}^I(\text{CO})_n]^+$ species ($n = 1-3$) in ZSM-5 zeolite in the C=O (a) and framework stretching (b) regions. The spectrum obtained before CO addition was used as background and was subtracted from the spectra in (a). The spectrum of the $[\text{Cu}^I(\text{CO})_3]^+$ adduct is shown after additional subtraction of the band of the physisorbed component at 2138 cm^{-1} .^[17]