FUNCTIONAL SILOXANES AS SCAFFOLDS FOR GOLD NANOPARTICLES AND THEIR APPLICATIONS

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ABSTRACT

In recent years, considerable attention has been focused on the development of catalytic routes for molecularly precise siloxanes bearing a variety of functional groups on silicon atom(s). Siloxane-based amphiphiles constitute an important family and exhibit surface-active properties in both water and non-aqueous systems. The study presented in the thesis relates to the synthesis, self-assembly behaviour and application of functional siloxanes, **1-5** (Figure 1) as scaffolds for the stabilization of gold nanoparticles in aqueous or organic medium.

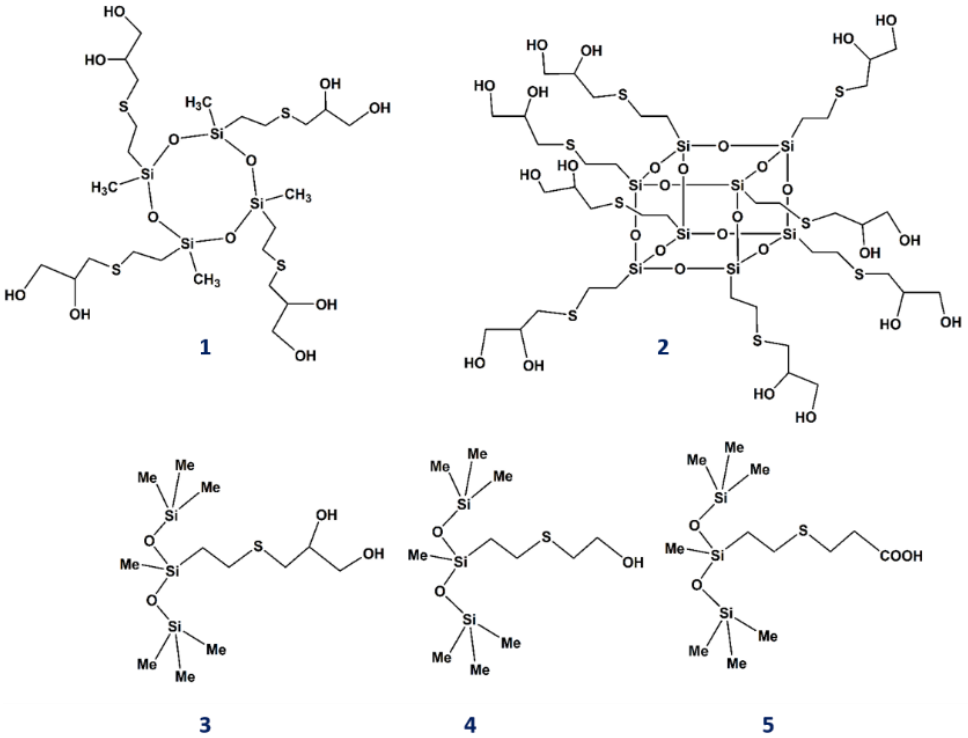

Figure 1. Functionally modified siloxanes **1-5**.

Surface activity of the AuNPs in aqueous medium results in *en route* formation of Pickering emulsions during hydrolytic oxidation of organosilanes, RR^1SiH_2 (R = Me; R^1 = *cyclo*-Hex, Ph). A major advantage of this protocol is to overcome the diffusion limitations, bringing

together immiscible organosilane-water system due to an enhanced contact area during the catalytic process. The method offers a useful alternative for the synthesis of disiloxane-1,3-diols, $[RR^1Si(OH)]_2O$ (R, R^1 = Me, *cyclo*-Hex or Ph). The Si-OH groups are involved in hydrogen-bonding interactions with Cl^- ions suggesting 2:1 host guest complexation with binding constants K_{11} = 85.11 ± 14, K_{21} = 150.62 ± 11 for $(MePhSiOH)_2O$ and K_{11} = 9.80 ± 3, K_{21} = 103.79 ± 2 M^{-1} for $[Me(cyclo\text{-}Hex)Si(OH)]_2O$.

The trisiloxanes, $(Me_3SiO)_2(Me)Si\{(CH_2)_3OC(O)(C)Me_2Br\}$ (**I**) and $SiMe_2(OSiMe_2)_2\{(CH_2)_3OC(O)(C)Me_2Br\}$ (**II**) have been used as initiators for atom transfer radical polymerization (ATRP) of methylmethacrylate (MMA). Following nanoprecipitation approach, polymers of varying molar mass are transformed to spherical particles and subsequently used to organize polymer-AuNP hybrids at water-chloroform interface. The self-assembly of AuNPs finds application as surface enhanced Raman scattering (SERS) substrate for the detection of methylene blue dye.