Do silsesquioxane cages and polymers offer semiconducting properties

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We report here the functionalization of a series of phenyl silsesquioxanes including $[PhSiO_{1.5}]_8$, $[PhSiO_{1.5}]_7[RSiO_{1.5}]$ where R = Me, propyl or $[PhSiO_{1.5}]_7[OSiMe_3]_3$ or the double decker compound $[PhSiO_{1.5}]_8[OSiMe_3]_4$. Each of these cages was functionalized by bromination followed by Heck catalytic cross coupling. Sets of polymers were also prepared from derivatives of $[PhSiO_{1.5}]_8[OSiMe_3]_4$.

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.[1,2] However, only for $[PhSiO_{1.5}]_8$ and $[vinylSiO_{1.5}]_8$ 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

[1] S. Sulaiman, A. Bhaskar, J. Zhang, R. Guda, T. Goodson III, R.M. Laine, "Molecules with perfect cubic symmetry as nanobuilding blocks for 3-D assemblies. Elaboration of octavinylsilsesquioxane. Unusual luminescence shifts may indicate extended conjugation involving the silsesquioxane core." Chem Mater. **2008**, *20* 5563 – 5573.

[2] R. M. Laine, S. Sulaiman, C. Brick, M. Roll, R. Tamaki, M. Z. Asuncion, M. Neurock, J-S. Filhol, C-Y. Lee, J. Zhang, T. Goodson III, M. Ronchi and M. Pizzotti, S. C. Rand, Y. Li, "Synthesis and photophysical properties of stilbeneoctasilsesquioxanes. Emission behavior coupled with theoretical modeling studies suggest a 3-D excited state involving the silica core," J. Am. Chem. Soc. **2010**, *132* 3708–3722.