Ferrocenyl Dendrimers Incorporated into Mesoporous Silica: New Hybrid Redox-Active Materials[†]

Isabel Díaz,[‡] Belén García,[§] Beatriz Alonso,[§] Carmen M. Casado,[§]
Moisés Morán,*[,§,#] José Losada,[||] and Joaquín Pérez-Pariente*[,‡,⊥]

Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049 Madrid, Spain,
Departamento de Química Inorgánica, Universidad Autónoma de Madrid, Cantoblanco,
28049 Madrid, Spain, and Escuela Técnica Superior de Ingenieros Industriales,
Universidad Politécnica de Madrid, 28006 Madrid, Spain

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A novel type of redox-active materials, which to our knowledge are the first examples of mesoporous silica hosts containing dendritic guest molecules within their highly ordered channels, is presented. A simple and efficient synthetic route has been used to incorporate poly(propyleneimine) dendrimers containing 4, 8, and 64 amidoferrocenyl moieties (**1**−**3**) into MCM-41. In these new composite materials (*dend*-***n***-MCM-41, ***n*** = **1**−**3**) the integrity of the guest after the inclusion process is maintained (as confirmed by elemental analyses, IR, and ^{13}C CP MAS NMR spectroscopy), resulting in stable dendrimer−matrix complexes. X-ray diffraction, nitrogen adsorption isotherms, and transmission electron microscopy are consistent with the full occupancy of the channels by the smallest dendrimer, whereas less effective inclusion is obtained with the bulkier macromolecules. One significant feature of these new composite materials is that the guest dendrimers, containing a controlled number of ferrocenyl units, are easily accessible to electrochemical oxidation. Platinum disk electrodes coated with layers of *dend*-***n***-MCM-41/graphite powder/polystyrene composites have been studied by cyclic voltammetry and differential pulse voltammetry. The electrochemical properties of these hybrid materials are related to the dendrimers different sizes and were found to differ significantly from those of the corresponding hybrid materials prepared with a nonporous silica.

Introduction

During the past 10 years much attention has been devoted to a new generation of mesoporous materials.[1] In particular, MCM-41, a mesoporous silicate with a highly regular structure composed of channels in a hexagonal arrangement, has stimulated interest since the pore sizes can be varied between 2 and 10 nm in diameter.[2] Thus, these materials have been shown to be suitable host frameworks for novel nanomaterials. For instance, these mesoporous silica are excellent matrixes for the anchoring of organometallic species,[3,4] and the resulting modified silicas have interesting applications, such as precursors of magnetic ceramics and as catalysts.[5]

Dendrimers[6] are appealing nanosized guest molecules for inclusion into mesoporous materials because their novel and unique architecture provides a very high and controlled number of functional groups in a compact space. The use of dendritic materials is currently generating increasing attention in a number of areas in science and technology.[7] To our knowledge, the idea of incorporating well-defined, highly branched dendritic molecules into the well-ordered channels of mesoporous silica has not been explored. However, this target is attractive as it may provide access to novel mesoporous materials having special properties and functions.

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* Corresponding authors.

[†] This paper is dedicated to the memory of Moisés Morán.

[‡] CSIC.

[§] Universidad Autónoma de Madrid.

[||] Universidad Politécnica de Madrid.

[⊥] E-mail: jperez@icp.csic.es.

[#] Recently deceased.

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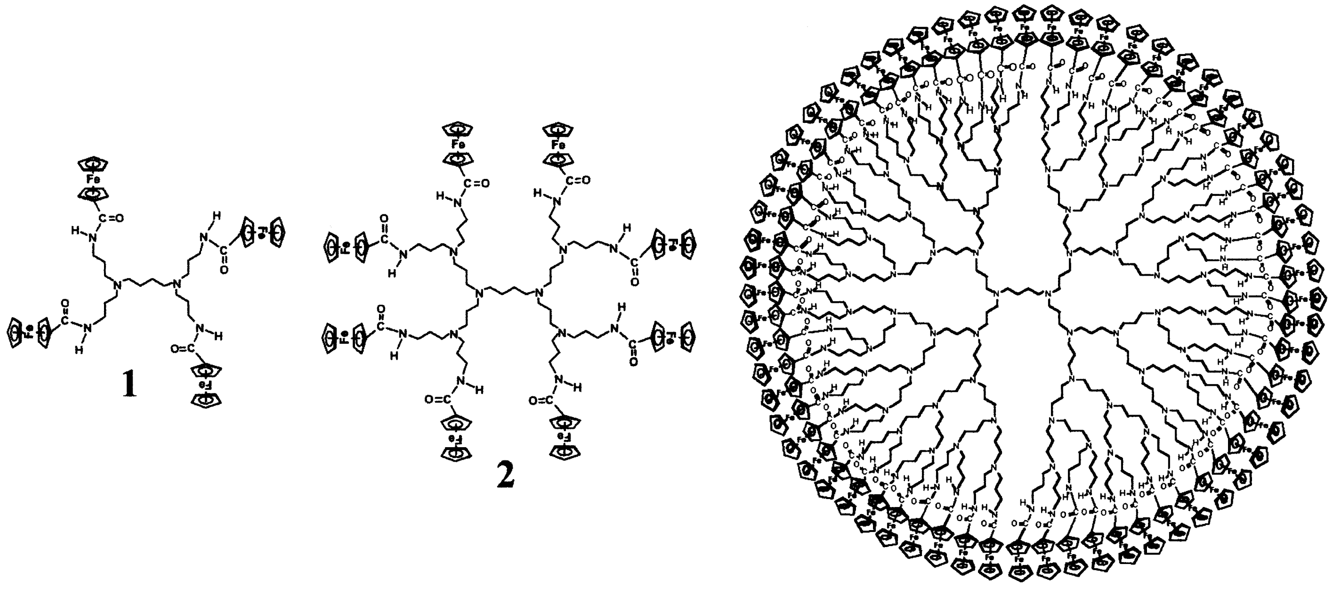
Chart 1



1 **2** **3**

As part of our research on metallodendrimers[8] and functionalized mesoporous materials,[9] we report here for the first time the synthesis and characterization of novel materials that incorporate redox-active ferrocenyl dendrimers into the host channels of a mesoporous silica framework.

Experimental Section

Sample Preparation. The synthesis of MCM-41 has been performed as previously described.[10] Included organic compounds were removed by heating the samples at 540 °C under a continuous flow of N_2 (130 cm^3/min) for 1 h, followed by a flow of air (130 cm^3/min) for 6 h. Dendrimers **1**−**3** (Chart 1) were synthesized as previously described.[11]

Preparation of *dend*-1-MCM-41, *dend*-2-MCM-41, and *dend*-3-MCM-41. MCM-41 (1 g) was treated with Me_2SiCl_2 (17 μL) in dry diethyl ether (30 mL) under stirring for 1 h. Then 0.2 g of this pretreated MCM-41 and 0.8 g of **1** (or 0.6 g of **2** or 0.6 g of **3**) in dry CH_2Cl_2 (30 mL) were left to reflux with stirring for 5 days. The solution was filtered off, and the orange solid was washed thoroughly with CH_2Cl_2, until the last three washings were colorless, and dried under vacuum. Elemental analysis found for pretreated MCM-41: C 0.82%, H 3.28%; *dend*-**1**-MCM-41: C 21.04%, H 2.79%, N 2.42%; *dend*-**2**-MCM-41: C 11.83%, H 2.24%, N 1.17%; *dend*-**3**-MCM-41: C 6.64%, H 1.73%, N 0.66%.

Preparation of *dend-n*-Aerosil. Aerosil 200 (Degussa) (0.25 g) and 0.15 g of dendrimer **1**, **2**, or **3** in dry CH_2Cl_2 (20 mL) were left to reflux with stirring for 12 h. The solution was filtered off, and the orange solids were washed thoroughly with CH_2Cl_2, until the last three washings were colorless, and dried under vacuum. Elemental analysis found for *dend*-**1**-Aerosil: C 3.84%, H 0.84%, N 0.42%; *dend*-**2**-Aerosil: C 4.04%, H 0.85%, N 0.50%; *dend*-**3**-Aerosil: C 2.44%, H 0.73%, N 0.33%.

Preparation of *dend*-3-Silica Gel. Silica gel (Fluka) (0.25 g) and 0.15 g of **3** in dry CH_2Cl_2 (20 mL) were left to reflux with stirring for 12 h. The solution was filtered off, and the orange solid was washed thoroughly with CH_2Cl_2, until the last three washings were colorless, and dried under vacuum. Elemental analysis found for *dend*-**3**-silica gel: C 6.74%, H 1.21%, N 0.78%.

Sample Characterization. Analyses of the organic material present in the solids were done in a Perkin-Elmer 2400 CHN analyzer. Iron was determined by atomic emission spectroscopy in an ICP−Perkin-Elmer 3300 DV after treatment of the solid with a 3:1:3 HNO_3:HCl:HF mixture under microwaves in a Milestone-mis1200mega apparatus. X-ray powder diffraction patterns were collected using Cu Kα radiation, on a SEIFERT XRD 3000P diffractometer operating at low angle (1−10°) using 1- and 0.5-mm font gratings and 0.1-mm detector grating. For the TEM measurements the solids were dispersed in acetone and dropped on a copper microgrid covered by a holey carbon film. Micrographs and selected area electron diffraction patterns (SAED) were recorded in a Jeol JEM 2000Fx microscope operating at 200 kV, equipped with a XEDS detector, and a Jeol JEM 3010 transmission electron microscope at 300 kV. Adsorption isotherms of nitrogen were obtained in an ASAP 2000 Micromeritics apparatus. Infrared data were collected with a Bomem MB-100 FTIR spectrometer. ^{13}C CP MAS NMR spectra were recorded on a Varian VXR S-400WB instrument. The $^1H-^{13}C$ contact time was 4 ms and the recycle delay was 3 s. Cyclic voltammetric and differential pulse voltammetric experiments were performed on either a BAS CV-27 potentiostat or a BAS CV-50W potentiostat. Electrochemical measurements were performed in acetonitrile freshly distilled from calcium hydride under nitrogen. The supporting electrolyte was in all cases tetra-*n*-butylammonium hexafluorophosphate (TBAH) (Aldrich), which was purified by recrystallization from ethanol and dried in a vacuum at 60 °C, and was used at a concentration of 0.1 M in all voltammetry experiments. A conventional sample cell operating under an atmosphere of prepurified nitrogen was used. All voltammetric experiments were performed using a platinum-disk working electrode (A = 0.020 cm^2), which was polished prior to use with 1-μm diamond paste (Buehler) and rinsed thoroughly with purified water. For the modification of platinum-disk electrodes with films of dendrimer-containing MCM-41, a suspension containing 0.013 g of the composite mesoporous material, 0.013 g of graphite powder, and 0.006 g of polystyrene in 0.5 mL of dichloromethane was prepared. Two drops of this suspension were placed on a freshly polished platinum-disk electrode and allowed to evaporate to dryness. The same procedure has been

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used to prepare electrodes modified with aerosil or silica gel derivatized with the ferrocenyl dendrimers. All potentials are referenced to the saturated calomel electrode (SCE). A coiled platinum wire was used as a counter electrode. DPV was done with a scan rate of 20 mV s^{-1}, a pulse height of 50 mV, duration of 50 ms, and pulse intervals of 2 s.

Results and Discussion

The pore size of the MCM-41 material that we have prepared[10] is close to 3 nm and makes this material a potential candidate for the encapsulation of dendrimers. Poly(propyleneimine) dendritic macromolecules **1**, **2**, and **3**[11] with estimated diameters of 2.5, 2.8, and 5.1 nm (CAChe molecular mechanic calculations), containing 4, 8, and 64 terminal ferrocenyl moieties, respectively, have been tested for inclusion. The MCM-41 sample was previously treated with the appropriate amount of Me_2SiCl_2 to cap the silanol groups on the external surface. This treatment has been performed using a proven methodology,[12] assuming a faster rate of reaction for the Si−OH groups on the outside surfaces compared to those of the internal surface and with the aim of minimizing the amount of dendrimer to be bound later on to the surface hydroxyl groups. Incorporation of dendrimers **1**−**3** into the mesoporous material MCM-41 was achieved by refluxing a CH_2Cl_2 solution of the corresponding dendrimer in the presence of a pretreated sample of MCM-41. The initial white color of MCM-41 changed to orange, which can be taken as an initial indication for the incorporation of the organometallic dendrimer guests. The success of these reactions to yield the loaded products *dend*-**1**-MCM-41, *dend*-**2**-MCM-41, and *dend*-**3**-MCM-41 was confirmed by different techniques. For example, elemental analyses indicated in all cases the retention of the dendrimer stoichiometry after inclusion in the mesoporous material and showed a content of organometallic dendrimer guests into the silicate of 34 wt % (51 mg of **1** (0.044 mmol) per 100 mg of host) for *dend*-**1**-MCM-41, of 15 wt % (18 mg of **2** (0.007 mmol) per 100 mg of host) for *dend*-**2**-MCM-41, and of 8 wt % (9 mg of **3** (4×10^{-4} mmol) per 100 mg of host) for *dend*-**3**-MCM-41. In the IR spectra of the mesoporous material derivatized with the amidoferrocenyl dendrimers **1** and **2**, the amide C=O stretching bands, which appear near 1615 cm^{-1}, were shifted approximately 10−15 cm^{-1} to lower energy in comparison with those of *dend*-**3**-MCM-41 and the free dendrimers (at ca. 1630 cm^{-1}), which possibly indicates a hydrogen bond type interaction C=O···H−O−Si. The solid-state ^{13}C cross-polarization magic-angle spinning (CP MAS) NMR spectra further supported the presence of the organometallic dendrimers. The resonances observed at about 70 ppm (see for example Figure 1a) are assigned to the cyclopentadienyl rings by comparison with the chemical shift observed for the free dendrimers (Figure 1b). In addition, a resonance is observed near 173 ppm, which is attributable to the carbon atom of the amide group. The spectra showed also resonances at approximately 53, 38, and 24 ppm, which are consistent with the presence of the propyleneimine dendritic framework. All these spectroscopic features suggest that the organometallic dendrimer guest has remained intact after the reaction with MCM-41.

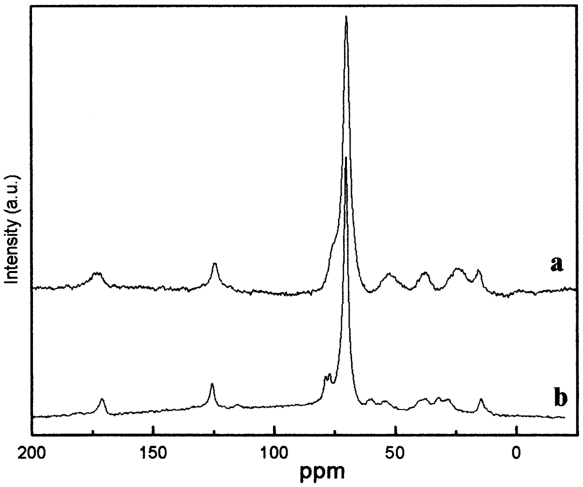

Figure 1. Room-temperature 100.6-MHz solid-state ^{13}C CP MAS NMR spectra of (a) *dend*-**1**-MCM-41 and (b) free dendrimer **1**.

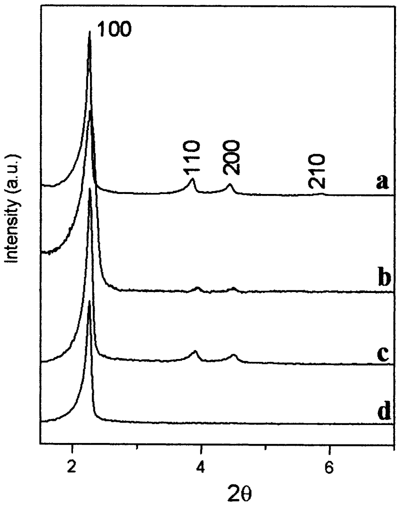

Figure 2. XRD of (a) calcined MCM-41, (b) *dend*-**3**-MCM-41, (c) *dend*-**2**-MCM-41, and (d) *dend*-**1**-MCM-41.

X-ray diffraction of the calcined MCM-41 sample shows the characteristic well-resolved pattern with an intense 100 reflection at low angle and three more weak intensities corresponding to 110, 200, and 210 reflections of the hexagonal *p*6*mm* plane group (Figure 2). From the d_{100} reflection it is possible to obtain the cell parameter $a_0 = 4.5$ nm. After the calcined sample was loaded with the dendrimers, the intensity of the reflections decreases, in such a way that the 110, 200, and 210 reflections are hardly observed in the sample containing the smallest dendrimer (Figure 2d). This behavior is consistent with the filling of the channels by the dendrimers and suggests a more effective inclusion of the smallest one. This result agrees with the chemical analyses, which show that the carbon content of the *dend*-**1**-MCM-41 sample is nearly 2 times that of the *dend*-**2**-MCM-41 and 3 times that of *dend*-**3**-MCM-41.

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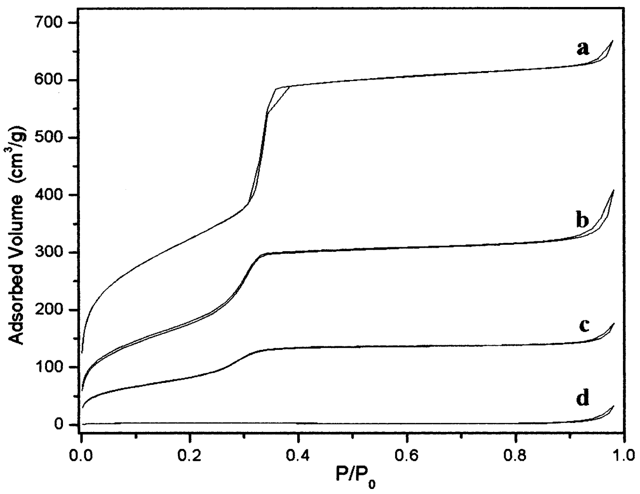


Figure 3. Nitrogen adsorption isotherms of (a) calcined MCM-41: $S_{BET} = 1154$ m^2 g^{-1}, Vp = 1.04 cm^3 g^{-1}; (b) *dend*-**3**-MCM-41: $S_{BET} = 691$ m^2 g^{-1}, Vp = 0.63 cm^3 g^{-1}; (c) *dend*-**2**-MCM-41: $S_{BET} = 325$ m^2 g^{-1}, Vp = 0.23 cm^3 g^{-1}; (d) *dend*-**1**-MCM-41: $S_{BET} = 10$ m^2 g^{-1}, Vp = 0.05 cm^3 g^{-1}.

The nitrogen adsorption isotherms shown in Figure 3 reflect the molecular size discrimination effect that operates upon contacting the MCM-41 host with the dendrimers. Nearly full occupancy of the channels by dendrimer **1** containing 4 ferrocenyl units is obtained, evidenced by the dramatic decrease of the surface area and pore volume of the loaded material (Figure 3d) as compared with the pristine MCM-41. Less effective inclusion is obtained upon increasing the number of ferrocene units in the dendrimers up to 8 (Figure 3c) and 64 (Figure 3b), owing to the steric restrictions to incorporate these bulkier molecules inside the MCM-41 channels. The effective pore diameter slightly decreases from 2.7 nm in calcined MCM-41 to 2.5 nm for materials *dend*-**2**-MCM-41 and *dend*-**3**-MCM-41.

Dendrimers-containing and also calcined MCM-41 were studied by transmission electron microscopy (TEM). Micrographs, selected area electron diffraction patterns (SAED), and X-ray energy-dispersed spectroscopy (XEDS) of the loaded *dend*-**1**-MCM-41 material are shown in Figure 4. The images and SAED patterns show the highly ordered hexagonal arrangement of the channels along two directions, perpendicular (Figure 4a) and parallel (Figure 4b) to the *c* axis. The cell parameter ($a_0 \cong 4.1$ nm) measured from SAED is comparable to the value observed by XRD ($a_0 = 4.5$ nm). The MCM-41 type structure is maintained after dendrimer loading and the inclusion of the macromolecules in the material is evidenced by XEDS (Figure 4c) where the iron peak is easily observed. Exhaustive XEDS analysis of different particles confirms the presence of Fe spread out homogeneously all over the materials. By comparing carefully the TEM results for sample MCM-41 calcined, where the channels are organic-free, with those of *dend*-**1**-MCM-41, fully occupied by the smallest dendrimer, and the intermediate samples *dend*-**2**-MCM-41 and *dend*-**3**-MCM-41, it can be concluded that no strong differences are observed in the images. The density filling the pores (mainly carbon) is not strongly scattered enough to inverse the contrast. However, when all the characterization results discussed in this work are combined, the incorporation of the ferrocenyl dendrimer **1** and at least a significant number of branches of dendrimers **2** and **3** inside the channels can be firmly established (Scheme 1).

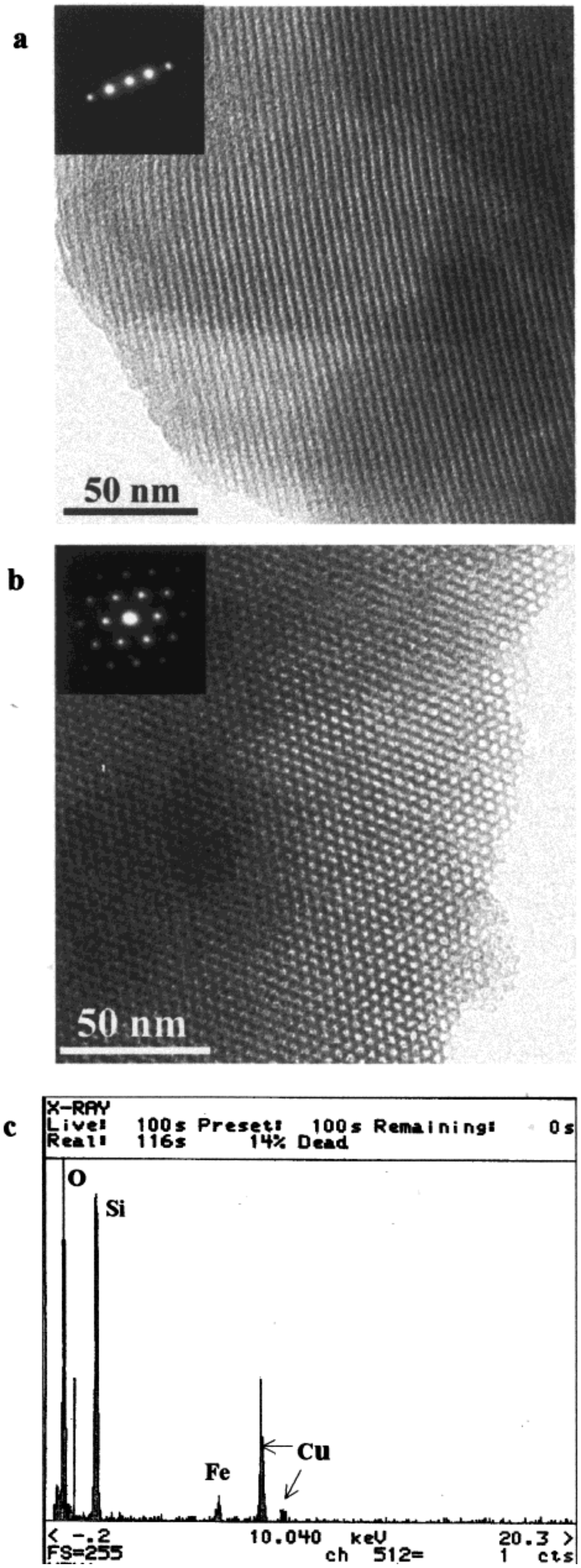
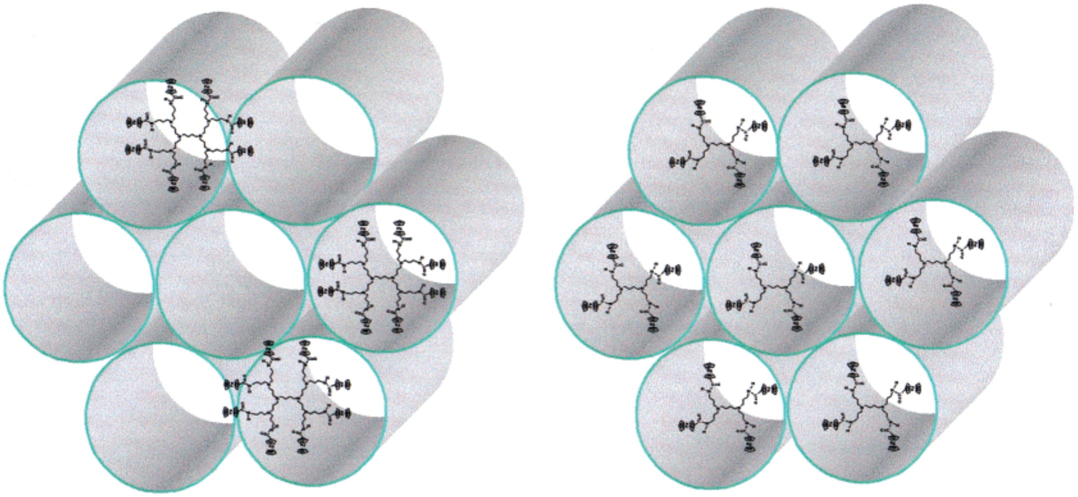


Figure 4. Images and selected area electron diffraction patterns of *dend*-**1**-MCM-41 along the direction (a) perpendicular and (b) parallel to the *c* axis. (c) Example of a representative XEDS pattern obtained for sample *dend*-**1**-MCM-41.

Scheme 1. Schematic Representation of the Encapsulation of Ferrocenyl Dendrimers 1 (Right) and 2 (Left) within MCM-41



We have also investigated the electrochemical behavior of the novel dendrimer-modified mesoporous silicate materials. For this purpose, platinum electrodes derivatized with films of *dend*-**1**-MCM-41 (ME-**1**-MCM-41), *dend*-**2**-MCM-41 (ME-**2**-MCM-41), and *dend*-**3**-MCM-41 (ME-**3**-MCM-41) were prepared and studied by cyclic voltammetry and differential pulse voltammetry in acetonitrile solution. In the cyclic voltammograms of ME-**1**-MCM-41 and ME-**3**-MCM-41 a well-defined reversible redox process is observed at $E_{1/2} = +0.65$ and $+0.61$ V vs SCE, respectively ($E_{1/2} = (E_{pa} + E_{pc})/2$) (see Figure 5 as an example).[13] The peak current ratio i_{pc}/i_{pa} is ca. 1, and the peak currents scale linearly with the square root of the scan rate, showing a diffusion control of the charge transfer. In addition, the potential separation ΔE_p is ca. 120 mV at 100 mV s^{-1}. These values are significantly larger than those found for the dendrimers in CH_2Cl_2/CH_3CN solution and can be attributed to kinetic limitations in charge transport through this type of films. For ME-**2**-MCM-41 a broader redox wave is observed, which could suggest two overlapped processes. These modified electrodes are very stable. Multiple successive cyclic voltammetric scans can be carried out with no loss of electroactivity. Likewise, after standing in air for several days, the redox response was practically unchanged.

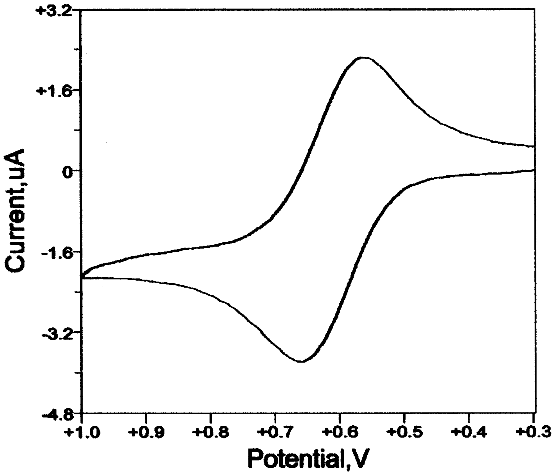


Figure 5. Cyclic voltammogram of a platinum disk electrode coated with layers of *dend*-**3**-MCM-41/graphite powder/polystyrene composite, measured in CH_3CN solution at 100 mV s^{-1}.

Differential pulse voltammograms (DPVs) provide further information about the electrochemical behavior. DPVs of ME-**1**-MCM-41 (Figure 6a) and ME-**3**-MCM-41 (Figure 6c) show a single wave at +0.63 and +0.59 V vs SCE, respectively (Table 1). These peak potential values are in accordance with the $E_{1/2}$ values obtained from cyclic voltammetry, taking into account that $E_{pk} = E_{1/2} - E_{pulse}/2$, where E_{pulse} is the pulse height. In contrast, the DPV of ME-**2**-MCM-41 (Figure 6b) shows two peaks of different heights at 0.60 and 0.64 V, which suggest the existence of two different ferrocene environments in this material.

It is interesting to note that the potential value of ME-**3**-MCM-41 is virtually the same as that obtained when a Pt electrode is modified with an admixture of dendrimer **3**, MCM-41, polystyrene, and powder graphite (ME-admixture-**3**-MCM-41). This fact reflects that in ME-**3**-MCM-41 most amidoferrocenyl units are not directly chemically bounded to the mesoporous material, and therefore their behavior is analogous to the ferrocenyl groups in ME-admixture-**3**-MCM-41. That is not surprising, taking into account that due to its size, dendrimer **3** cannot fit inside the MCM-41 pore system, and only a small number of ferrocenyl branches must be linked within the channels of MCM-41 and therefore their electrochemical response is masked by that of external ferrocenes.

For ME-**1**-MCM-41, containing the smallest dendrimer that can fit inside the MCM-41 channels, a more positive potential value is obtained. This behavior is in accordance with the decrease of the effective electron density on the redox centers, as a result of the binding of the amidoferrocenyl moieties to the silanol groups inside the channels of MCM-41, which makes the oxidation more difficult. In agreement with IR data this binding must be a hydrogen bond type interaction, C=O···H−O−Si.

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(13) $E_{1/2}$ values for dendrimers **1**−**3** from cyclic voltammetry (vs SCE), in 2:1 CH_2Cl_2/CH_3CN solution with 0.1 M TBAH, are +0.61 V in the three cases.

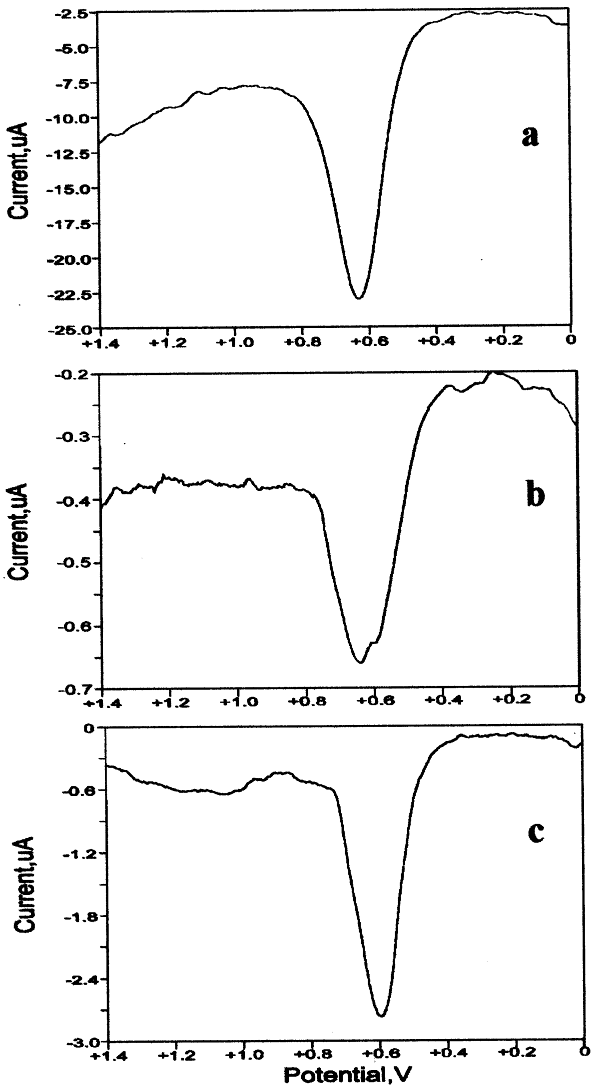

Figure 6. Differential pulse voltammograms of a platinum disk electrode coated with layers of *dend*-***n***-MCM-41/graphite powder/polystyrene composite, measured in CH_3CN solution: (a) $\boldsymbol{n} = \mathbf{1}$; (b) $\boldsymbol{n} = \mathbf{2}$; (c) $\boldsymbol{n} = \mathbf{3}$.

Table 1. Peak Potential Values (V, vs SCE) Obtained from DPV

	ferrocenyl dendrimer (***n***)		
material	**1**	**2**	**3**
solution[a]	0.58	0.58	0.58
ME-***n***-MCM-41[b]	0.63	0.60 and 0.64	0.59
ME-admixture-***n***-MCM-41			0.59
ME-***n***-aerosil[b]	0.58	0.58	0.59

[a] Measured in 0.1 M TBAH, CH_2Cl_2/CH_3CN 2:1 solution, 1.0 mM ferrocene centers, at a Pt disk electrode. [b] Measured in CH_3CN/0.1 M TBAH.

On the other hand, the potential values of the waves displayed in the DPV of ME-**2**-MCM-41 are very close to those exhibited by ME-**1**-MCM-41 and ME-**3**-MCM-41, respectively, which suggests the presence of both kinds of ferrocenes in *dend*-**2**-MCM-41. That is, in this material there must be ferrocenyl dendritic branches inside the MCM-41 channels as well as out of the mesoporous material, near the aperture of the cavities.

It should be noted that as a consequence of the linkage with the MCM-41, dendrimers cannot diffuse freely within the mesoporous channel system and therefore the electrochemical responses must be only due to the electron transfer by electron hopping between ferrocenyl moieties in sufficient proximity.[14]

Remarkably, a gradual decrease in the peak current upon continuous scanning is observed in the cyclic voltammograms of ME-admixture-**3**-MCM-41, which indicates that the solubility of the oxidized form is inevitably a source of instability, due to loss of oxidized dendrimers that can diffuse away from the layer on the electrode to the acetonitrile solution. In contrast, no loss of electroactivity is observed in ME-***n***-MCM-41, $\boldsymbol{n} = \mathbf{1}-\mathbf{3}$, after repeated scanning, demonstrating that these modified electrodes are stable to electrochemical cycling. This stability clearly supports the existence of effective bindings in ME-***n***-MCM-41, $\boldsymbol{n} = \mathbf{1}-\mathbf{3}$, between at least some of the amidoferrocenyl units in the dendrimers and the silanol groups in the mesoporous material. Therefore, the ferrocenyl dendrimers are persistently attached to the mesoporous material.

With the aim of investigating if the redox properties of dendrimers are affected by the porosity of the silica material, we have also examined the electrochemical behavior of a Pt electrode modified with hybrid materials obtained from dendrimers **1**−**3** and a nonporous silica such as aerosil. In contrast with that observed when MCM-41 is used as a silicate support, DPVs of ME-**1**-aerosil, ME-**2**-aerosil, and ME-**3**-aerosil show in all cases a single wave at approximately +0.58 V vs SCE (see Table 1). These results indicate that when the ferrocenyl dendrimers are attached to the nonporous material, the electrochemical behavior of the three ferrocenyl dendrimers is essentially the same regardless of the dendrimer size. This result is not unexpected as the intrapore confinement effect proposed with the MCM-41 is discarded when aerosil is used.

Finally, it has been observed that the electrochemical behavior of electrodes modified with silica materials derivatized with the ferrocenyl dendrimers depends on the structure of the silica support. DPVs of ME-**3**-silica gel and ME-admixture-**3**-silica gel show a single wave at +0.60 and +0.64 V vs SCE, respectively. In contrast with that observed when MCM-41 is used as a silicate support, the potential of the modified silica is cathodically shifted by 40 mV with respect to that of the admixture. That is, upon incorporation of ferrocenyl dendrimer into silica gel, the oxidation of the ferrocenyl units in the dendrimer is easier, which could be attributable to a hydrogen bond type interaction, CONH···OH−Si, in ME-**3**-silica gel, which increases the electron density at the iron center. Therefore, the type of interaction between the dendrimer and the silicate materials, and hence the potential values for both kinds of hybrid materials (with MCM-41 and silica gel), seems to be related to the silicate structure. Thus, the amorphous silica determines a different kind of interaction between the dendrimer and the support that is not observed with the highly regular structured MCM-41, which clearly affects its electrochemical behavior.

Variations in the behavior of the guests related to the different natures or structures of the silicate hosts have been previously observed. For instance, structural differences between MCM-41 and silica gel have been

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(14) Bedioui, F.; Roué, L.; Briot, E.; Devynck, J.; Bell, S. L.; Balkus, K. J., Jr. *J. Electroanal. Chem.* **1994**, *373*, 19.

reported as a determining factor in the coordination mode and reactivity of some cobalt complexes.[15]

Preliminary data show that electrodes modified with dendrimer-containing MCM-41 appear to be sensitive to the presence of dihydrogenphosphate anion since a shift of the anodic peak to less positive potentials is observed (ca. 60 mV in the presence of 5×10^{-3} M [n-Bu_4N][$H_2PO_4^-$]), which suggests that these mixed materials could potentially be used as redox-responsive receptor systems for anion recognition.[16]

In summary, MCM-41 has been demonstrated to be an effective solid support for redox-active organometallic dendrimer guests. These novel materials promise to be valuable candidates for applications that require facile handling and stable and durable systems capable of simultaneously transferring several electrons at the same potential, such as redox catalysis, sensing, and other electrochemical applications. Work is now focused on exploiting the structural possibilities of both the mesoporous materials and dendritic structures, in the design of novel hybrid materials that can act as selective redox-responsive receptor system for molecular recognition.

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