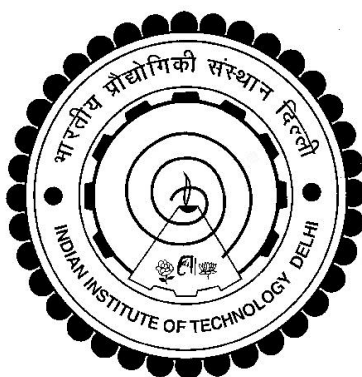


**FUNCTIONAL CYCLOTETRASILOXANES AS
SCAFFOLDS FOR GOLD NANOPARTICLES AND
THEIR APPLICATION IN CATALYSIS**

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**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
AUGUST 2015**

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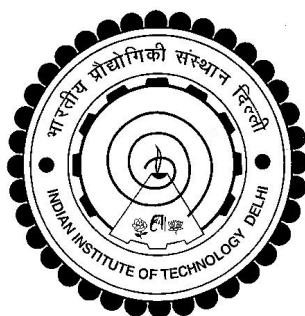
Department of Chemistry

Submitted

In fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

AUGUST 2015

Dedicated to My Parents

CERTIFICATE

This is to certify that the thesis entitled “*Funtional cyclotetrasiloxanes as scaffolds for gold nanoparticles and their application in catalysis*” being submitted by **Ms. Manchal Chaudhary** 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.

Manchal Chaudhary has worked under my guidance and supervision and has fulfilled the requirements for the submission of this 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.

Prof. Ravi Shankar

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Manchal Chaudhary

ABSTRACT

A great deal of attention has been focused in recent years to develop catalytic methods for the synthesis of homo-/heteroatom, Si-E (E = Si, O, N, P) bonds. These studies have offered an attractive alternative to traditional routes for the synthesis of wide ranging molecular as well as oligomeric/polymeric structures with control over their molecular weight and dimensionality. The work embodied in the thesis is devoted to the synthesis and characterization of hitherto unknown cyclotetrasiloxanes, $[\text{RMe}_2\text{SiCH}_2\text{CH}_2(\text{Me})\text{SiO}]_4$ (R = Ph, 2-thienyl, 2-furyl) and $[\text{R}^1\text{SCH}_2\text{CH}_2(\text{Me})\text{SiO}]_4$ (R^1 = *n*-Bu, *n*-Hex, dodecyl, CH_2COOH , $\text{CH}_2\text{CH}_2\text{COOH}$, $\text{CH}_2\text{CH}_2\text{OH}$) and their application as scaffolds for the construction of stable gold nanoparticles (AuNPs) which are of relevance to catalysis.

The content of the thesis is divided into five chapters. The introductory chapter deals with a brief review on recent developments in the synthesis, structural aspects and applications of functional organosilicon compounds containing silicon-oxygen bond(s). In chapter II, synthetic methods and the analytical/instrumental techniques for the characterization of compounds/AuNP assemblies are included. Chapters III-V are devoted to the results and discussion of the present work.

Chapter III relates to synthesis, characterization and X-ray crystallographic studies of the cyclotetrasiloxanes, $[\text{RMe}_2\text{SiCH}_2\text{CH}_2(\text{Me})\text{SiO}]_4$ (R = Ph, 2-thienyl, 2-furyl) bearing appended sila-alkyl groups. X-ray crystallographic studies reveal that the structures represent a scarce family featuring an all-*trans* conformation of Si-Me groups with respect to the siloxane core. The formation of three-dimensional supramolecular self-assembly is effected by extensive C-H--- π interactions. The scope of these functional cyclotetrasiloxanes for the stabilization of gold nanoparticles has been examined in detail. The results reveal that these molecular cyclotetrasiloxanes are interesting scaffolds to afford the formation of AuNP assemblies featuring nanowire-like morphology. Chapter IV deals with the

synthesis of functional cyclosiloxanes bearing thioether groups of varying alkyl chain lengths as well as additional terminal carboxylic acid or hydroxyl group. Further studies have shown that these thioether-substituted cyclosiloxanes act as tetrapodal ligands to provide long term stability to gold nanoparticles (AuNPs) in solution. The role of varying alkyl chain lengths of thioether groups appear to be significant in modulating size and self-organization of AuNPs. The results obtained from transmission electron microscopy (TEM) reveal that long *n*-hexyl/dodecyl chains favor organization of mono-dispersed AuNPs of average size of 7-9 nm. On the other hand, stabilization of AuNP surface with the cyclosiloxane, $[R^1SCH_2CH_2(Me)SiO]_4$ ($R^1 = CH_2CH_2COOH$) allows the formation of super structures of nearly 100 nm size which are made up by stacking of discrete spherical shaped AuNPs of average size of ~ 10 nm. The application of these AuNPs as catalysts for oxidation of organosilanes, R_2SiH_2 ($R = \text{alkyl or aryl}$) as well as reduction of nitroarenes is discussed in chapter V. Since hydrolytic oxidation of organosilanes requires a biphasic water-chloroform medium, we carefully monitored physical changes that took place during the course of these reactions under AuNP-catalyzed conditions. A notable revelation during the course of these studies is the formation of gold-stabilized water in chloroform “Pickering emulsion” which acts a unique catalyst with excellent activity and selectivity to afford the transformation of secondary organosilanes to the corresponding 1,3-dihydrotetraorganodisiloxanes. Similar reactions with primary organosilanes, $RSiH_3$ ($R = \text{Ph, PhMe}_2\text{SiCH}_2\text{CH}_2$) reveal a facile formation of linear poly(hydrosiloxane)s with $M_w = 3000\text{-}5500$ and $PDI = 1.2$. In addition, the AuNPs are found to be active catalyst for the synthesis of aminoarenes *via* reduction of the nitroarenes using $NaBH_4$ as the reducing agent. A comparative assessment of the rate constants (k) with those reported earlier for similar transformation suggest high catalytic efficacy of the AuNPs under study.

CONTENTS

	Page No.
<i>Abstract</i>	<i>i</i>
<i>List of Figures</i>	<i>iii</i>
<i>List of Tables</i>	<i>vi</i>
<i>Glossary of Symbols and Abbreviations</i>	<i>vii</i>
CHAPTER I	
Introduction	1-16
Scope and aim	17-18
CHAPTER II	
Materials and Methods	19-34
CHAPTER III	
Functional cyclotetrasiloxanes with appended sila-alkyl groups as scaffolds for the synthesis of gold nanowires	35-57
CHAPTER IV	
Functional cyclotetrasiloxanes with appended thioether groups and their application as scaffolds for gold nanoparticle assemblies	58-81
CHAPTER V	
Gold nanoparticles as catalysts for the oxidation of organosilanes and reduction of nitroarenes	82-107
REFERENCES	108-120
APPENDIX	
Summary of crystallographic data and structure of 2	121-122
BIODATA OF THE AUTHOR	

LIST OF FIGURES

Figure No.	Description	Page No.
Chapter III		
3.1	Electron spray ionisation Mass (ESI-MS) (positive ion mode) spectrum of [2-Th(CH ₂) ₃ (Me)SiO] ₄ , 4 .	43
3.2	¹ H NMR spectrum of [2-ThMe ₂ SiCH ₂ CH ₂ (Me)SiO] ₄ , 2 .	43
3.3	¹³ C{ ¹ H} NMR spectrum (DEPT-135) of [2-Th(CH ₂) ₃ (Me)SiO] ₄ , 4 .	44
3.4	²⁹ Si{ ¹ H} NMR spectrum of [2-FuMe ₂ SiCH ₂ CH ₂ (Me)SiO] ₄ , 3 .	44
3.5	(a) X-ray crystal structure of [PhMe ₂ SiCH ₂ CH ₂ (Me)SiO] ₄ , (1) and (b) Three-dimensional view of the structure along <i>c</i> -axis.	47
3.6	(a) Perspective view of three-dimensional structure of 1 viewed along <i>b</i> -axis and (b) Scanning electron microscopic image of 1 , showing one dimensional nanowires.	48
3.7	TEM images of gold nanoparticle assemblies: (a) GNP-1 , (b) GNP-2 and (c) GNP-3 .	53
3.8	High resolution transmission electron microscopic (HRTEM) image of gold nanowires [GNP-2].	54
3.9	UV-Vis spectra (chloroform, RT) showing surface plasmon resonance of gold nanoparticle assemblies, GNP-1 to GNP-3 .	54
3.10	TEM image and UV-Vis spectrum of AuNP assembly [GNP-5].	56
Chapter IV		
4.1	¹ H NMR spectra of [RSCH ₂ CH ₂ (Me)SiO] ₄ {R = <i>n</i> -Bu (6), <i>n</i> -Hex (7), dodecyl (8)}.	63
4.2	(a) ¹³ C{ ¹ H} (DEPT-135) and (b) ²⁹ Si{ ¹ H} NMR spectra of 7 .	64
4.3	(a) ESI-MS and (b) ¹ H NMR spectra of [RSCH ₂ CH ₂ (Me)SiO] ₄ {R = CH ₂ CH ₂ OH} (11).	66
4.4	Attenuated total reflectance infrared (ATR-IR) spectrum of [RSCH ₂ CH ₂ (Me)SiO] ₄ {R = CH ₂ CH ₂ COOH} (10).	67
4.5	X-ray photo electron spectrum AuNP assembly [GNP-8].	70

Figure No.	Description	Page No.
4.6	TEM images of the AuNP assemblies (GNP-6 to GNP-8).	72
4.7	High resolution transmission electron microscopic (HRTEM) and Field emission scanning electron microscopic (FESEM) images of AuNP assembly [GNP-10].	73
4.8	ATR-IR spectra of cyclosiloxane 10 and AuNP assembly [GNP-10].	74
4.9	UV-Vis spectra (a) AuNP assemblies (GNP-6 to GNP-8) and (b) Time dependent UV-Vis spectra of GNP-10 .	76
4.10	HRTEM images of AuNP assembly [GNP-10] after treatment with iodine.	78
4.11	UV-Vis spectra of GNP-10 after incremental addition (10 μ L) of iodine solution (7.8×10^{-4} M in chloroform).	79
Chapter V		
5.1	Images of AuNP-stabilized “Pickering emulsion”.	85
5.2	Time dependent ^1H NMR spectra showing the oxidation of PhMeSiH_2 to $[\text{PhMeSiH}]_2\text{O}$.	88
5.3	GC-MS profile of the product from the oxidation of PhMeSiH_2 .	89
5.4	(a) Plot of $-\ln(C_t/C_0)$ vs. time (t) and (b) Plot of concentration of the reactant vs. time for the oxidation reaction of PhMeSiH_2 catalyzed by gold nanoparticles (GNP-10).	90
5.5	Optical microscopic image of AuNP-stabilized “Pickering emulsion” formed during the oxidation of PhMeSiH_2 .	93
5.6	HRTEM image of AuNPs after catalytic oxidation of PhMeSiH_2 .	93
5.7	GC-MS profiles of (a) $[\text{PhMe}_2\text{Si}]_2\text{O}$ and (b) $[\text{Ph}_2(\text{H})\text{Si}]_2\text{O}$.	95
5.8	IR spectrum of $[\text{Ph}(\text{H})\text{SiO}]_n$.	97
5.8	GPC profiles of poly(hydrosiloxane)s, $[\text{Ph}(\text{H})\text{SiO}]_n$ and $[\text{PhMe}_2\text{CH}_2\text{CH}_2(\text{H})\text{SiO}]_n$.	97
5.10	HRTEM image of AuNP assembly [GNP-10A].	100
5.11	ATR-IR spectra of AuNPs (a) GNP-10 and (b) GNP-10A .	100

Figure No.	Description	Page No.
5.12	Chemical transformation of 4-nitrophenol to 4-aminophenol. (a) UV-Vis spectral studies and (b) Plot of $-\ln(C/C_0)$ vs. time (t) (Au: Substrate = 1:15).	102
5.13	UV-Vis spectra for the reduction of 4-nitrophenol [Au: Substrate (a) 1:9 and (b) 1:7].	103
5.14	^1H NMR spectra of 4-nitrophenol and 4-aminophenol.	106
Appendix		
S1	Perspective view of $[2\text{-ThMe}_2\text{SiCH}_2\text{CH}_2(\text{Me})\text{SiO}]_4$, 2 .	122

LIST OF TABLES

Table No.	Description	Page No.
Chapter III		
3.1	^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{29}\text{Si}\{^1\text{H}\}$ NMR and ESI-MS spectral data of cyclotetrasiloxanes, 1-4	42
3.2	Summary of crystallographic data for 1	49
3.3	Selected bond lengths (Å) and angles (°) for 1	50
Chapter IV		
4.1	^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR and ESI-MS spectral data of cyclosiloxanes, 6-11	62
4.2	Color and plasmonic absorption data of AuNPs [GNP-6 to GNP-10]	69
Chapter V		
5.1.	Summary of hydrolytic oxidation of primary/secondary/tertiaryorganosilanes in presence AuNP catalyst [GNP-10]	92
5.2	Rate constant (k) for AuNP-catalyzed reduction of 4-nitrophenol to 4-aminophenol	102
5.3	Summary of aminoarenes obtained by catalytic reduction usingAuNPs [GNP-10A] catalyst	104
Appendix		
S1	Summary of crystallographic data for 2	121

GLOSSARY OF SYMBOLS AND ABBREVIATIONS

Å	Ångström
%	percent
δ	chemical shift
ν	frequency
°C	degree centigrade
ϵ	molar absorptivity
λ_{max}	absorption maxima
AIBN	2,2'-azobis(isobutyronitrile)
AuNPs	gold nanoparticles
AuNWs	gold nanowires
ATR	attenuated total reflectance
b.p.	boiling point
br	broad
<i>n</i> -Bu	<i>n</i> -butyl
cm	centimeter
Cp	cyclopentadienyl
CH ₂ Cl ₂	dichloromethane
d	doublet
DEPT	distortionless enhancement by polarization transfer
D ₄ ^H	2,4,6,8-tetramethylcyclotetrasiloxane
D ₄ ^{Vi}	2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane
e.g.	for example
ESI	electrospray ionization
Et	ethyl
Et ₂ O	diethyl ether
FESEM	field emission scanning electron microscopy
FT	Fourier transform
Fu	furyl
fwhm	full width at half maximum
g	gram
GC	gas chromatography

GPC	gel permeation chromatography
h	hour
Hz	Hertz
HPLC	high performance liquid chromatography
HRTEM	high resolution transmission electron microscopy
<i>n</i> -Hex	<i>n</i> -hexyl
i.e.	that is
IR	infrared
J	coupling constant
m	multiplet
m.p.	melting point
m/z	mass/charge
MHz	Mega Hertz
M ⁺	molecular ion
Me	methyl
mmol	millimole
mol	mole
mL	milliliter
M _n	number average molecular weight
M _w	weight average molecular weight
nm	nanometer
NMR	nuclear magnetic resonance
OAc	acetate
OTf	triflate
<i>p</i> -	para
PDI	polydispersity index
Ph	phenyl
<i>n</i> -Pr	<i>n</i> -propyl
PL	photoluminescence
q	quartet
RT	room temperature
s	singlet
t	triplet

TEM	transmission electron microscopy
Th	thienyl
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMS	tetramethylsilane
UV	ultraviolet
XPS	X-ray photoelectron spectroscopy