

Unconventional conjugation via vinylMeSi(O-)₂ siloxane bridges may imbue semiconducting properties in double-decker and ladder silsesquioxane copolymers

Jun Guan¹ and Richard Laine¹

1. University of Michigan, Ann Arbor, Michigan, United States

Silsesquioxane (SQ) based polymers are of increasing interest due to their enhanced thermal stability, high compatibility with organic materials as well as high processability. However, to our knowledge, no one has sought to explore through-chain conjugation between double-decker (DD) and ladder (LL) SQs and organic linkers. We recently demonstrated that stilbene derivatives of simple DD SQs exhibit photophysical properties commensurate with formation of cage-centered LUMOs, supporting the existence of 3-D excited-state conjugation. We describe here Heck catalyzed co-polymerization of vinyl(Me)Si(O_{0.5})₂[PhSiO_{1.5}]₈(O_{0.5})₂Si(Me)vinyl (vinylDDvinyl) with Br-Ar-Br where Br-Ar-Br = multiple aromatic and heteraromatic moieties.

Apparent excited state conjugation via vinyl(Me)Si(O-)₂ siloxane bridges is observed in the DD copolymers, as evidenced by 50-120 nm red-shifts in emission from corresponding model compounds. To identify minimum SQ structures that may offer such extended conjugation vinyl(Me)Si(O_{0.5})₂[PhSiO_{1.5}]₄(O_{0.5})₂Si(Me)vinyl [vinyl-ladder(LL)-vinyl] derived copolymers were also synthesized. Surprisingly, most of the resulting oligomers show 30-60 nm emission red-shifts *beyond* those seen with the vinylDDvinyl analogs despite lacking a true cage.

We also find that brominating DD/LL copolymer vinyl groups eliminates emission red-shifts. Zn debromination thereafter restores vinyl groups and emission red-shifts but brominated phenyls remain providing potential access to families of “hairy” conjugated SQ polymers. Further proof of semiconducting properties led to studies wherein DD/LL-co-thiophene, bithiophene and thienothiophene were doped with 10 mol% F₄TCNQ resulting in integer charge transfer (ICT) behavior.

