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

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by

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Submitted

In fulfillment of the requirements of the degree of

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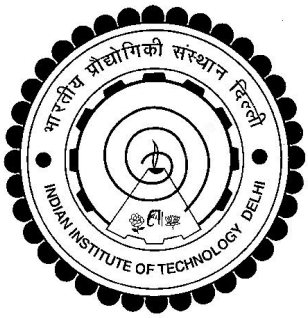

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AUGUST 2015

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.

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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, $[RMe_2SiCH_2CH_2(Me)SiO]_4$ (R = Ph, 2-thienyl, 2-furyl) and $[R^1SCH_2CH_2(Me)SiO]_4$ (R^1 = *n*-Bu, *n*-Hex, dodecyl, CH_2COOH, CH_2CH_2COOH, CH_2CH_2OH) 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 cyclosiloxanes, $[RMe_2SiCH_2CH_2(Me)SiO]_4$ (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 cyclosiloxanes for the stabilization of gold nanoparticles has been examined in detail. The results reveal that these molecular cyclosiloxanes 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 = 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 = Ph, $PhMe_2SiCH_2CH_2$) reveal a facile formation of linear poly(hydrosiloxane)s with M_w = 3000-5500 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.

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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
n-Bu	*n*-butyl
cm	centimeter
Cp	cyclopentadienyl
CH_2Cl_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_2O	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
n-Hex	*n*-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
p-	para
PDI	polydispersity index
Ph	phenyl
n-Pr	*n*-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 specroscopy