Synthesis, Characterization, and Thermal Behavior of Carboranyl-Styrene Decorated Octasilsesquioxanes: Influence of the Carborane Clusters on Photoluminescence

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Abstract: Novel polyhedral oligomeric silsesquioxanes (POSS) or octasilsesquioxanes with carboranyl–styrene fragments attached to each corner are described. These compounds have been synthesized by olefin-metathesis reactions between octavinylsilsesquioxane and carboranyl–styrene compounds that possess different substituents (Ph, Me, or H). In all cases, these reactions, which were catalyzed by the Grubbs catalyst, are highly regioselective and yield exclusively the E isomers. The existence of the carborane cage in the POSS structure induces a remarkable thermal stability in these compounds. After combustion at 1000 8C, these carboranyl–POSS compounds exhibit a mass loss lower than 10 %. The UV/ Vis absorption data of these carboranyl–POSS compounds shows a slight bathochromic shift with respect to the carboranyl–styrene monomers, with an absorption maximum around 262 nm. Nevertheless, important differences in the emission spectra of the carboranyl– POSS compounds with regard to their carboranyl–styrene precursors are observed; the phenyl-o-carborane-containing POSS compound exhibits the highest fluorescence intensity (FF = 44 %), whereas for the POSS compound bearing the methyl substituent, and for the unsubstituted o-carborane clusters, the fluorescence intensity is much lower (FF = 9 and 2 %, respectively). This is precisely the reverse of what occurs with the monomers, in which the unsubstituted o-carboranyl– styrene compound exhibits the highest FF, and a quenching of the fluorescence is observed in the phenyl-o-carboranyl–styrene compound. In addition, a large red shift of around 100 nm is observed for the POSS compounds with respect to their precursors. These experimental results can only be accounted for by the spatial ordering induced by the POSS core that eases interactions, which otherwise would not occur. These results have been confirmed by time-dependent density functional theory (TDDFT) calculations that exclude a photoinduced electron transfer (PET) process in the POSS compounds.

Keywords: boron cluster · carboranes · cluster compounds. · octasilsesquioxanes · photoluminescence · styrene