

**Synthesis and Characterization of conjugated Silsesquioxanes (SQs)
and their Beads on a chain (BoC) polymers**

by

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Abstract

Organic/inorganic hybrid materials play a major role in developing high performance and high functional materials. Octameric polyhedral silsesquioxanes (SQs), $(\text{RSiO}_{1.5})_8$, are unique hybrid materials which indicate that the silsesquioxane cage appears to be involved in electron delocalization with conjugated organic tethers in the excited state. This dissertation describes the synthesis and characterization of organic/inorganic hybrid beads on a chain (BoC) type polymers with SQ cages in the polymer backbones and functionalization of silsesquioxanes to offer semiconducting properties for optoelectronic devices and microporous materials.

This dissertation first discusses the synthetic routes to BoC epoxy resins which were synthesized by the reaction of di- and tri-aminophenyl, phenyl $\text{T}_{10/12}$ SQ mixtures. The di- and trifunctional SQs were prepared by the F^- catalyzed rearrangement reaction of octaaminophenylSQs (OAPS) and octaphenylSQs (OPS). Moreover, we present the synthesis and characterization of sets of BoC polymers derived from octaiodophenylSQs (I_8OPS) via Heck or Sonogashira cross coupling with divinylbenzene (DVB) or 1,4-diethynylbenzene (DEB). The DEB polymers reveal unique photophysical properties suggesting electronic communication along the polymer chains and through the cages via the conjugated linkers.

The metathesis and Heck cross coupling reactions of vinyl $\text{T}_{10/12}$ and octa(2,5-dibromophenyl) SQs (Br_{16}OPS) provides a convenient synthetic route to various conjugated SQs. The photophysical studies indicate that $\text{T}_{10/12}$ systems also show 3-D conjugation in the excited state similar to T_8 analogs. Furthermore, cyclic voltammetry studies reveal that the LUMO of functionalized Br_{16}OPS offer optimal values to apply as an electron acceptor with P3HT in organic photovoltaic (OPV) cells. Nevertheless, a BHJ device of $5\text{FSty}_{16}\text{OPS}$ and P3HT showed poor power conversion efficiency, partial substitution of PCBM by $5\text{FSty}_{16}\text{OPS}$ retained OPV performance of reference cell which was fabricated with mixture of P3HT and PCBM (4.1 %) if the content of $5\text{FSty}_{16}\text{OPS}$ was less than 15 %.

Lastly, we demonstrated the synthesis of a variety of *p*-hydroxySQs based on T_8 and $\text{T}_{10/12}$ vinylSQs and explored the application of these SQs as precursors to nanoporous polymeric

materials. The cross-linked polyester prepared from GEN1 T₈ SQ exhibited up to 25 m²/g of BET surface area in spite of the flexible C₆ linker.