FUNCTIONAL SILOXANES AS SCAFFOLDS FOR GOLD NANOPARTICLES AND THEIR APPLICATIONS

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by

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In fulfilment of the requirements of the degree of Doctor of Philosophy

to the

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Dedicated to My Family

CERTIFICATE

This is to certify that the thesis entitled "***FUNCTIONAL SILOXANES AS SCAFFOLDS FOR GOLD NANOPARTICLES AND THEIR APPLICATIONS***" being submitted by **Ms. Nidhi Mahavar** to the Department of Chemistry, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her.

She has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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NIDHI MAHAVAR

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.

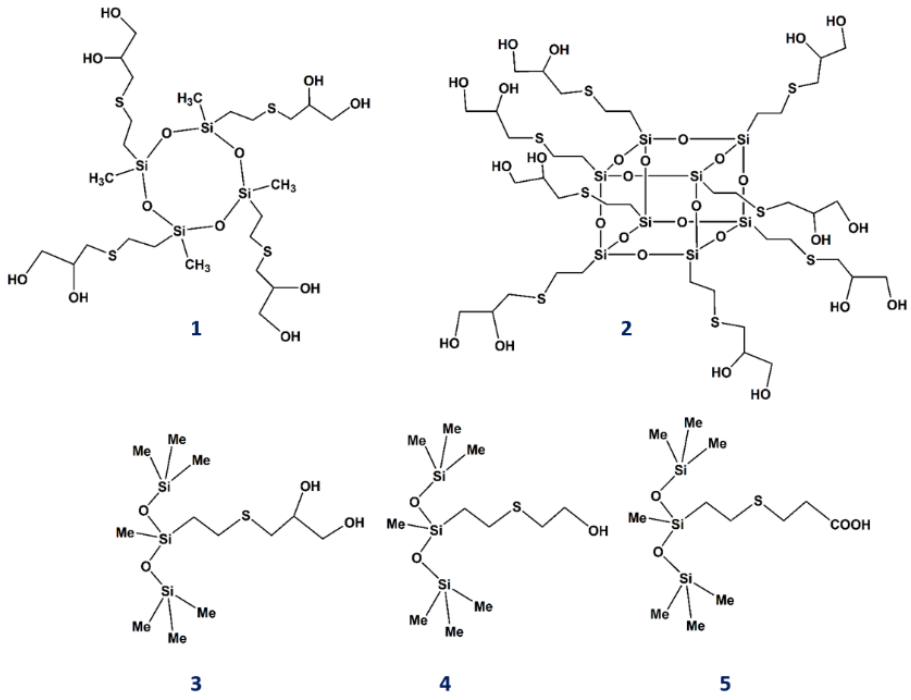


Figure 1. Functionally modified siloxanes **1-5**.

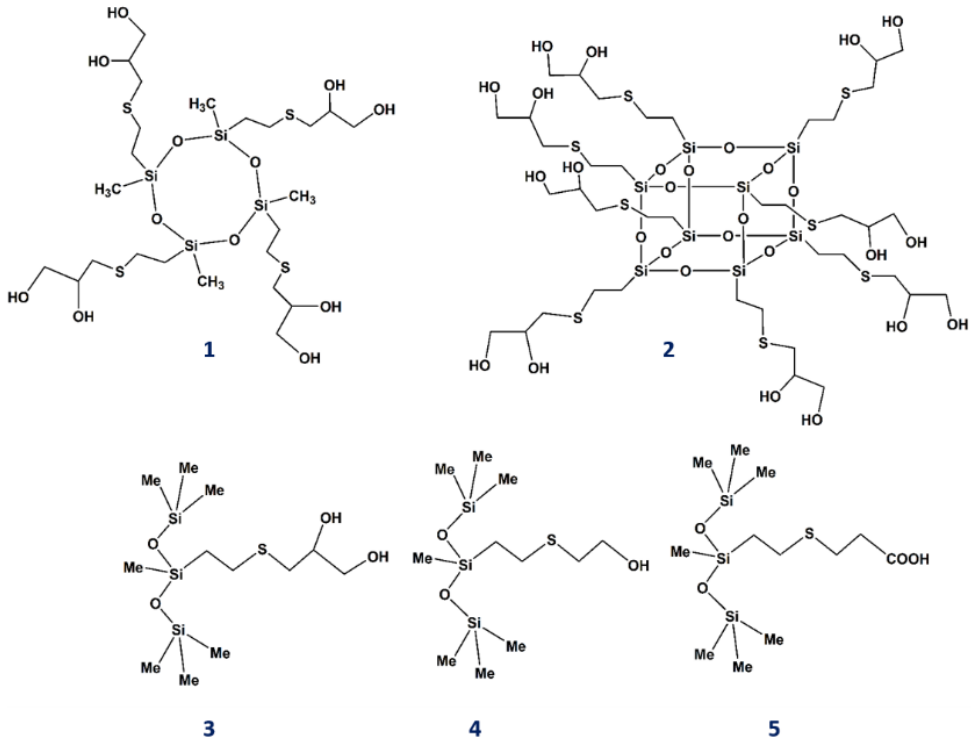
Surface activity of the AuNPs in aqueous medium results in *en route* formation of Pickering emulsions during hydrolytic oxidation of organosilanes, RR^1SiH_2 (R = Me; R^1 = *cyclo*-Hex, Ph). A major advantage of this protocol is to overcome the diffusion limitations, bringing together immiscible organosilane-water 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 $K_{11} = 85.11 \pm 14$, $K_{21} = 150.62 \pm 11$ for $(MePhSiOH)_2O$ and $K_{11} = 9.80 \pm 3$, $K_{21} = 103.79 \pm 2\ M^{-1}$ 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.

विषय-सार

हाल के वर्षों में, सिलिकॉन परमाणुओं पर विभिन्न प्रकार के कार्यात्मक समूहों को प्रभावित करने वाले आणविक रूप से सटीक सिलोक्सेन के लिए उत्प्रेरक मार्गों के विकास पर काफी ध्यान केंद्रित किया गया है। सिलोक्सेन-आधारित एम्फीफाइल्स एक महत्वपूर्ण परिवार का गठन करते हैं और पानी और गैर-जलीय दोनों प्रणालियों में सतह-सक्रिय गुणों का प्रदर्शन करते हैं। थीसिस में प्रस्तुत अध्ययन जलीय या कार्बनिक माध्यम में सोने के नैनोकणों के स्थिरीकरण के लिए मचान के रूप में संश्लेषण, स्व-संयोजन व्यवहार और कार्यात्मक सिलोक्सेन के अनुप्रयोग, 1-5 (चित्र 1) से संबंधित है।



चित्र 1. कार्यात्मक रूप से संशोधित सिलोक्सेन 1-5.

जलीय माध्यम में AuNPs की सतह गतिविधि के परिणामस्वरूप ऑर्गोसिलेन्स, RR^1SiH_2 (R = Me; R^1 = *cyclo*-Hex, Ph) के हाइड्रोलाइटिक ऑक्सीकरण के दौरान पिकरिंग इमल्शन का निर्माण होता है। इस प्रोटोकॉल का एक प्रमुख लाभ उत्प्रेरक प्रक्रिया के दौरान प्रसार सीमाओं को दूर करने के लिए, बढ़े हुए

संपर्क क्षेत्र के कारण अमिश्रणीय ऑर्गेनोसिलेन-जल प्रणाली को एक साथ लाने के लिए है। विधि डिसिलोक्सेन-1,3-डायोल, $[RR^1Si(OH)]_2O$ (R, R^1 = Me, *cyclo*-Hex या Ph) के संश्लेषण के लिए एक उपयोगी विकल्प प्रदान करती है। Si-OH समूह Cl^- आयनों के साथ हाइड्रोजन-बॉन्डिंग इंटरैक्शन में शामिल हैं, जो बाध्यकारी स्थिरांक $K_{11} = 85.11 \pm 14$, $K_{21} = 150.62 \pm 11$ $(MePhSiOH)_2O$ और $K_{11} = 9.80 \pm 3$, $K_{21} = 103.79 \pm 2$ एम$^{-1}$ [Me(*cyclo*-Hex)$Si(OH)_2O$] के साथ 2:1 मेजबान अतिथि जटिलता का सुझाव देते हैं।

ट्राइसिलोक्सेन, $(Me_3SiO)_2(Me)Si\{(CH_2)_3OC(O)(C)Me_2Br\}$ (I) और $SiMe_2(OSiMe_2)_2\{(CH_2)_3OC(O)(C)Me_2Br\}$ (II) को मिथाइलमेथैक्रिलेट (एमएमए) के परमाणु हस्तांतरण कट्टरपंथी पोलीमराइजेशन (एटीआरपी) के लिए सर्जक के रूप में इस्तेमाल किया गया है। नैनो-अवक्षेपण दृष्टिकोण के बाद, अलग-अलग दाढ़ द्रव्यमान के बहुलक गोलाकार कणों में बदल जाते हैं और बाद में पानी-क्लोरोफॉर्म इंटरफेस में बहुलक-AuNP संकर को व्यवस्थित करने के लिए उपयोग किए जाते हैं। AuNPs की सेल्फ-असेंबली मेथिलीन ब्लू डाई का पता लगाने के लिए सतह वर्धित रमन स्कैटरिंग (एसईआरएस) सब्सट्रेट के रूप में आवेदन पाती है।

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
δ	chemical shift
ν	frequency
˚C	degree centigrade
AuNPs	gold nanoparticles
ATRP	atom transfer radical polymerization
b. p.	boiling point
m. p.	melting point
b	block
Bu^t	*tert*-butyl
cyclo-Hex	*cyclo*-hexyl
cm	centimeter
$CDCl_3$	deuterated chloroform
DLS	dynamic light scattering
DEPT	distortionless enhancement by polarization transfer
DSC	differential scanning calorimetry
e.g.,	for example
ESI	electrospray ionization
FESEM	field emission scanning electron microscopy
ATR	attenuated total reflectance
FT	fourier transform
GPC	gel permeation chromatography

H	hour
min	minutes
i.e.	that is
IR	infrared
m	multiplet
br	broad
s	singlet
t	triplet
m/z	mass/charge
M^+	molecular ion
Me	methyl
mL	millilitre
mol	mole
M_n	number average molecular weight
nm	nanometer
NMR	nuclear magnetic resonance
PDI	polydispersity index
Ph	phenyl
PMMA	polymethylmethacrylate
PMDETA	N, N, N', N'', N''-pentamethyldiethylenetriamine
Pd	palladium
Ag	silver
MHz	mega hertz

Hz	hertz
RT	room temperature
TEM	transmission electron microscopy
SEM	scanning electron microscopy
T_g	glass transition temperature
TGA	thermogravimetric analysis
THF	tetrahydrofuran
wt	weight
UV	ultraviolet
BFTEM	bright field transmission electron microscopy
µm	micrometer
SERS	surface enhanced Raman scattering
Å	armstrong
dm	decimeter
POSS	polyhedral octavinyl silsesquioxane