

Organometallic Chemistry: Synthesis, Structure and Applications of Organochalcogens (S, Se, Te)

Synthetic Metals:

Synthesis and structural characterization of organosulfur π -donors and acceptors for **structure-property correlation**

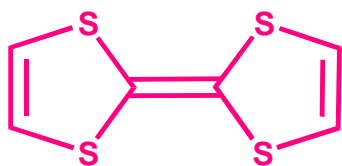
Systematic study of intramolecularly coordinated organochalcogens (S, Se, Te):



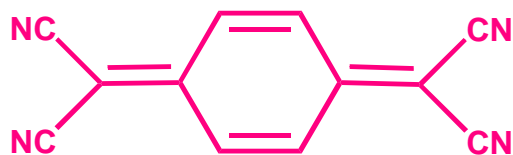
D = N, O
E = O, S, Se, Te
X = E, Halogens, Organyl groups

1. E...D secondary bonding by X-ray and NMR etc.
2. Isolable reagents/reagent precursors for organic synthesis catalysis; RE⁺, RE⁻
3. Hybrid multidentate ligands containing both “hard” and “soft” donor atoms: chiral, macrocyclic ligands
4. Synthetic organochalcogens with Glutathione Peroxidase (GPx)-like activity
5. Monomeric, volatile stoichiometric organometallic precursors for MOCVD of Group II-VI semiconductors

Synthetic metals and Superconductors



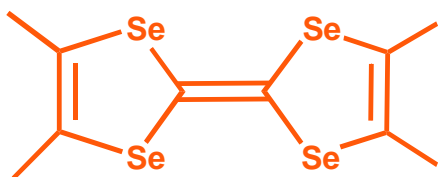
TTF



TCNQ

1973

TTF.TCNQ First Organic Metal

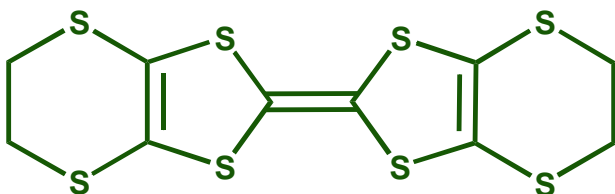


TMTSF

$(\text{TMTSF})_2\text{ClO}_4$

First Organic Superconductor

$T_c \sim 1 \text{ K}$

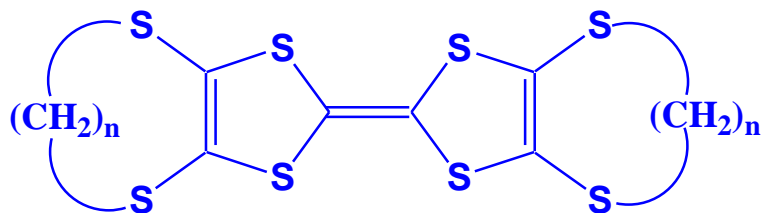


BEDT-TTF

$(\text{BEDT-TTF})_2[\text{Cu}\{\text{N}(\text{CN})_2\}\text{Cl}]$

$T_c 12.5\text{-}12.8 \text{ K}$

Synthesis and Structural Characterization of BEDT-TTF type p - Donors/Acceptors

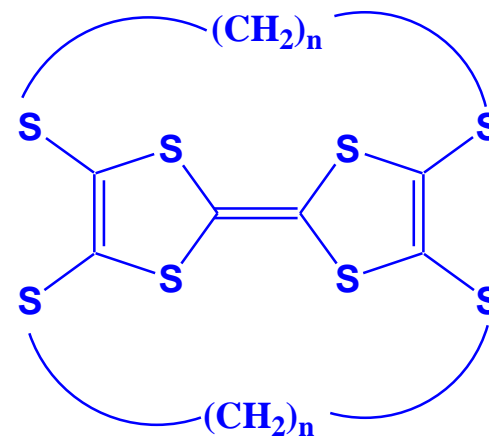


$n = 4, 5, 6, 12$

Major findings

- (a) Core C_6S_8 more planar
- (b) Donor properties unchanged
- (c) S...S nonbonded interactions decrease
- (d) $n = 6$ onwards, isomers

Phane type TTFs isolated



- (i) C_6S_8 core not planar
- (ii) Poor donors

Singh et al.

J. Chem. Soc., Chem. Commun., **1991**, 952.

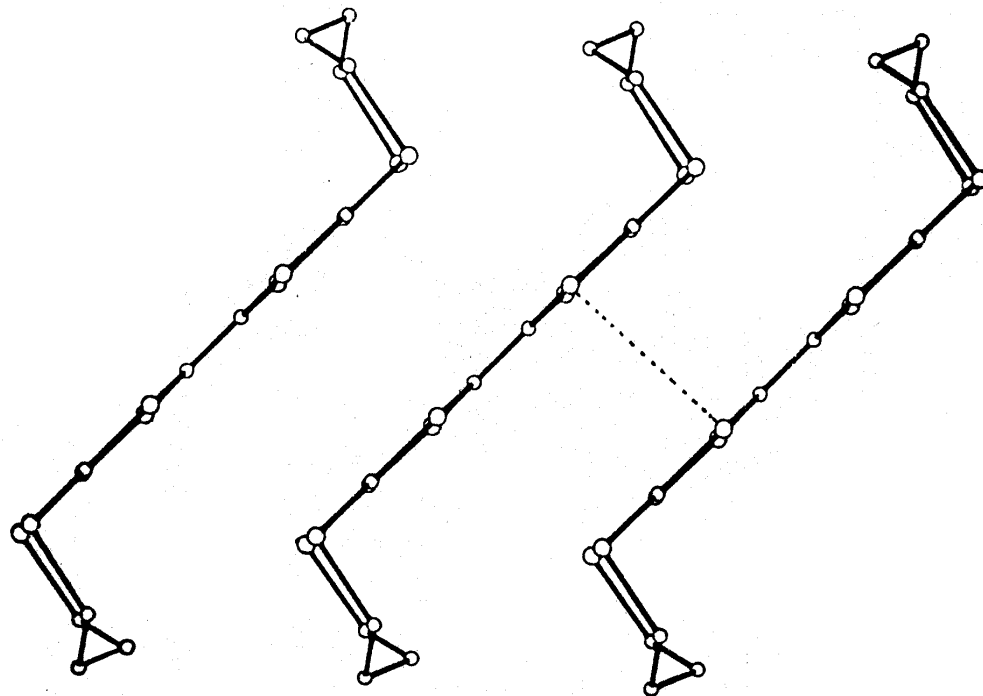
J. Chem. Soc., Perkin Trans I, **1991**, 3341.

Chemistry and Industry, Applied Highlights, **1991**, P805.

J. Chem. Soc., Perkin Trans I, **1992**, 2913.

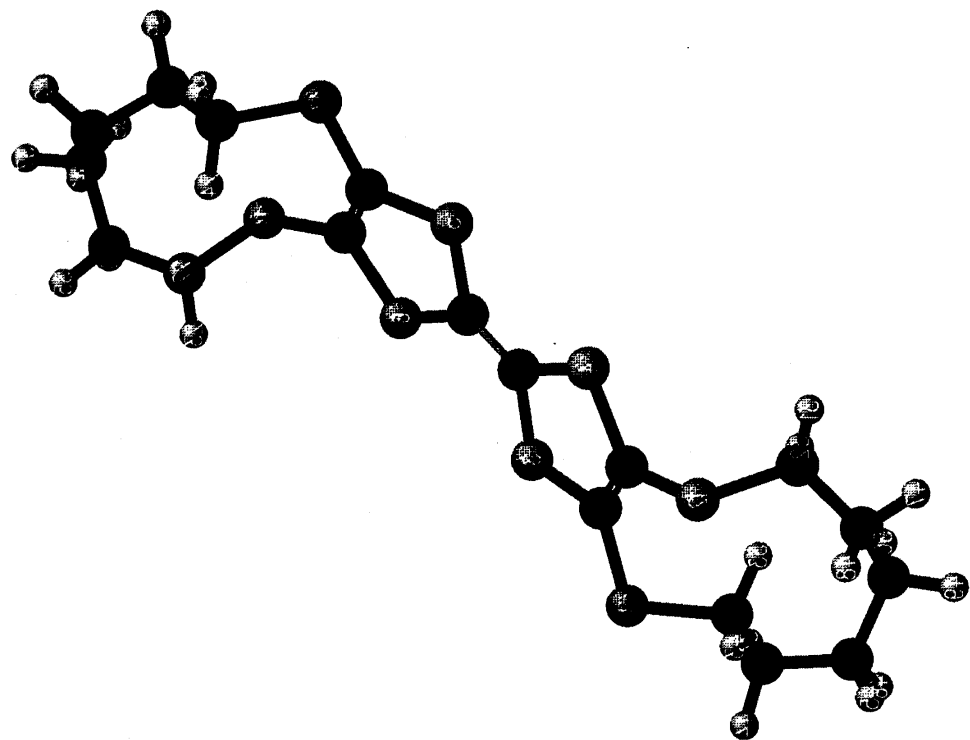
J. Org. Chem., **1995**, 60, 508.

J. Chem. Soc., Perkin Trans I, **1998**, 1769.

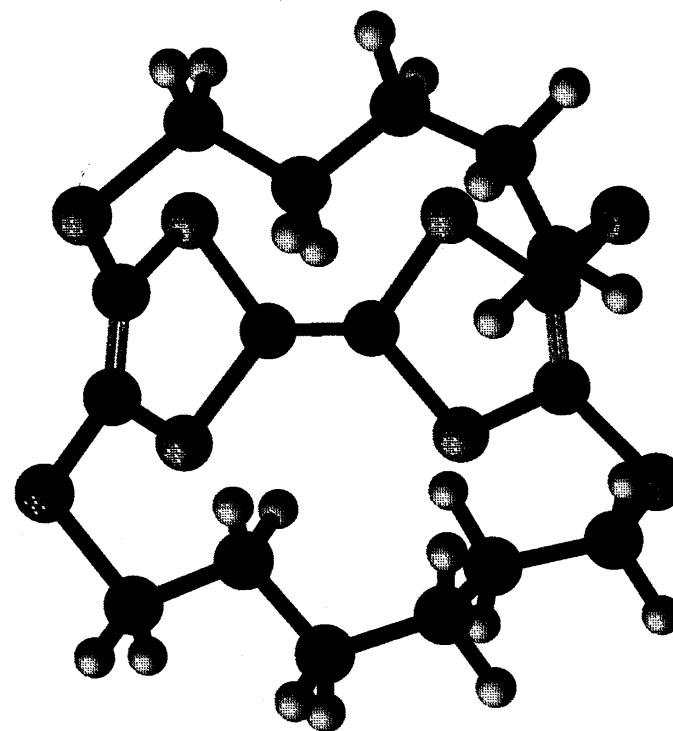


1. C_6S_8 Core planar
2. Stacked uniformly along a axis
3. $S^{1/4}S$ 3.686 Å
BEDT-TTF 3.686 Å (core tube-shape)

TTF-6 Isomers



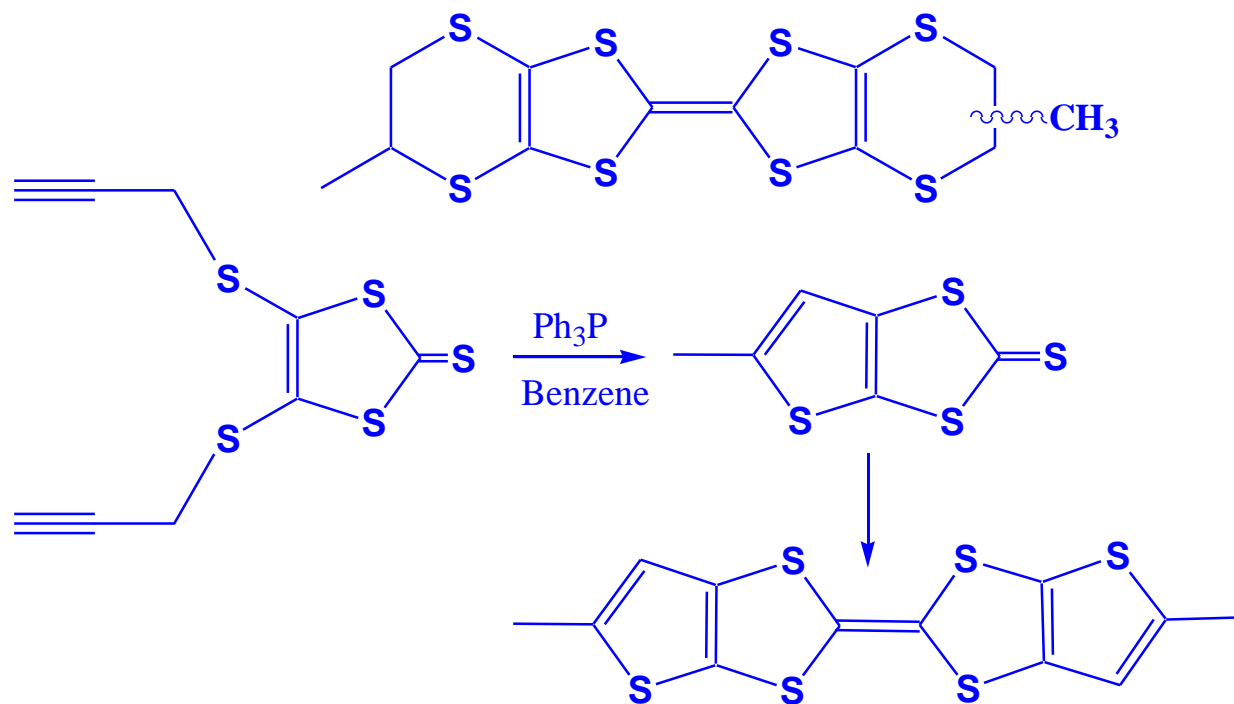
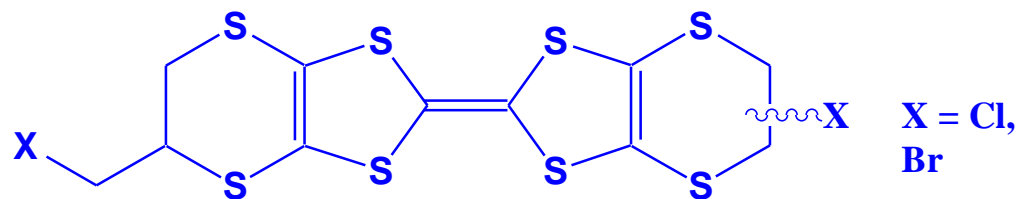
Energy = 68.56 kcal/mol



Energy = 79.42 kcal/mol

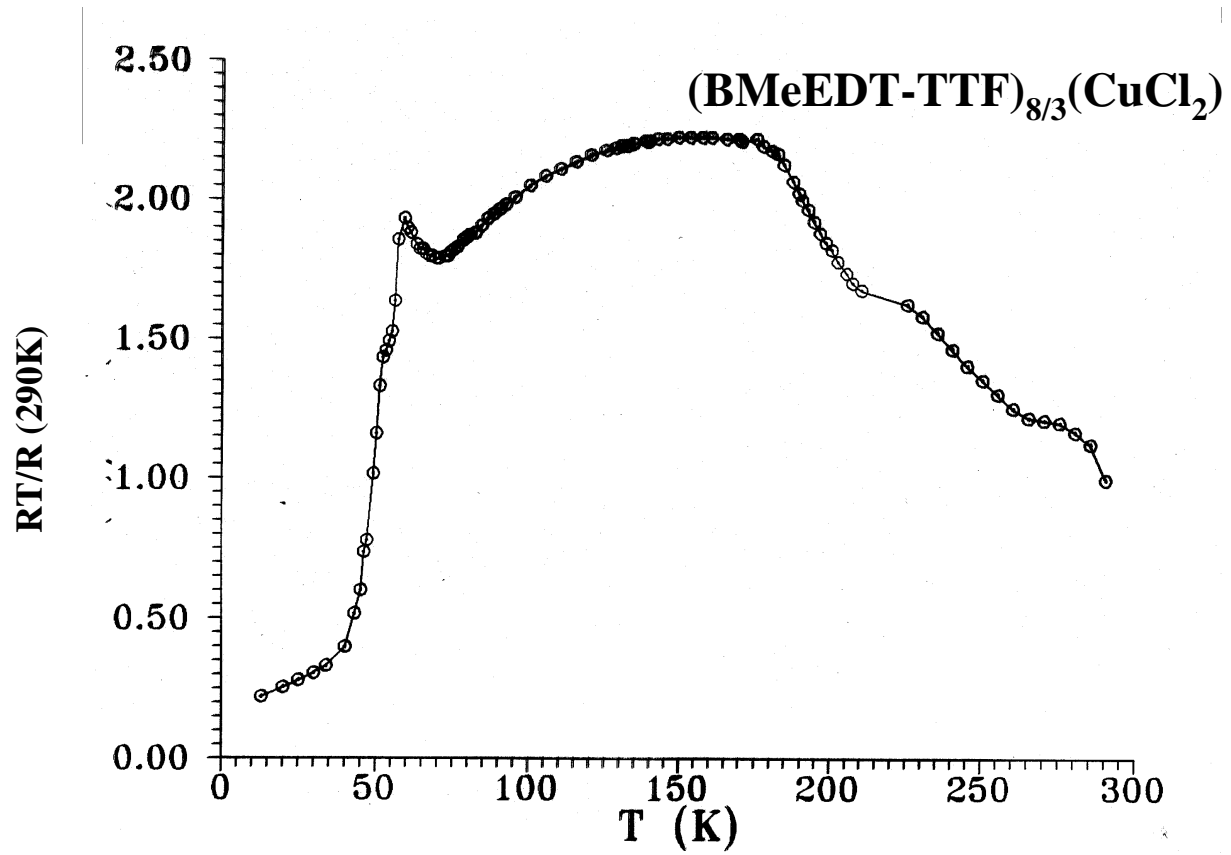
PM-3 computed parameters

Functionalised TTFs



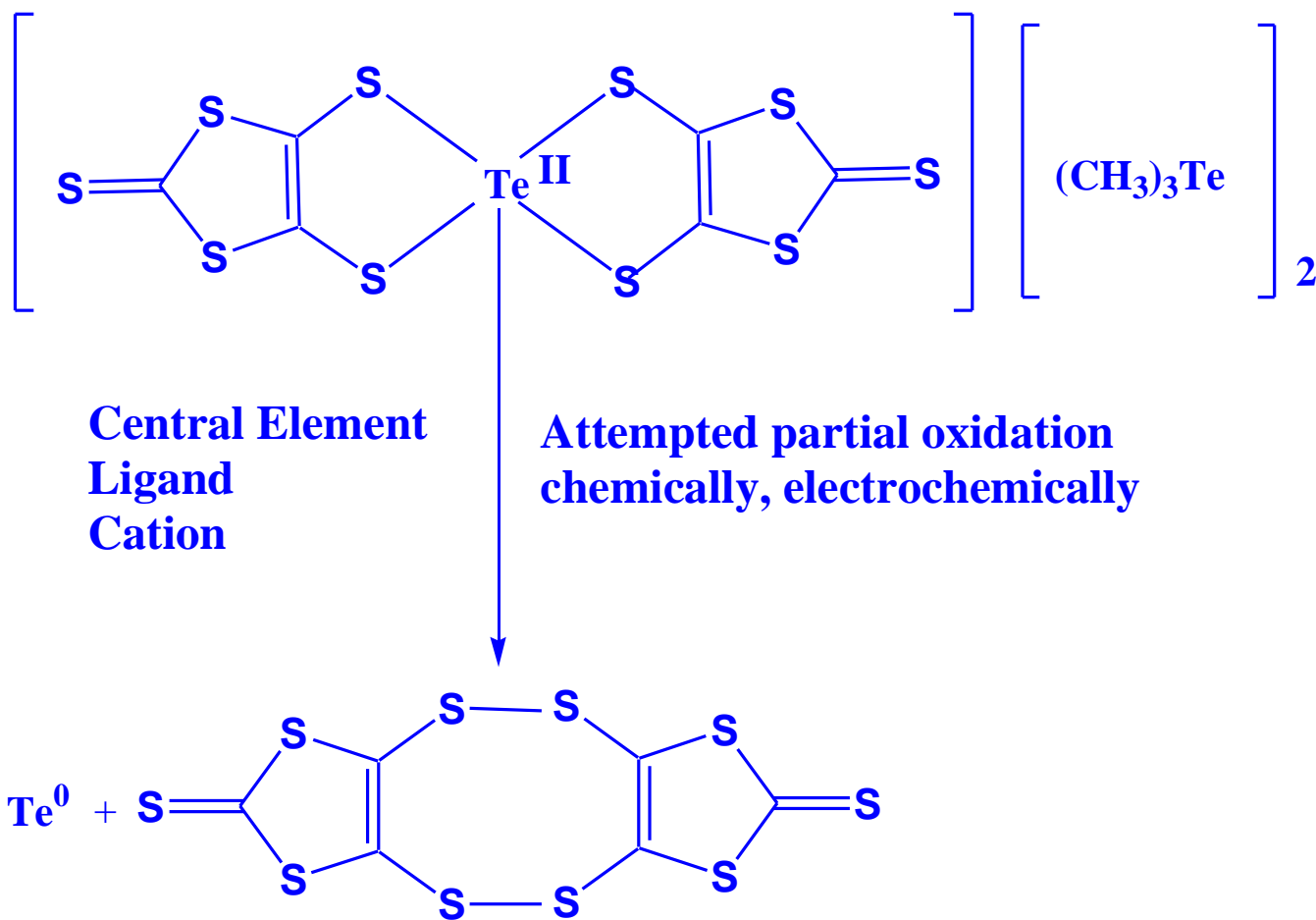
Thio-Claisen Rearrangement

Singh et al. *Tetrahedron* **1977**, 11627.



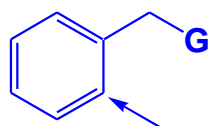
Normalised resistance vs temperature plot

All Chalcogen Acceptors

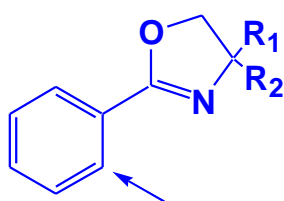
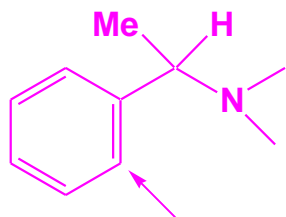


Singh et al. *Polyhedron* **1993**, 2849.

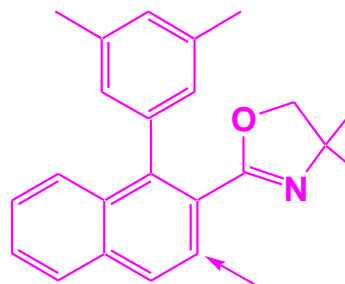
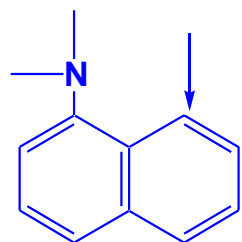
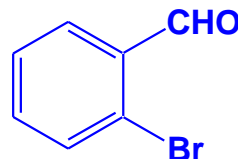
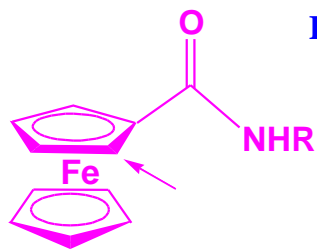
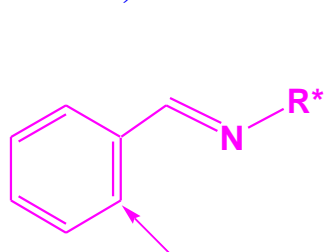
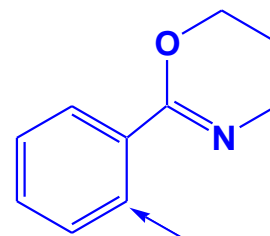
Substrates for Intramolecularly Coordinated Organochalcogens



G = NMe₂, Cl,
OH, SPh



R₁ = H, R₂ = H
R₁ = H, R₂ = Et
R₁ = Me, R₂ = Me



Singh et al.

J. Chem. Soc., Dalton Trans., 1990, 907.

Inorg. Chem., 1992, 32, 1431.

Coord. Chem. Rev., 1994, 135-136, 469.

Organometallics, 1995, 14, 4755.

J. Chem. Soc., Dalton Trans., 1996, 2718.

J. Chem. Soc., Dalton Trans., 1996, 1203.

Organometallics, 1996, 15, 1707.

Organometallics, 1997, 16, 563.

Organometallics, 1999, 18, 1986.

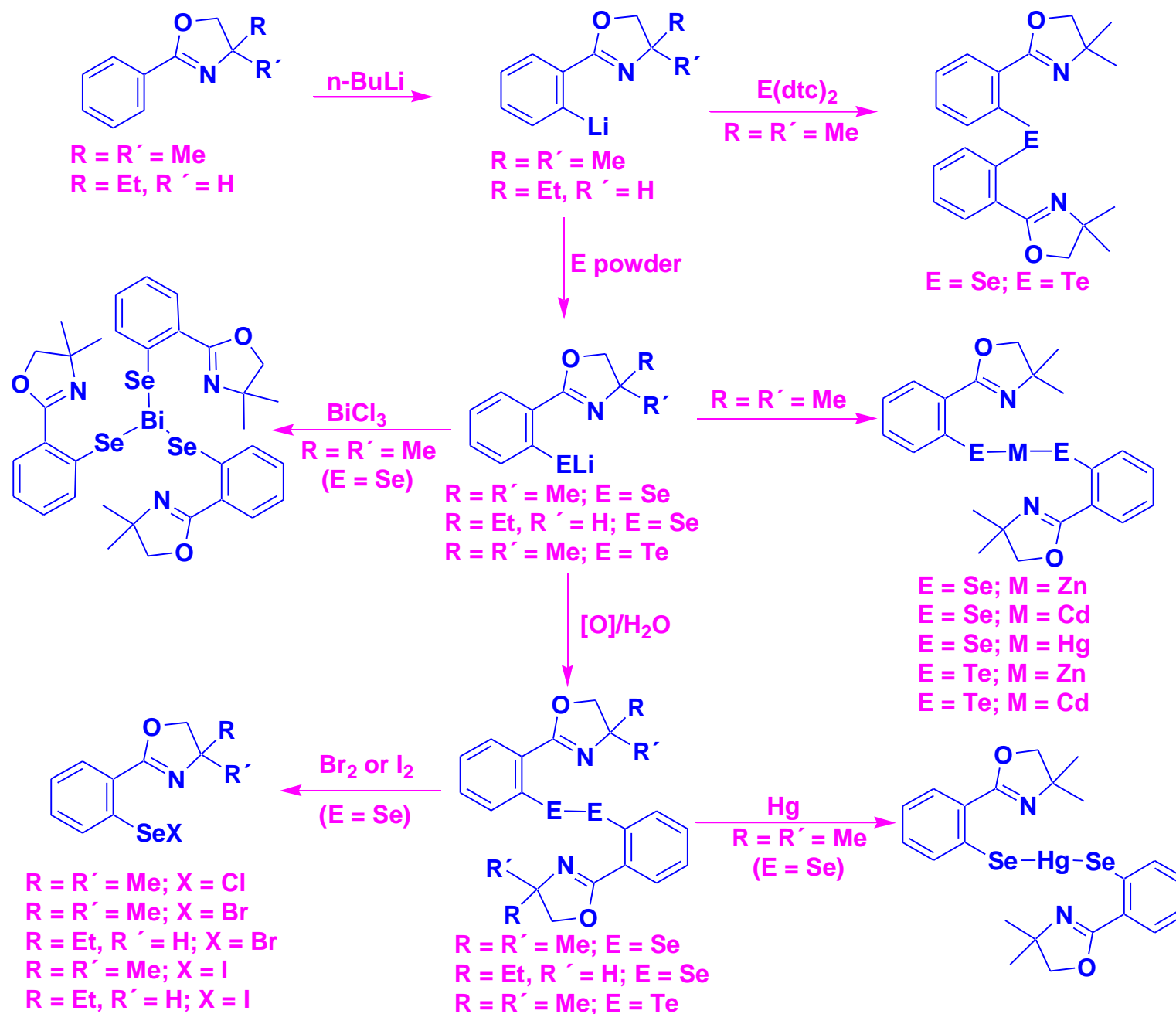
Chem. Eur. J., 1999, 5, 1411.

Tetrahedron: Asymmetry, 1999, 10, 237.

Chem. Commun., 2000, 143.

Acc. Chem. Res., 2002, 35, 226.

A Typical Sequence of Reactions

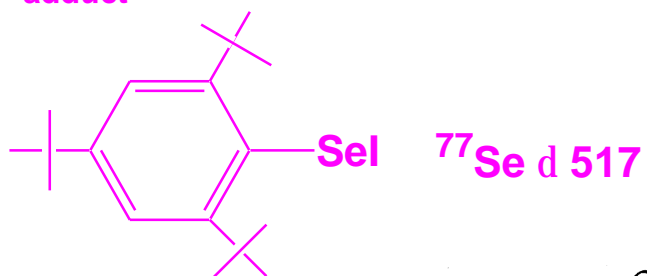
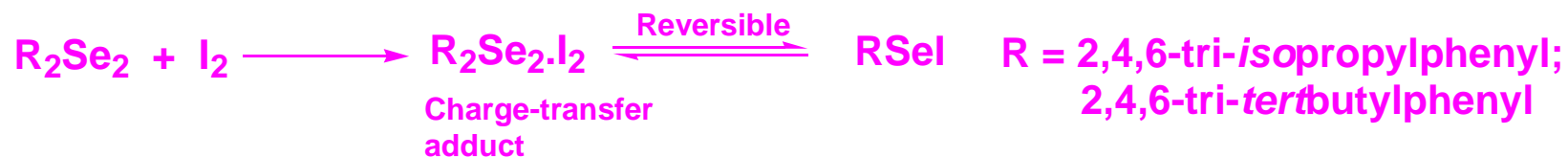


Stabilised RSeI

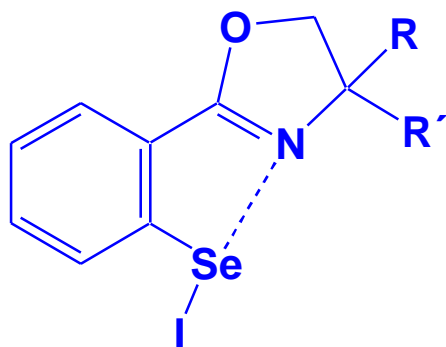
Toshimitsu Reagent: $\text{Ph}_2\text{Se}_2/\text{I}_2$

PhSeI ?

Du Mont *et al.*: *Inorg. Chem.* 1990, 29, 4847



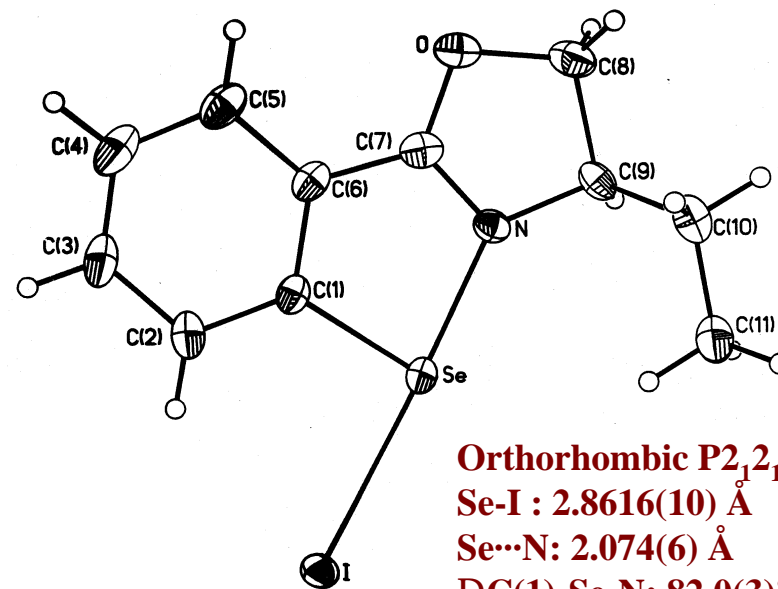
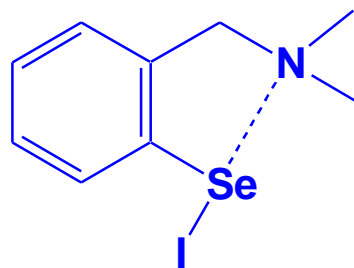
Stabilized by Intramolecular Coordination



$\text{R} = \text{R}' = \text{Me}; \text{X} = \text{I}$

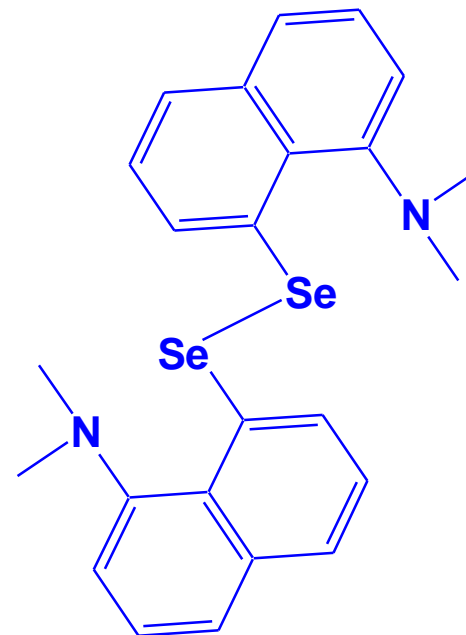
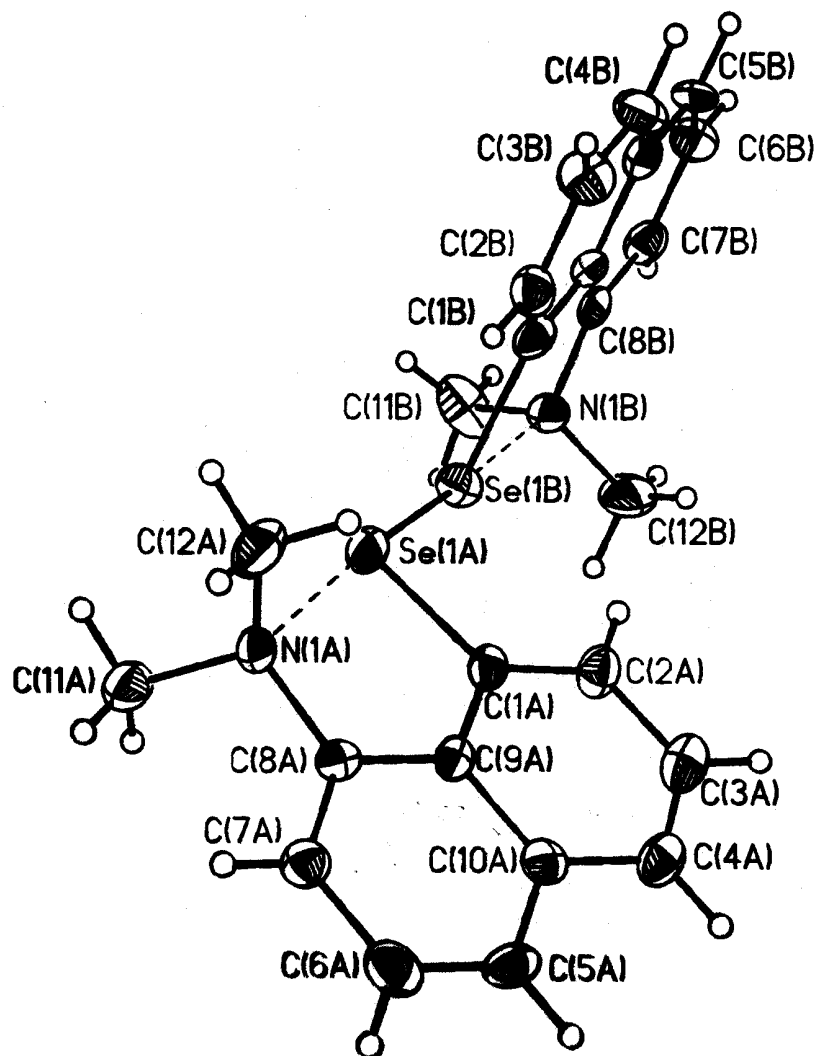
$\text{R} = \text{Et}, \text{R}' = \text{H}; \text{X} = \text{I}$

Stable, Irreversible



Orthorhombic $\text{P2}_1\text{2}_1\text{2}_1$
 Se-I : 2.8616(10) Å
 Se...N: 2.074(6) Å
 DC(1)-Se-N: 82.0(3)°
 DN-Se-I: 176.1(2)°

Chiral Molecule without chiral center



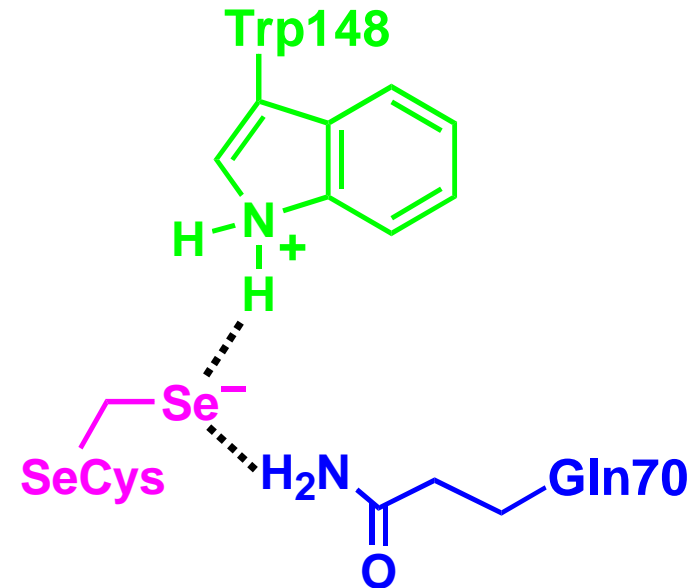
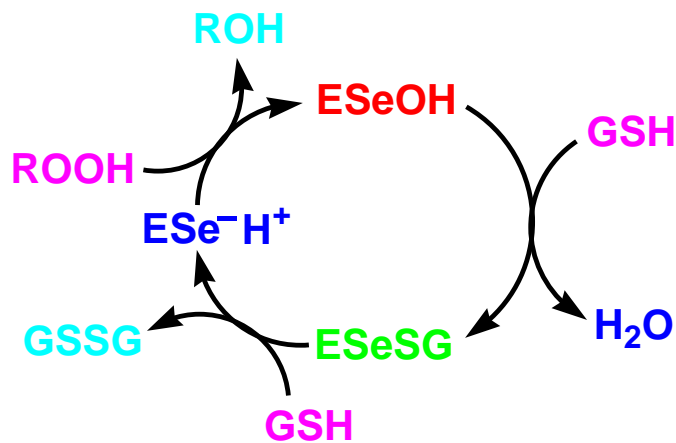
Orthorhombic $P2_12_12_1$
Flack enantiopole parameter = 0
R value: 0.0564
Se-Se: 2.383 (2) Å
Se(1A)⋯N(1A): 2.652 Å
Se(1B)⋯N(1B): 2.628 Å

Glutathione Peroxidase (GPx)

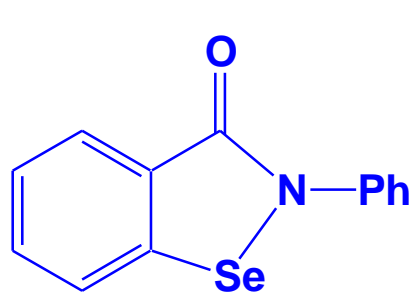
- ❖ Cytosolic GPx (cGPx) – uses GSH as co-substrate
- ❖ Reduction of hydrogen peroxides and organic peroxides



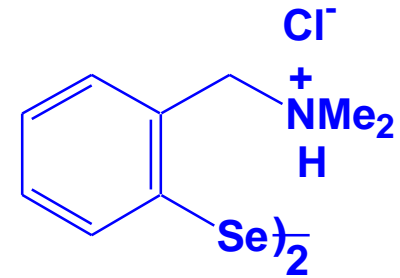
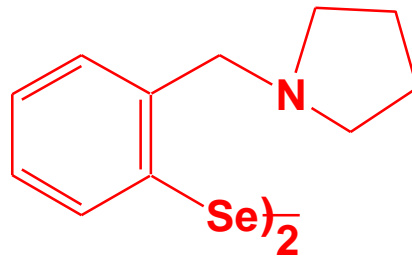
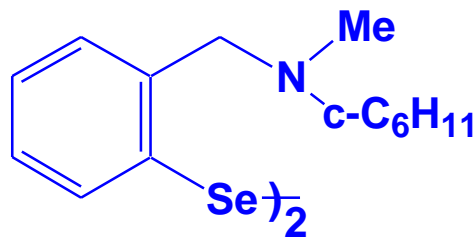
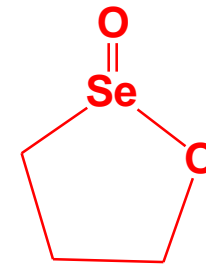
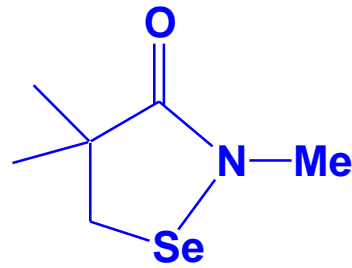
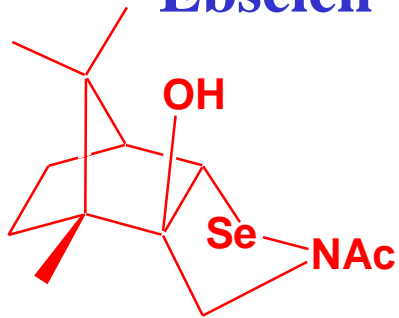
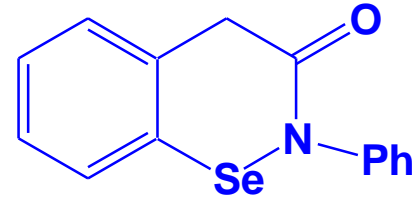
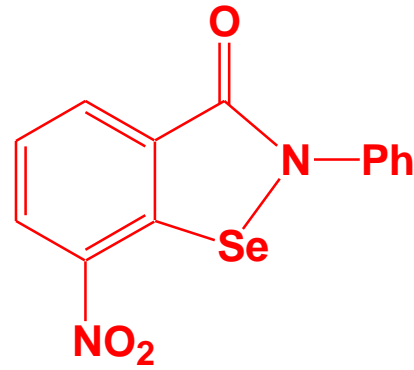
- Tetramer of four identical subunits; each subunit contains a selenocysteine residue
- Catalytic triad – SeCys, Gln, Trp - Selenolate is highly stabilized



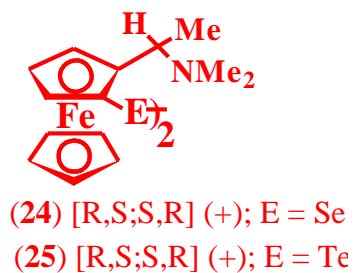
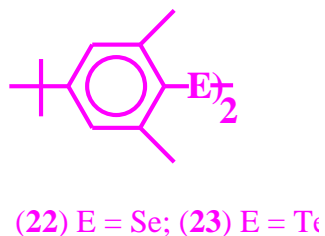
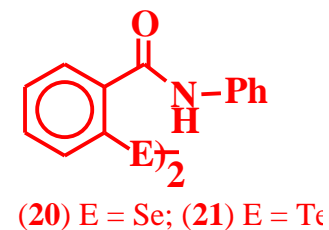
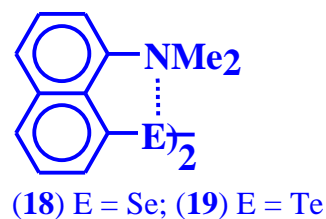
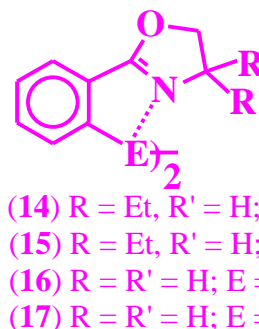
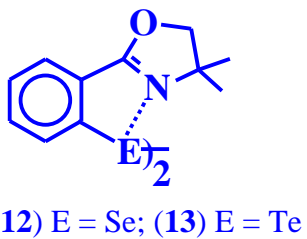
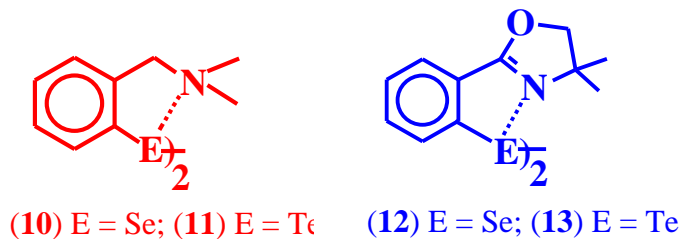
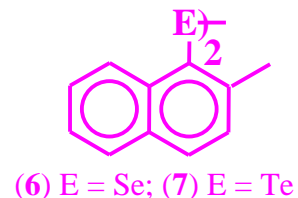
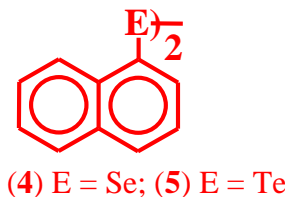
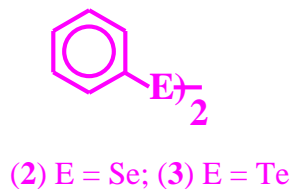
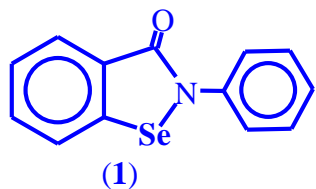
GPX Mimics



Ebselen



Organochalcogen Compounds As a GPx Mimics



Singh et al.

Chem. Soc. Rev. 2000, 29, 347

Proc. Natl. Acad. Sci. 2000, 70, 207

J. Am. Chem. Soc. 2001, 123, 839-850

Chem. Commun. 2000, 143

Organometallics 2002, 21, 884

Table: Initial reduction rates (v_0)^[a] of H₂O₂ (3.75 mM) with PhSH (1 mM) in the presence of various dichalcogenide catalysts (0.1 mM).

entry	catalyst (E = Se)	v_0 ^[b] $\mu\text{M}\cdot\text{min}^{-1}$	entry	catalyst (E = Te)	v_0 ^[b] $\mu\text{M}\cdot\text{min}^{-1}$
a	2	24.08(1.04)	b	3	59.52(3.58)
c	4	53.21(5.81)	d	5	142.97(5.17)
e	6	31.48(3.07)	f	7	70.47(5.40)
g	8	33.92(0.37)	h	9	77.61(6.08)
i	10	124.02(7.89)	j	11	1629.56(5.67)
k	12^c	28.87(1.72)	l	13	135.09(10.04)
m	14^c	18.53(1.32)	n	15	109.38(6.95)
o	16	41.64(1.48)	p	17	- ^e
q	18^c	45.34(2.81)	r	19	239.00(8.99)
s	20	3.52(0.87)	t	21	9.83(1.82)
u	22	inactive	v	23	inactive
w	24	574.01 (23.98) ^d	x	25	- ^e

^[a]Obtained by Lineweaver-Burk Plots. ^[b]Standard deviations are shown in parentheses.

^[c]Inactive at lower concentration.⁹ ^[d]Since the reduction rate was too fast to be determined at 0.1 mM concentration range, 0.01 mM was used for the experiments.⁹ ^[e]decomposed

Single source precursors for Group 12-16 semiconductors



**Metal
Chalcogenolates**

M E

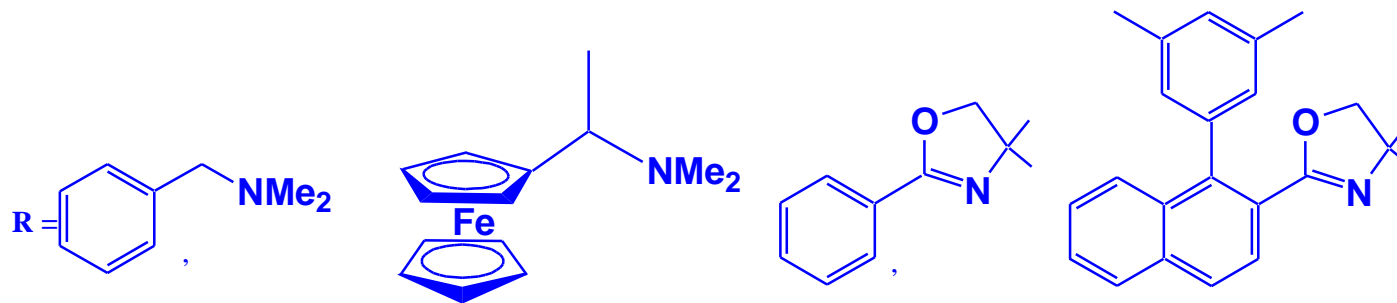
**Polymeric
Insoluble
Low volatility**

Zn S

Cd Se

Hg Te

**Strategies: a) Use of bulky R groups
b) Adduct formation with neutral ligands**



Zinc, Cadmium and Mercury Chalcogenolates

**Monomeric,
hydrocarbon soluble,
Crystalline**

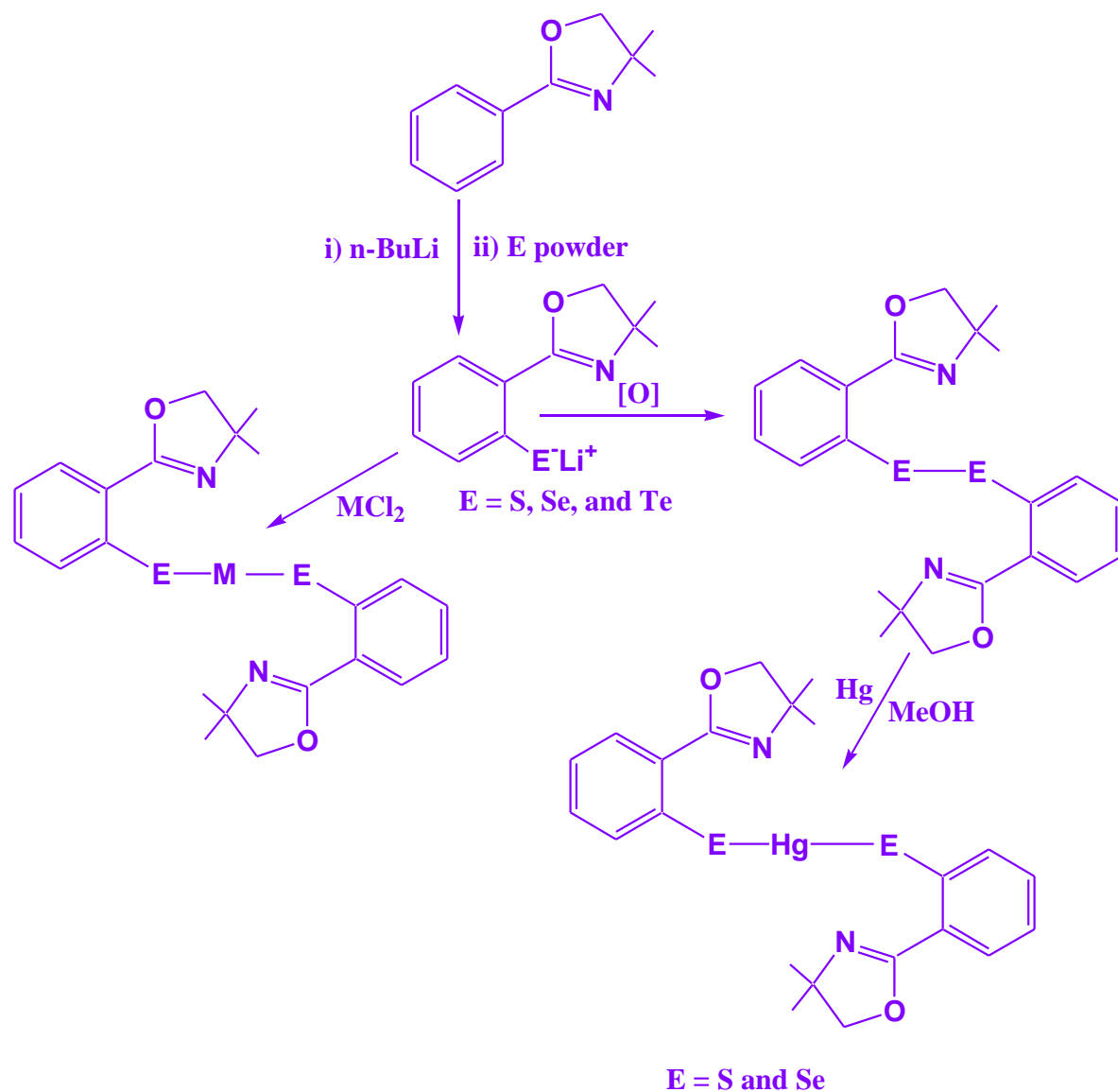
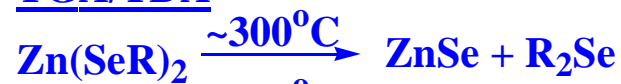
Mass Spectroscopy

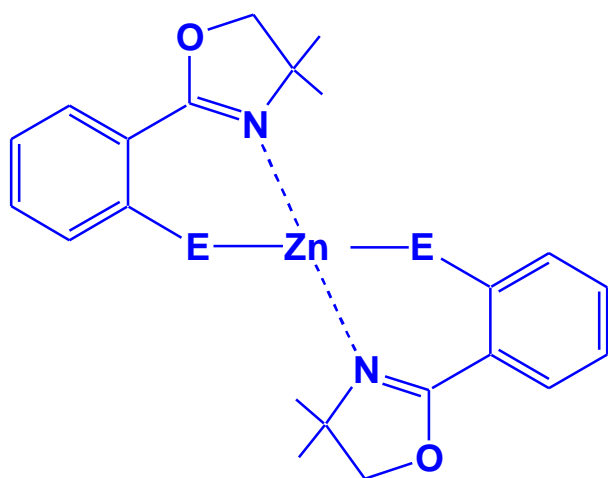


(no peak corresponding
to dimer)



TGA/TDA



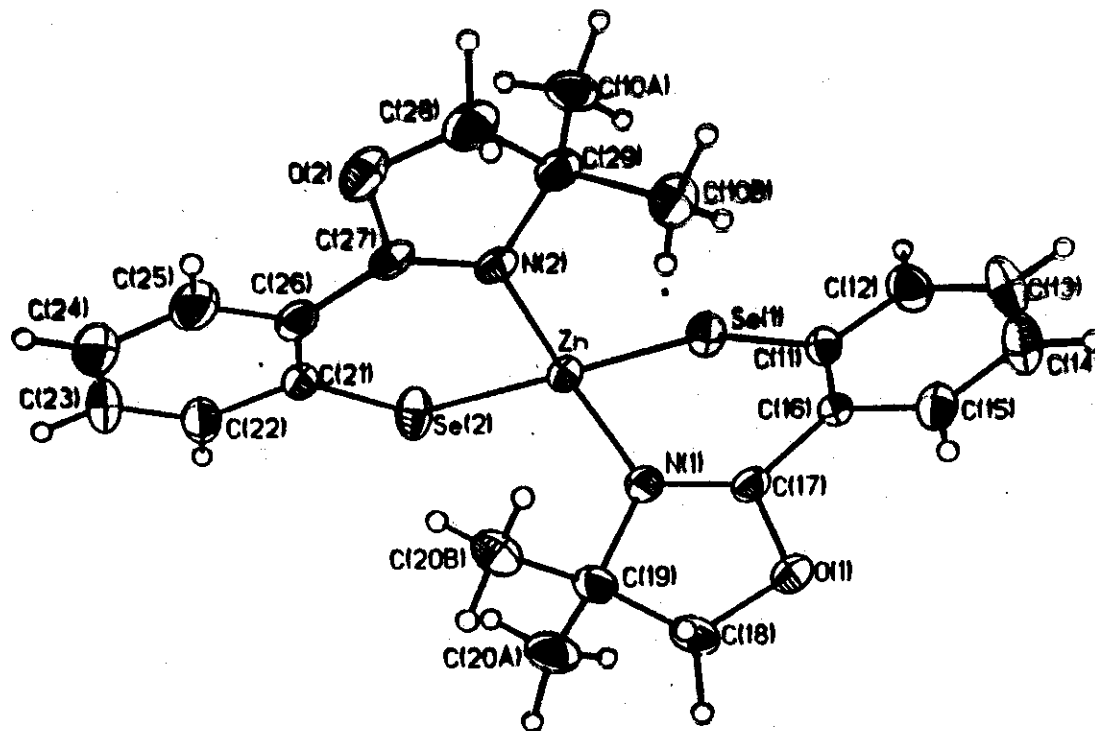


E = O, S, Se, Te

P₂₁

Chiral space group

- 1. Enantiomerically pure, interconversion between (P) and (M) helix
slow at room temperature**
- 2. Thiolato- both pure enantiomers and racemic forms isolated**
- 3. Zinc phenolate- -55⁰C AB quartet**
- 4. Zinc tellurolate- -60⁰C AB pattern resolved**



Singh et al.

Polyhedron (Report), **1996**, 15, 745
J. Chem. Soc., Dalton Trans., **1996**, 461.
Inorg. Chem., **1998**, 37, 2663.
Eur. J. Inorg. Chem., **1999**, 1229.
J. Organomet. Chem., **1999**, 577, 293.
Eur. J. Inorg. Chem., **2001**, 669.

Acknowledgement

**Drs. S. Kalyan Kumar, J. D. Singh, E. V. K. Suresh Kumar
Drs. S. Narsimhan, R. Kaur, S. C. Menon, G. Mugesh, A. Panda,**

**Mr. S. D. Apte, S. S. Zade, Sangit Kumar, K. Kandasamy
Ms. S. Panda**

Funding Agencies

CSIR

DST

BRNS

**Professor R. J. Butcher
Dr. G. Wolmershauser
X-ray Crystallography**