






# Redox-Active Metallacarborane-Decorated Octasilsesquioxanes. Electrochemical and Thermal Properties

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**ABSTRACT:** Polyanionic and electroactive hybrids based on octasilsesquioxanes bearing metallacarborane units are developed. They show remarkable solubility in organic solvents and outstanding thermal stability. The metallacarboranes act as independent units simultaneously undergoing the reversible redox process.

Metallodendrimers are metal-containing macromolecules that have attracted an increased interest in the development of nanometer-scale materials.<sup>1</sup> The incorporation of redox-active units into dendritic structures leads to a wide range of applications such as sensors, catalysts, biomedical materials, and multielectron storage devices,<sup>2,3</sup> among others. Dendrimer-type molecules are ideal platforms to construct these devices, which must be designed to satisfy some conditions such as possessing robust and reversible redox moieties.<sup>4</sup> Polyhedral octasilsesquioxanes (POSSs) are 3D scaffolds that, unlike most dendrimers, are easy to synthesize and exhibit robustness, versatility in functionality, and high solubility.<sup>5,6</sup> The inorganic core of POSS cages provides mechanical stiffness and thermal stability, whereas the organic pendant groups provide oxidative stability, as well as mechanical, optical, electrical, or electronic properties.<sup>7,8</sup> These characteristics make POSSs promising building blocks for hybrid nanomaterials toward technological applications.<sup>9–13</sup> As a particular case, silsesquioxane-cored dendrimers bearing ferrocenyl units were reported to confer electroactive properties.<sup>14–16</sup> However, an important drawback of some ferrocene (Fc)-functionalized silsesquioxane dendrimers is their lack of solubility in common solvents.<sup>17</sup>

Metallacarboranes  $[M(C_2B_9H_{11})_2]^-$  are unique redox-active molecules, in which a central metal ion, commonly Co (cobaltabisdicarbollide or COSAN) or Fe (ferrabisdicarbollide or FESAN), is  $\eta^2$ -bonded to two dicarbollide anions  $[C_2B_9H_{11}]^{2-}$ .<sup>18</sup> In addition to their high thermal and chemical stability,<sup>19</sup> metallacarboranes show unusual supramolecular interactions and self-assembling properties.<sup>20–22</sup> Because of the presence of Co or Fe, these complexes display one well-studied reversible wave under cyclic voltammetry (CV) conditions, at  $-1.74$  V for  $Co^{3+/2+}$  in COSAN and at  $-0.78$  V for  $Fe^{3+/2+}$  in FESAN versus Fc.<sup>23,24</sup> Another remarkable property is the stepwise tuning of the redox potential upon dehydrohalogenation of the metallacarboranes.<sup>25–27</sup> Moreover, the ionic character of COSAN and FESAN provide them a high versatility to be

soluble in a broad scope of organic and inorganic media by modification of the cation nature.

Our laboratory and others have contributed to the advancement of metallacarborane-containing dendrimers;<sup>28–31</sup> however, a few studies have been carried out from an electrochemical viewpoint.<sup>31</sup> This paper does not specifically deal with electroactive metallodendrimers, but we will focus on conceptually similar large molecules but small enough to learn about their electron-transfer (ET) capacity with the electrode. Contrary to Fc,<sup>15,16</sup> the investigation of silsesquioxanes functionalized with metallacarboranes has not yet been explored. Regarding the special electronic, physicochemical, anionic nature but lower charge densities of metallacarboranes on the one hand<sup>32,33</sup> and architecture properties of silsesquioxanes on the other,<sup>5–8</sup> the target here is to produce new multifunctional molecular materials to combine the unique properties of metallacarboranes with the robustness and stability of POSS. To this end, we report the synthesis and complete characterization of COSAN- and FESAN-terminated octasilsesquioxanes, combined with diffusion studies performed by CV and NMR spectroscopy in solution to determine their overall sizes; we also study the electrochemical behavior of the new materials to learn about their ET properties, and finally we analyze how the presence of metallacarboranes produces enhancement of the thermal stability.

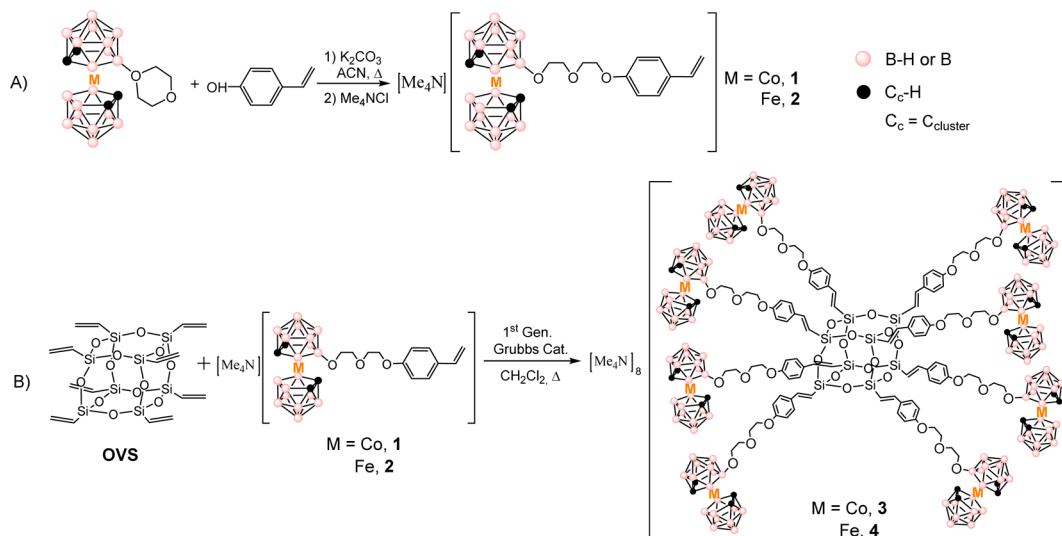
The decoration of octavinylsilsesquioxane (OVS) was performed via a cross-metathesis reaction.<sup>34,35</sup> Starting from  $[3,3'-Co(8-C_4H_8O_2-1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})]$  and  $[3,3'-Fe(8-C_4H_8O_2-1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})]$ , two new anionic precursors bearing a terminal styrene group (**1** and **2**) were synthesized by a nucleophilic oxonium ring-opening reaction using the deprotonated 4-vinylphenol as the nucleophile (Scheme 1A). The reaction was monitored by <sup>11</sup>B NMR spectroscopy by comparison with their parent species,<sup>36,37</sup> and compounds **1** and **2** were isolated as  $[NMe_4]^+$  salts in 98.5% and 32% yield, respectively.

Cross-metathesis reactions of **1** and **2** with OVS were performed using the first-generation Grubbs's catalyst. Regio- and stereoselective *E* isomers of metallacarborane-containing POSSs **3** and **4** were obtained, isolating both compounds in 83% and 45% yield, respectively (Scheme 1B). The cross-metathesis

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Scheme 1. (A) Synthesis of Metallocarborane Derivatives 1 and 2 and (B) Cross-Metathesis Reactions To Obtain 3 and 4



reactions were monitored by  $^1\text{H}$  NMR upon the total disappearance of the vinyl proton resonances from  $\text{SiCH}=\text{CH}_2$  (Figure S2 in the Supporting Information, SI). Compounds 1–4 were characterized by attenuated total reflectance IR, NMR ( $^1\text{H}$ ,  $^1\text{H}\{^{11}\text{B}\}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{11}\text{B}\{^1\text{H}\}$ , and  $^{11}\text{B}$ ), and elemental analysis, whereas matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) was possible only for 1 and 2 (see the SI).

To confirm the total functionalization of OVS, we used the method developed by Kim and Jung,<sup>38</sup> as for previous COSAN-containing dendrimers,<sup>28–30,39</sup> based on the estimation of the metallocarborane units by the Lambert–Beer law. Figure 1 shows the UV–vis spectra for 1–4 in acetonitrile and their line-fitting analysis with Gaussians, for an adequate discernment of the spectral bands.<sup>40,41</sup>

The maximum at 260 nm for 1 and 2, which is 15 nm red-shifted in POSS cages 3 and 4 (275 nm), is mainly endorsed to the styrene group; the maxima, near 310 and 370 nm, are attributed to metallocarboranes.<sup>30,40</sup> Therefore, the number of metallocarboranes for 3 and 4 was estimated by comparing their molar extinction coefficients ( $\epsilon$ ) for deconvoluted curves at

304–314 nm (pink curves in Figure 1) with those from the respective monomers 1 and 2 ( $\epsilon_0$ ). The number of COSAN and FESAN units fits very well with the theoretical ones, corroborating the complete functionalization of OVS (Table S1). These results, along with the NMR spectra, establish the presence of eight metallocarboranes in the final POSS materials 3 and 4.

Improvement in the thermal, mechanical, and oxidative resistance of polymers and composites after the incorporation of silsesquioxanes is known.<sup>7</sup> Furthermore, materials incorporating boron clusters have a high thermal stability.<sup>35,42,43</sup> In this line, thermogravimetric analysis (TGA) of 3 and 4 under argon shows a thermal behavior very different from that of nonfunctionalized OVS (Figure S3). The pristine OVS shows an 82% weight loss near 290 °C,<sup>44</sup> whereas both 3 and 4 undergo a very low weight loss between 350 and 600 °C, and after heating to 900 °C, around 88% of the initial weight was recovered. Compounds 3 and 4 contain 43% of the organic part, while the percentage of hydrogen would correspond to 7.6%; therefore, we could interpret that after thermal treatment only  $\text{H}_2$  and a small percentage of the organic part was lost. The former thermal studies confirm the relevance in terms of the thermal stability of incorporating anionic metallocarboranes in the POSS cage.

Considering the reversible redox electroactivity of metallocarboranes, similar to Fc, we aimed to investigate the electroactivity of these materials and their performance in the ET process by CV (Figure 2). Contrary to the poor solubility of the Fc-containing POSS,<sup>17</sup> 3 and 4 show very good solubility in organic solvents, so that the CVs were carried out in dry  $\text{CH}_3\text{CN}$  at  $10^{-3}$  M for 1 and 2 and  $1.25 \times 10^{-4}$  M for 3 and 4, using a three-electrode setup and tetrabutylammonium hexafluorophosphate (0.1 M) as an inert electrolyte. Compounds 1 and 3 show a redox potential near  $-1.74$  V vs Fc ( $\text{Co}^{3+/2+}$  in COSAN),<sup>23</sup> whereas for 2 and 4, the pair appears around  $-0.74$  V ( $\text{Fe}^{3+/2+}$  from FESAN).<sup>27</sup>

Despite 3 and 4 bearing eight metallocarboranes each, they exhibit only one redox process in the CV. Besides, no shift in  $E^0$  is observed between the monomer and the POSS derivative,<sup>45</sup> which indicates that all units act independently and that there is no electronic communication between the electroactive parts. A similar behavior was observed for octasilsesquioxanes functionalized with eight ferrocenes<sup>17</sup> and other dendrimers containing

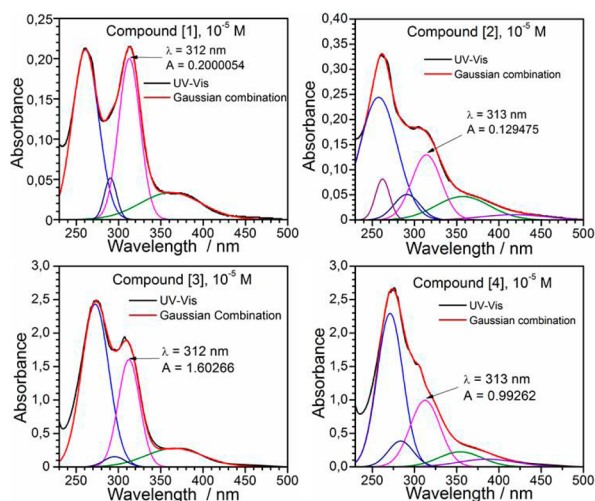
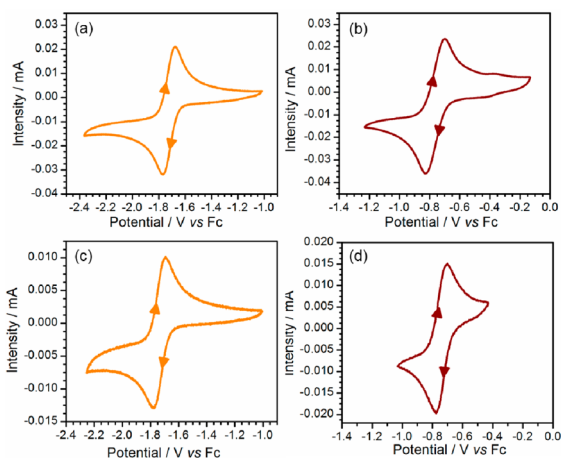


Figure 1. UV–vis spectra of compounds 1–4 at  $10^{-5}$  M in  $\text{CH}_3\text{CN}$  and the results of the line fitting with Gaussians.



**Figure 2.** CVs of (a) **1**, (b) **2**, (c) **3**, and (d) **4** in  $\text{CH}_3\text{CN}$  at 300 mV/s and Fc as the internal reference.

ferrocenes or cobaltocinium.<sup>4</sup> However, for larger globular molecules, all redox-active moieties could not simultaneously be in contact with or in proximity to the electrode. The fact that all eight electroactive members can interact with the electrode implies that the whole molecule has a dimension that permits ET to all of them simultaneously, either by the tunnel effect or due to the rapid rolling of molecules on the electrode surface.<sup>46</sup> Apparently, the size, shape, and charge of metallacarboranes do not exert any influence on this feature. To learn about the dimensions of compounds **3** and **4**, we first determined diffusion coefficients ( $D$ ) and later hydrodynamic radii ( $R_H$ ). The  $D$  values were obtained by the Randles–Sevcik equation ( $D_{CV}$ ) and pulsed-field-gradient spin–echo NMR techniques ( $D_{NMR}$ ). The Randles–Sevcik method requires us to carry out CVs, under the same conditions as previously pointed out, at different scan rates (see the SI).<sup>47</sup>  $D_{NMR}$  was performed in  $\text{CD}_3\text{CN}$  solutions (concentrations of ca.  $10^{-2}$ – $10^{-3}$  M) at 298 K; as a reference, we also measured  $D_{NMR}$  for the starting OVS and pristine COSAN. Unfortunately, the large broad signals observed in the  $^1\text{H}$  NMR spectrum of the pristine FESAN prevent the measurement of  $D_{NMR}$ . The results (Table S2) indicate that the  $D_{CV}$  values for **1** and **2** are 2.5 and 3 times smaller with regard to  $D_{NMR}$  values, whereas the difference is between 37 and 39 times smaller for **3** and **4**.

Kaifer et al. described a methodology to relate the  $D_{NMR}$  and  $D_{CV}$  values in noncharged Fc-containing dendrimers ( $D_{CV} = 1.04D_{NMR}$ ).<sup>48</sup> However, this method does not fit our results probably because of the stronger interaction of the anionic metallacarboranes with the electrolyte,<sup>20,21</sup> which prevents good diffusion of our molecules. Regarding the discrepancies between  $D_{CV}$  and  $D_{NMR}$  values and the fact that the  $R_H$  value for OVS calculated from  $D_{NMR}$  (5.49 Å) is in good agreement with that reported for the crystal structure (5.66 Å),<sup>49</sup> the  $R_H$  values for **1**–**4** were calculated by the Stokes–Einstein equation using  $D_{NMR}$  values and assuming spherical shapes (Table 1). Compounds **1** and **2** show sizes of around 5–5.5 Å, whereas POSSs **3** and **4** have  $R_H$  values of 16.2 and 17.0 Å, respectively. These results indicate that the sizes of **3** and **4** are adequate to simultaneously perform the redox process of the eight peripheral metallacarboranes.<sup>50</sup>

To confirm the simultaneous reduction of the eight metallacarboranes, 8 equiv of sodium naphthalenide as the reducer was added to a 3 mg solution of **4** in dry tetrahydrofuran, obtaining a pinky solid (inset in Figure S5).  $^{11}\text{B}$  NMR after reduction of **4** confirms that all of the FESANE units have been reduced, from

**Table 1.** Experimental  $D_{NMR}$  and Estimated Hydrodynamic Radius of **1**–**4** in  $\text{CD}_3\text{CN}$  and 298 K

compound	molecular weight, g/mol	$D_{NMR}$ , $\text{m}^2/\text{s}$	$R_H$ , Å
OVS	632.8	$1.148 \times 10^{-9}$	5.49
cosane	456.67	$1.549 \times 10^{-9}$	4.07
fesane	453.58		
<b>1</b>	604.13	$1.175 \times 10^{-9}$	5.37
<b>2</b>	601	$1.259 \times 10^{-9}$	5.01
<b>3</b>	5241.7	$3.89 \times 10^{-10}$	16.2
<b>4</b>	5217	$3.72 \times 10^{-10}$	17.0

the paramagnetic  $\text{Fe}^{3+}$  to the diamagnetic  $\text{Fe}^{2+}$  (Figure S5),<sup>36</sup> showing new resonances from 19 to –38 ppm, including the signal at 18.30 ppm typical for B–O in diamagnetic metallacarboranes.<sup>51</sup> This result corroborates the simultaneous reduction of all of the metallacarboranes.

In conclusion, two new polyanionic and electroactive hybrids based on octasilsesquioxanes bearing eight COSAN or FESAN units are developed and fully characterized. The grafting of metallacarboranes to OVS produces an outstanding thermal stability on the final hybrids. Remarkably, these materials exhibit high solubility in organic solvents that could be modified by changing the cation nature. Electrochemical studies show that the peripheral metallacarboranes act as independent redox units and simultaneously undergo the redox process, providing insight into ET in dendrimers. This feature also brings an additional advantage in the preparation of materials for catalyst, additives, or sensor applications.

## ■ ASSOCIATED CONTENT

### § Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02394.

Experimental details, the Randles–Sevcik equation, NMR spectra, TGA data, CV, UV–vis data, diffusion coefficients, and  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{11}\text{B}$  NMR, IR, and MALDI DOSY experiments (PDF)

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### Notes

The authors declare no competing financial interest.

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