

Supplementary Information

**Thiol Functionalized Polyhedral Oligomeric Silsesquioxanes as Building Blocks for LB
Films in Sensing and Nanoparticle Patterning**

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MP₈ POSS can easily be analyzed using ¹H- and ²⁹Si ²⁹Si-NMR. As shown in Figure S1, a clean, isolated and well-defined product is obtained.

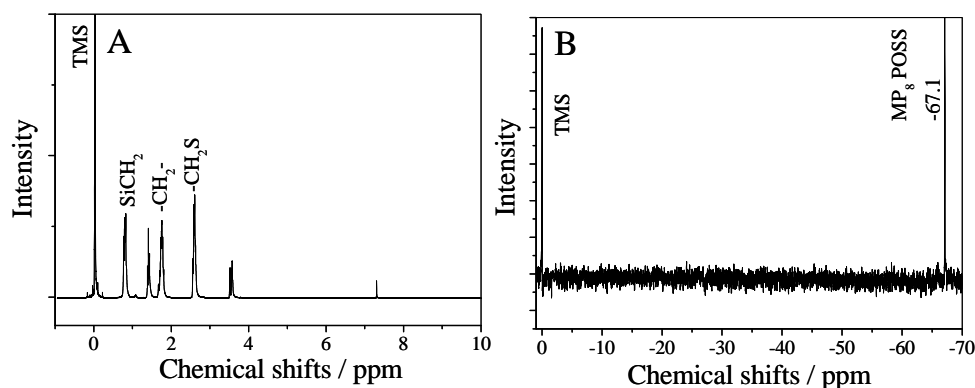


Figure S1: ¹H NMR (A) and ²⁹Si NMR spectra (B) of MP₈.

However, synthesis of multifunctional POSS from different triethoxysilanes ends with different structure isomers. This has been already noted in the case of mono-substituted heptapropylmercapto-T₈POSS by Marsmann¹. Hence, the synthesis of dimercaptohexapropyl-T₈POSS could lead to a wider spectrum of products. The co-hydrolysis of isooctyltrimethoxysilane (IOTMS) and 3-aminopropyltriethoxysilane (APMTS), which was applied in our previous studies,² could lead³ to even less well-defined products composed of aminopropyl and isooctyl functionalized T₆, T₈, T₉(OH)₃ and other products. We demonstrate here, for the first time, that the co-hydrolysis of IOTMS and 3-mercapto-propyltrimethoxysilane (MPTMS) (not yet tested as a precursor) under basic conditions and by using hydrothermal synthesis led to T₈POSS compounds that could be well separated.

The identification of isomers can be readily analyzed by ²⁹Si NMR spectroscopy. Namely, in contrast to a broad signal(s) ²⁹Si NMR spectra,⁴ observed in T³ region, rather sharp and well separated signals characteristic for each of the isomers are expected.

The product MP₂IO₆ of the co-hydrolysis of MPTMS and IOTMS performed under basic conditions using hydrothermal synthesis route was analyzed. Preparative medium pressure

liquid chromatography (MPLC) was employed and four fractions were separated. The detection (UV 254 nm) was satisfactory and total amount of ~250 mg of a mixture of compounds were collected for each run. Each of the separated components was analyzed by measuring the corresponding ^{29}Si NMR spectra (Figure S2). ^{29}Si NMR spectra revealed unified structure of isomers. A marked difference between the fractions is apparent in the NMR spectra. Expectedly, the ^{29}Si NMR spectra of the single fraction revealed the various T^3 signals between -66.16 and -68.25 ppm, corroborating the presence of different isomer species, in contrast to only one sharp T^3 signal (-66.16 or -68.25 ppm) (not shown) observed in the liquid ^{29}Si NMR spectra of MP_8 - or IO_8 -POSS. The observation of two or more signals in our ^{29}Si NMR confirms the formation of octameric disubstituted POSS due to different silicon environments as has been reported¹. ^{29}Si NMR spectra of MP_2IO_6 persuasively confirms the presence of ortho, meta and para substituents in the reaction product and the absence of uncondensed products like $\text{T}_7(\text{OH})_3$, and ladder like polymers.

In conclusion, the mixture of products could be separated by chromatography and a singly well-defined product, i.e., the ortho substituted product, was used.

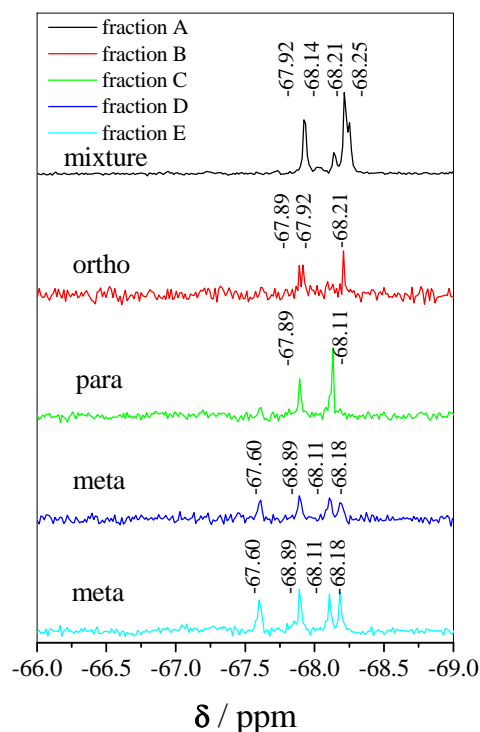


Figure S2: ^{29}Si NMR spectra of MP_2IO_6 T8 POSS prepared via the hydrothermal synthesis and separated by NPLC (fraction A - mixture of ortho and para substituents with small amount of IO_8 T8 POSS, fraction B - ortho product, fraction C – para substituted product, fraction D and E – meta substituted MP_2IO_6 T8 POSS product).

- ¹ Hendan, B. J.; Marsmann, H. C. *Journal of Organometallic Chemistry* 1994, **483**, 33.
- ² Jerman, I.; Vuk, A. U.; Kozelj, M.; Orel, B.; Kovac, J. *Langmuir* 2008, **24**, 5029.
- ³ Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chemical Reviews* 2010, **110**, 2081.
- ⁴ Anderson, S. E.; Bodzin, D. J.; Haddad, T. S.; Boatz, J. A.; Mabry, J. M.; Mitchell, C.; Bowers, M. T. *Chemistry of Materials* 2008, **20**, 4299.