

DESIGN, SYNTHESIS AND CHARACTERIZATION OF POLYORGANOSELENIUM COMPOUNDS AND THEIR UNIQUE FUNCTIONAL BEHAVIOR AS CHEMICAL SENSORS

By

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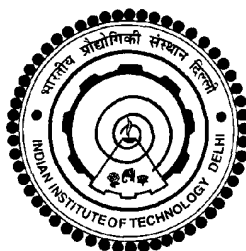
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Dedicated
to
respected mausi Late Mrs. Shashi Srivastava and mausaji
Late Dr. Onkar Nath Srivastava
&
to my parents

I am blessed to have these wonderful people in life as my
family

Certificate

*This is to certify that the thesis entitled “**Design, Synthesis and Characterization of Polyorganoselenium Compounds and Their Unique Functional Behavior as Chemical Sensors**” being submitted by **Mr. Abhishek Kumar**, to the Indian Institute of Technology Delhi, for the award of degree of ‘Doctor of Philosophy’ in Chemistry is a bonafide research work carried out by him. Mr. Abhishek Kumar has worked under my guidance and supervision and has fulfilled the requirement for the submission of 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 award of any degree or diploma.*

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ABSTRACT

The thesis entitled “**Design, Synthesis and Characterization of Polyorganoselenium Compounds and Their Unique Functional Behavior as Chemical Sensors**” deals with the design and synthesis of polyorganoselenium compounds and their identification and evaluation as chemical sensors for biologically and environmentally crucial metal ions, such as Cu^{2+} and Hg^{2+} ions.

Chapter I provides a brief overview on organoselenium compounds in view of various significant results and applications of organoselenium compounds that have been realised in past several decades. This chapter also defines the aims and objectives of the present research work.

Chapter II describes the synthetic strategies and experimental details involved in the preparation of starting materials and a list of chemicals procured from various sources for the current study. It also describes various physicochemical studies used for characterization of newly synthesized compounds.

Chapter III deals with the synthesis of arylchalcogen containing tripodal systems of the type $\text{N}(\text{CH}_2\text{CH}_2\text{EPh})_3$. The identified systems were subjected for their performance in cation recognition phenomenon in solution state through UV-visible and fluorescence spectroscopy. The marked specificity for the Hg^{2+} ion, low response time at ambient temperature, and fluorescence “turn-on”-type behavior of selenium based tripod are remarkable and the system supersedes over other Hg^{2+} sensors studied in the past several decades. Undoubtedly, selenium based tripod is a unique non-fluorophore bearing Hg^{2+} probe that exhibits direct fluorescence “turn-on” behaviour as a function of Hg–Se bond formation in solution, which is the first of its kind.

Chapter IV deals with the synthesis and characterization of alkylselenium containing tripodal systems of the type $N(CH_2CH_2SeR)_3$, with a view to examine the reactivity pattern difference between aromatic and aliphatic organoselenium derivatives. These systems were evaluated further for their cation recognition phenomenon. The change of organic group from phenyl to n-propyl chain clearly shows a reversal in selectivity of the NSe_3 system from Hg^{2+} to Ag^+ . The result from the present chapter indicates that the organic group appended to the selenium centre plays an important role in metal ion binding affinity.

Chapter V deals with the targeted synthesis of (3+3) mixed hexa-substituted benzene systems containing two different arylselenium groups at alternate positions. A two-step synthetic methodology was successful in achieving new type of (3+3) mixed arylselenium derivatized hexa-substituted benzenes in high yields under mild conditions. The isolated intermediate species and the final species have been established by using physicochemical techniques and single crystal X-ray diffraction studies.

Chapter VI deals with the synthesis of (3+3) mixed arylchalcogen substituted hexa-benzenes (Aryl = phenyl, *p*-substituted phenyl; Chalcogen = O, S, Se). Representative example of the four type of species synthesized were evaluated for recognition behavior towards various metal ions. The mixed (O, Se) bearing system exhibits remarkable binding affinity towards Cu^{2+} as evident from the UV-visible and fluorescence spectroscopy. This system has combined electronic influence of different heteroatom centres in its binding affinity.

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