

# Finding LUMOs in Unusual Places. Silsesquioxane cages and their polymers appear to offer semiconducting properties

J. Guan, J. R. Arias, K. Tomobe, S. Jungstittiwong, N. Yodsin, Richard M. Laine

Dept. of Materials Science and Engineering,<sup>1</sup> Chemistry<sup>2</sup> and Macromolecular<sup>3</sup> Science and Engineering, University of Michigan, Ann Arbor, Michigan, U.S.A., Dept of Chemistry,<sup>4</sup> Ubon Ratchathani University, Thailand

talsdad@umich.edu

We report here the functionalization of a series of phenyl silsesquioxanes including  $[\text{PhSiO}_{1.5}]_8$ ,  $[\text{PhSiO}_{1.5}]_7[\text{RSiO}_{1.5}]$  where R = Me, propyl or  $[\text{PhSiO}_{1.5}]_7[\text{OSiMe}_3]_3$  or the double decker compound  $[\text{PhSiO}_{1.5}]_8[\text{OSiMe}_3]_4$ . Each of these cages was functionalized by bromination followed by Heck catalytic cross coupling. Sets of polymers were also prepared from derivatives of  $[\text{PhSiO}_{1.5}]_8[\text{OSiMe}_3]_4$ .

Photophysical characterization of these series of compounds allow one to establish the existence of a LUMO that interacts with the conjugated moieties linked to the cage presenting red emission shifts indicating 3-D conjugation in the excited state. This behavior has been reported before as indicative of semiconducting like behavior.<sup>1,2</sup> However, only for  $[\text{PhSiO}_{1.5}]_8$  and  $[\text{vinylSiO}_{1.5}]_8$  cages and their derivatives. Here we demonstrate similar behavior where only partial cages are used and the first examples of conjugation in the ground state pointing the potential of these materials as new types of semiconducting polymers

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