

Preparation and Application of a Novel Hybrid Nanomaterial Based on Silsesquioxane Cubic

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Abstract – Here we start from a silsesquioxane functionalized with eight chloropropyl chains $T_8\text{-PrCl}$ (**1**) and report two new derivatives, one functionalized with a pendant linear chain (dipyridilamine – DPA) $T_8\text{-Pr-DPA}$ (**2**) and the other with a Mo(II) complex $T_8\text{-Pr-DPA-Mo}$ (**3**). To the best of our knowledge only a few works in the literature have reported this type of substitution. The new organometallic nanomaterial $T_8\text{-Pr-DPA-Mo}$ (**3**) and the precursors $T_8\text{-PrCl}$ (**1**) and $T_8\text{-Pr-DPA}$ (**2**) were characterized by ^1H , ^{13}C NMR, FTIR, XRD and elemental analysis.

Polyhedral oligomeric silsesquioxanes (POSS) have emerged as a new class of organic-inorganic hybrid porous materials that offer novel and attractive properties and applications. The cubic structures of POSS macromonomers have inorganic cores that are basically the smallest particle of rigid silica. These cubic silica cores possess 0.53 nm diameter and a spherical radius of 1-3 nm including peripheral organic units. These nanocage cores are surrounded by eight organic groups with the general formula $(\text{RSiO}_{1.5})_n$, where n is an even number and R can be any of a large number of groups [1].

The objective of this research was the preparation and characterization of nanocage silsesquioxane cores functionalized with eight chloropropyl chains (**1**, $T_8\text{-PrCl}$) and of two new derivatives, one functionalized with a pendant linear chain (2,2'-dipyridilamine – DPA; **2**, $T_8\text{-Pr-DPA}$) and the other with a Mo(II) organometallic complex ($[\text{Mo}(\text{allyl})\text{Br}(\text{CO})_2(\text{NCMe})_2]$; **3**, $T_8\text{-Pr-DPA-Mo}$) (**3**) (Figure 1).

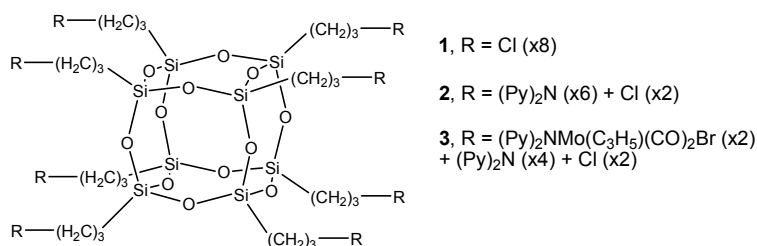


Figure 1 – Silsesquioxane cores functionalized.

Only a few works in the literature have reported this type of substitution, and none dealt with DPA or Mo(II) complexes.

The three materials were characterized by ^1H , ^{13}C NMR, FTIR, XRD and elemental analysis. Although the parent material $T_8\text{-PrCl}$ (**1**) has eight Cl groups, elemental analysis indicated that in material $T_8\text{-Pr-DPA}$ (**2**) all Cl atoms have been substituted by the deprotonated DPA group, but for $T_8\text{-Pr-DPA-Mo}$ (**3**) a distribution of two or three coordinated $[\text{Mo}(\text{allyl})\text{Br}(\text{CO})_2(\text{DPA})]$ units was obtained. The new Mo-silsesquioxane organometallic nanomaterial $T_8\text{-Pr-DPA-Mo}$ (**3**) has been tested as precursor in the epoxidation of olefins – cyclooctene and styrene and compared with $[\text{Mo}(\text{allyl})\text{Br}(\text{CO})_2(\text{DPA})]$. Both species are highly selective toward epoxide formation, but the activity (conversion and turnover frequency) are not improved when the complex is immobilized in the POSS cage.

[1] R. H. Baney, M. Itoh, A. Sakakibara, and T. Suzuki, Chem. Rev. **95** (1995) 1409.