

**DESIGN, SYNTHESIS AND CHARACTERIZATION OF
NOVEL HETEROFUNCTIONALIZED
TETRATHIAFULVALENE DERIVATIVES**

by

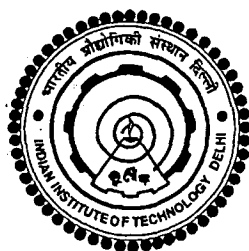
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Submitted

In fulfillment of the requirements of the degree of Doctor of Philosophy

to the



Indian Institute of Technology, Delhi

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*“Dedicated to my beloved
parents &
those who, inspired me”*

*Woods are Lovely, Dark' n Deep,
But I have promises to keep!
And miles to go, before I sleep!
And miles to go, before I sleep!*

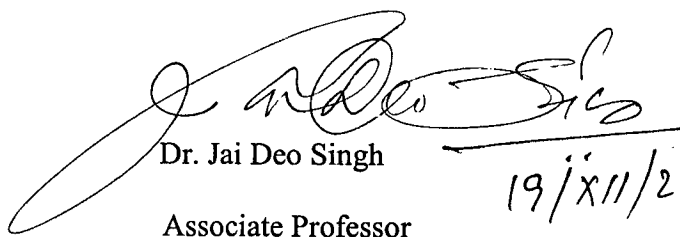
“Robert frost”

CERTIFICATE

This is to certify that the thesis entitled "Design, Synthesis and Characterization of Novel Heterofunctionalized Tetrathiafulvalene Derivatives" by Mr. Jagat Singh, to the Indian Institute of Technology, Delhi, for the award of degree of 'Doctor of Philosophy' in chemistry, is a record of bonafide research work carried by him. Mr. jagat Singh has work under 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 the thesis have not been submitted in part or in full, to any other University or institute for the award of any degree or diploma.

Date 19 Dec 2003


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Jagat singh
Jagat Singh

ABSTRACT

The thesis entitled “Design, Synthesis and Characterization of Novel Heterofunctionalized Tetrathiafulvalene Derivatives” deals with some aspects of chemistry of functionalized tetrathiafulvalene.

Among the various functionalized tetrathiafulvalenes (TTFs) described in the literature, only a few examples of these organic donors substituted with heavier chalcogens have been reported. The approach of chalcogen functionalized TTF derivatives become important to obtain new donors with enhanced dimensionality and low oxidation potentials.

Chapter 1 discusses an overview of the recent advances made in the field of organic donors with special reference to design and synthesis of functionalized tetrathiafulvalene derivatives. This chapter also discusses the objective of the present work.

Chapter 2 deals with the synthetic strategies and experimental details involved in the synthesis of starting precursors. This chapter also contains the source of various chemicals used for this work and a brief description of various techniques used for the characterization of compounds synthesized in this thesis.

Chapter 3 deals with the incorporation of heavier organochalcogens as building blocks (both polydentate and polynucleating) for the formation of predefined structures which may not be reasonably straightforward unlike their organic counterparts. There is still much to learn about designing factors prior to achieving a satisfactory level of

predictability of the final arrangement of molecules, especially when the designed TTF are being incorporated with heavier chalcogens such as selenium and tellurium.

Chapter 4 deals with the synthesis of multiarmed tetrathiafulvalene derivatives functionalized through heavier chalcogens, where each arm of the central TTF contains terdentate (E, N, E; E= S, Se or Te) binding units and is connected through nitrogen linkages.

Chapter 5 deals with the synthesis of multifunctional tetrathiafulvalene derivatives, where TTF unit connected to C_3 -symmetric spacers such as 2, 4, 6-trimethylbenzene through sulfur linkage. These kinds of systems may display multi-stage redox behavior which might provide the possibility to control stoichiometry in desired conductive species.

Chapter 6 deals with the synthesis of tetrathiafulvalene derivatives functionalized with calixarene. We realized that TTF functionalized with calixarene would be an ideal candidate for study as calixarene has received well defined importance in supramolecular chemistry. Such system may also have potential applications in supramolecular host-guest chemistry and may act as either sensors, molecular switches or as catalysts for specific reactions.

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