Unexplored features of cage silsesquioxane chemistry: synthesis of large T_{18} POSS and fluxional Si...F interactions in T_8-F cages

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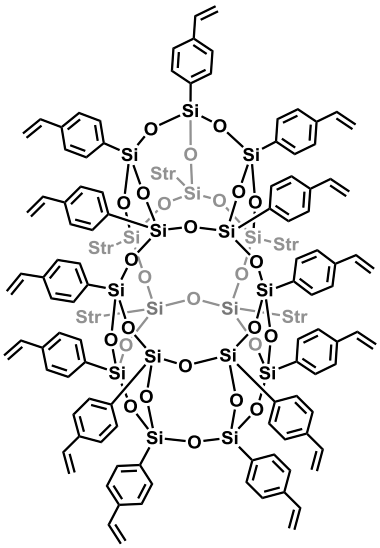
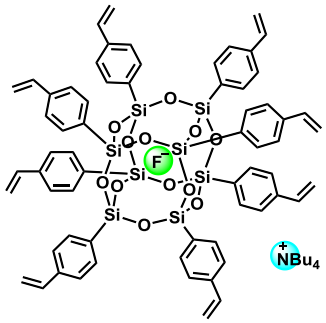
The T_n cage silsesquioxanes (also referred to as polyhedral oligomeric silsesquioxanes, POSS) are a class of hybrid molecules with the formula $(RSiO_{3/2})_n$, with R being an organic group (e.g. chloropropyl, vinyl, phenyl, etc.).[1] Different cages have been reported, with the largest POSS previously isolated and fully characterized being a T_{14} cage.[2] A variety of T_8 cages with fluoride encapsulated within the silsesquioxane core (T_8-F) have also been described.[3] Despite the variety of T_n cages known to date (particularly with n=6, 8, 10, and 12), most interest has been focused on T_8 cages[1] for a wide range of applications including polymer hybrids, catalysis, photoluminescence, sensing, etc.



Unprecedented T_{18} cage

Here, we explore the properties of less common cage silsesquioxanes. Firstly, we report the isolation and characterization of an unprecedented T_{18} cage silsesquioxane as a pure product.[4] The structure of the T_{18} cage is identified unambiguously among the nine possible isomers previously proposed for the T_{18} system.[2] The structure and properties of the compound are established by multinuclear NMR, mass spectrometry, etc. Secondly, we report the synthesis of a new styryl-functionalized T_8-F cage.[5] The interaction between the Si atoms and the F^- ion is investigated through multinuclear and variable temperature NMR experiments. The latter evidenced the presence of fluxional covalent interactions between the encapsulated fluoride and the eight surrounding Si atoms. We also report the first successful functionalization of T_8-F cages, involving the grafting of hydrolysable alkoxysilane groups onto each of the eight styryl arms. The subsequent incorporation of the precursors into materials via sol-gel processing will be discussed.



Styryl T_8-F cage

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