Available online at **www.joac.info**

ISSN: 2278-1862

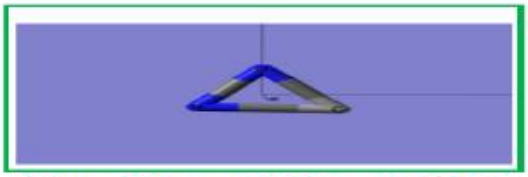
Journal of Applicable Chemistry

2022, 11 (3): 432-500

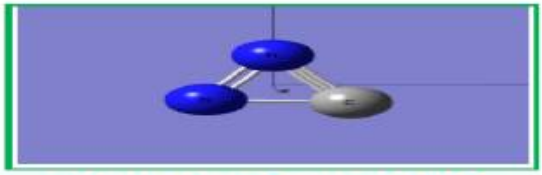
(International Peer Reviewed Journal)

New Chemistry News

$^{-}N=C=N^{-}$



New News of Chem (NNC)



ChemNewsNew (CNN)

CNN – 45 Sup Inf Fig (Sif)
Chalcogenbonds

Information Source	ACS.org ; sciencedirect.com
K. Somasekhara Rao, Dept. of Chemistry, Acharya Nagarjuna Univ., Dr. M.R.Appa Rao Campus, Nuzvid-521 201, India	R. Sambasiva Rao, School of Chemistry, Andhra University, Visakhapatnam 530 003, India

Cox-2

Chalcogen Bond [S]	Cox-2	ChB.	ACS.	23

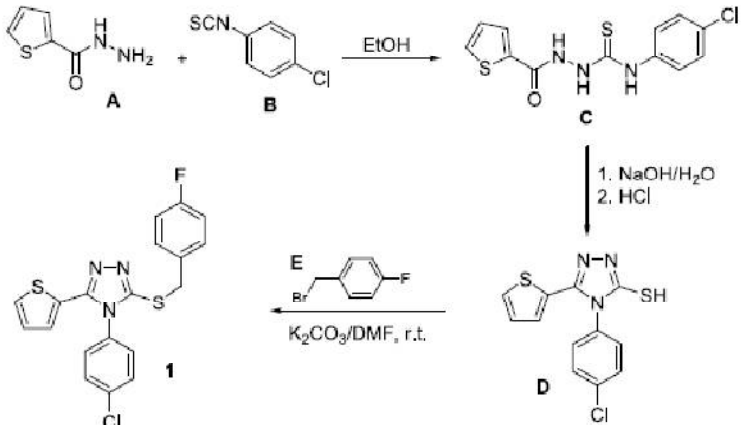
Experimental	
o **Synthesis** o In Vitro COX Inhibition Assay	**Spectroscopy** ➔ **Single-Crystal X-ray Diffraction**
	NMR o 500.16 MHz for ^{1}H

	o 125.77 MHz for ^{13}C o Jeol ECA 500 III NMR spectrometer

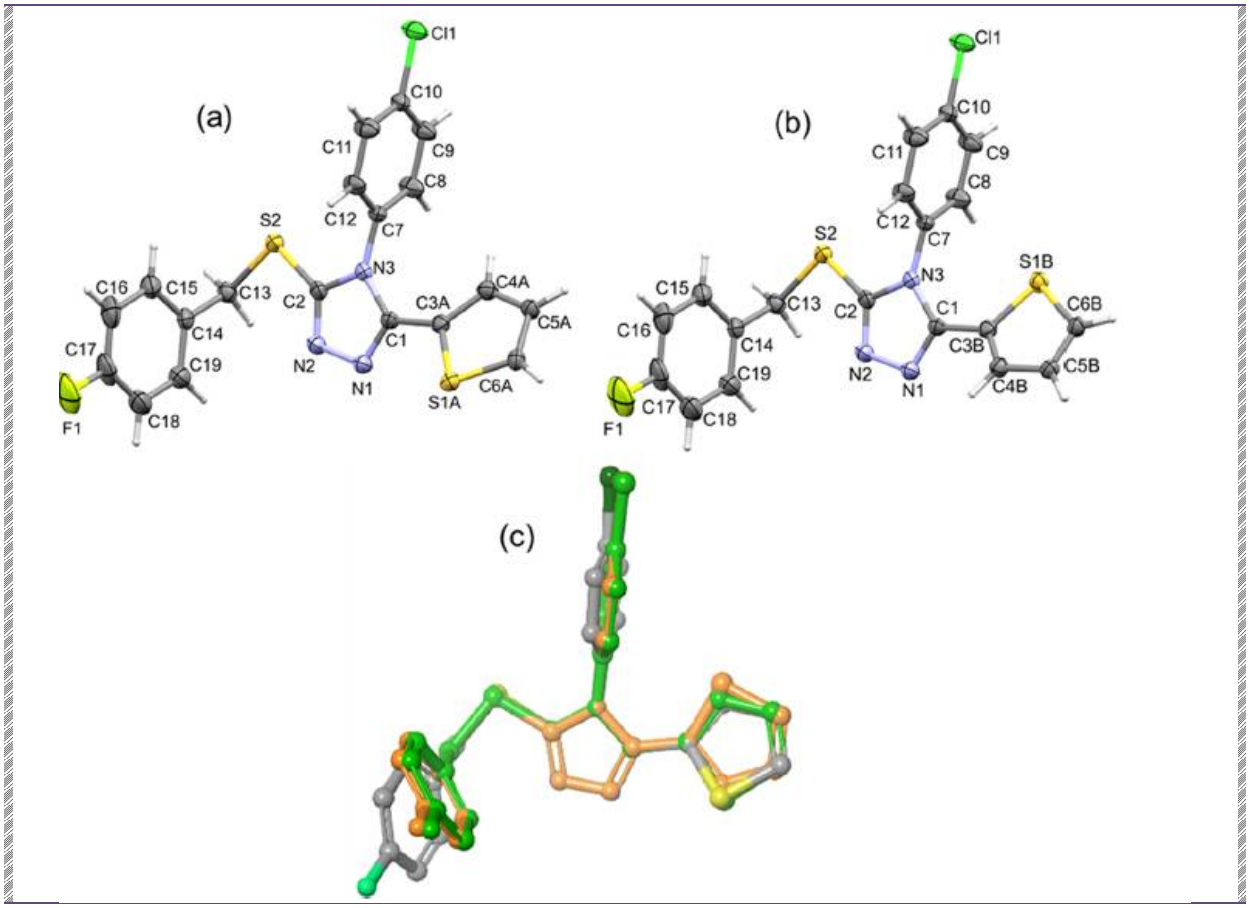
Comp Quan Chem (CQC)	
Theoretical charge density analysis	✓ Crystal structure geometry + ✓ AIMALL package
Wave Functions generated	☞ M062X-D3/ccpVTZ
Topological parameters	o Electron density ($\rho(r)$) o Laplacian of the electron density ($\nabla^2\rho(r)$) o Potential energy density ($V(r)$) o Kinetic energy density ($G(r)$) o Total electronic energy density ($H(r) = V(r) + G(r)$)
Dissociation energy for interaction =	EML empirical scheme, i.e., $D_e = -0.5 \times V(r)$

Chalcogen Bond [S]	Cox-2	ChB.	ACS.	23

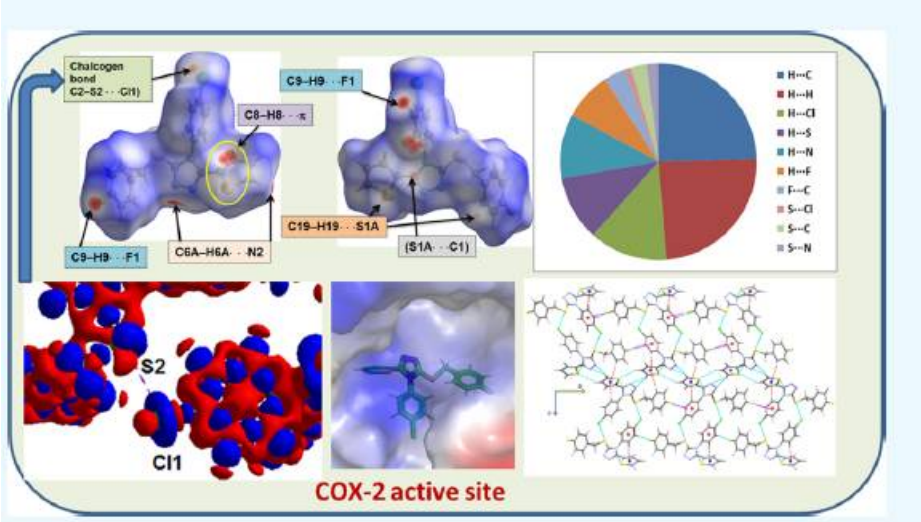
Title Compound

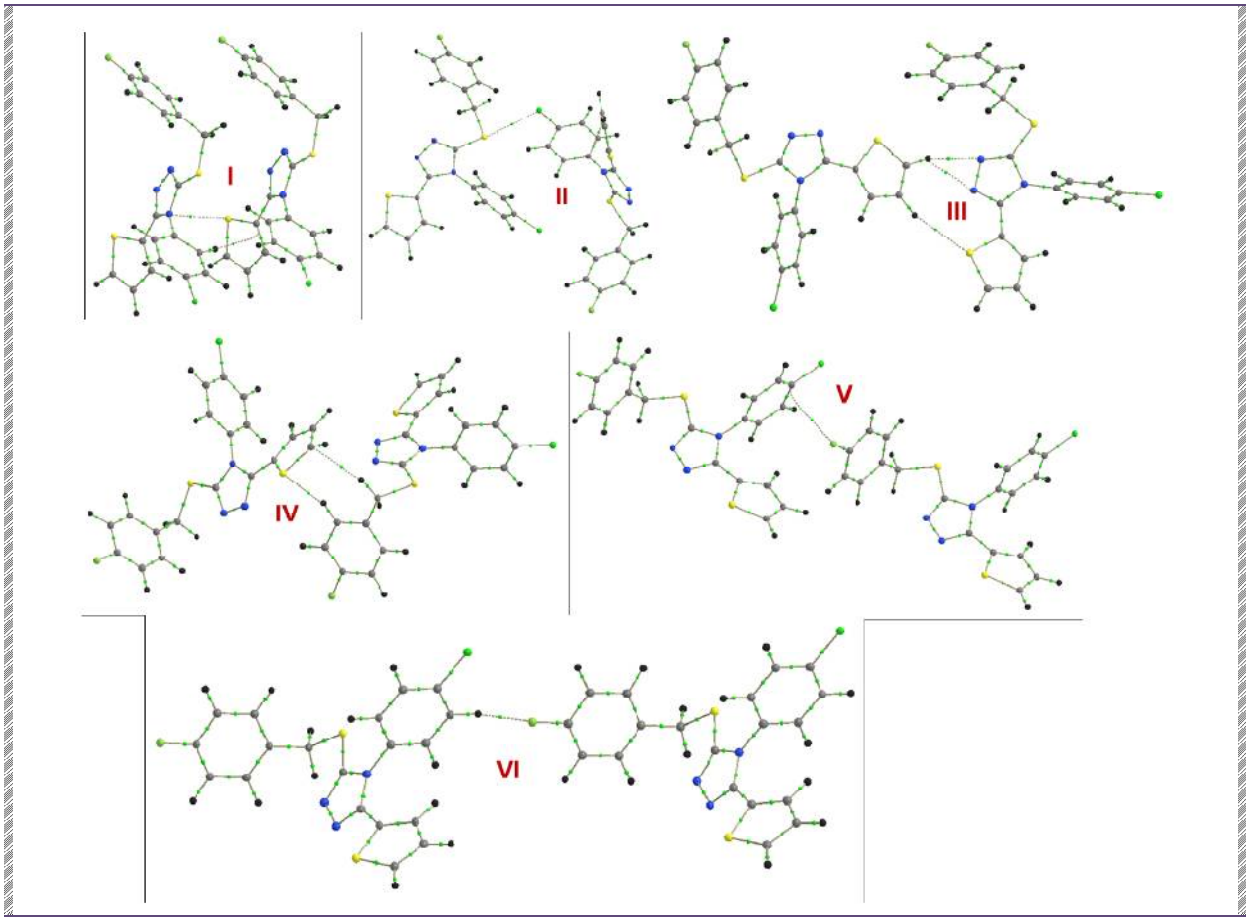


Displacement ellipsoids
Title compound



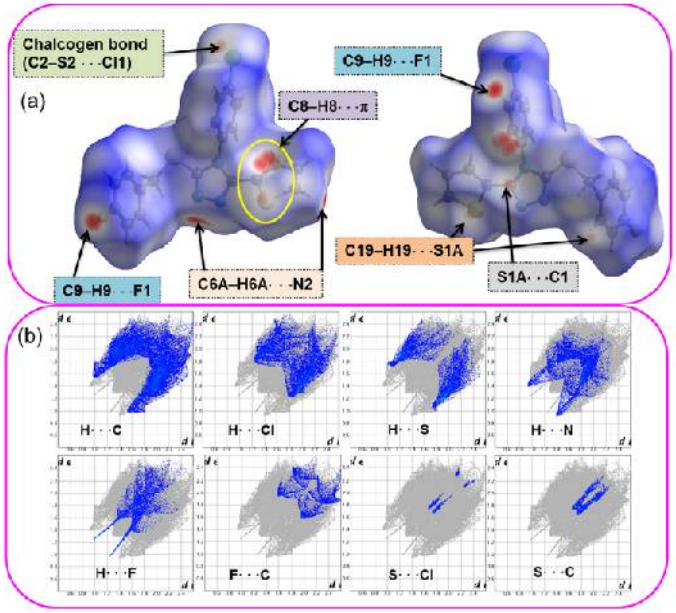
Intermolecular interactions in different molecular pairs (I-VI)



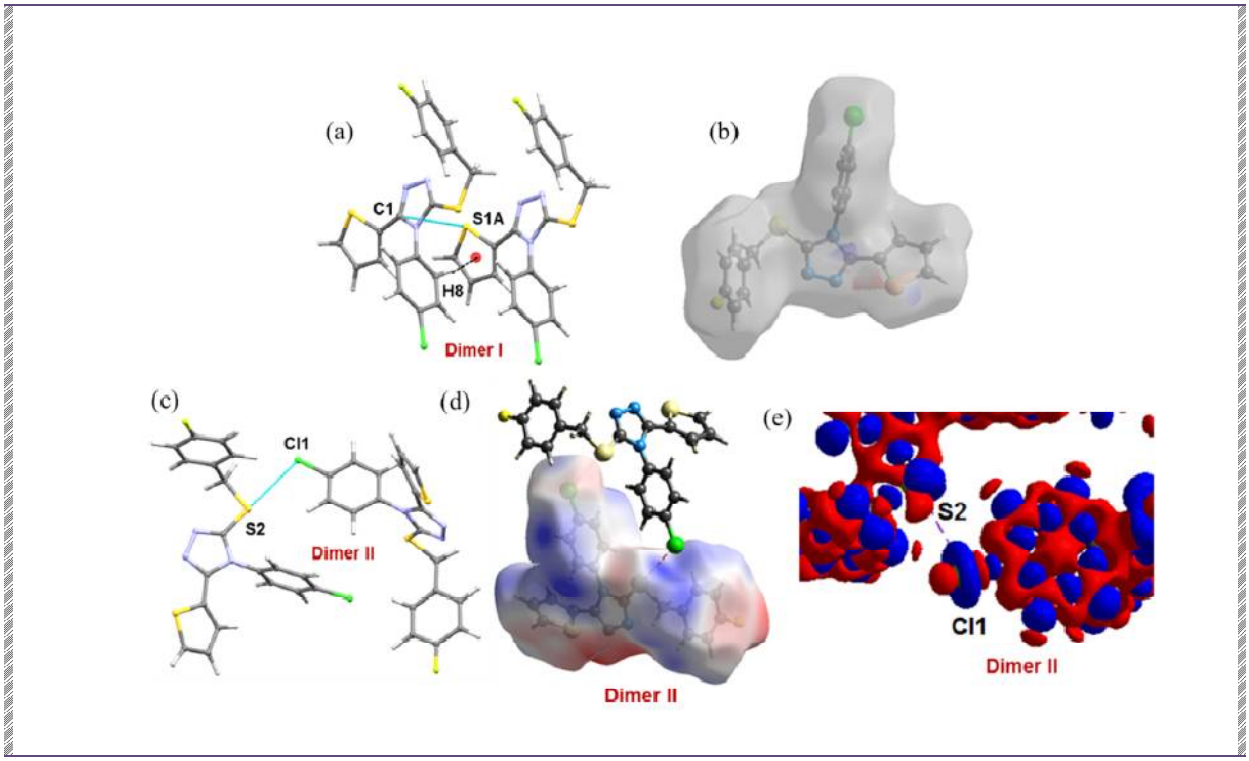


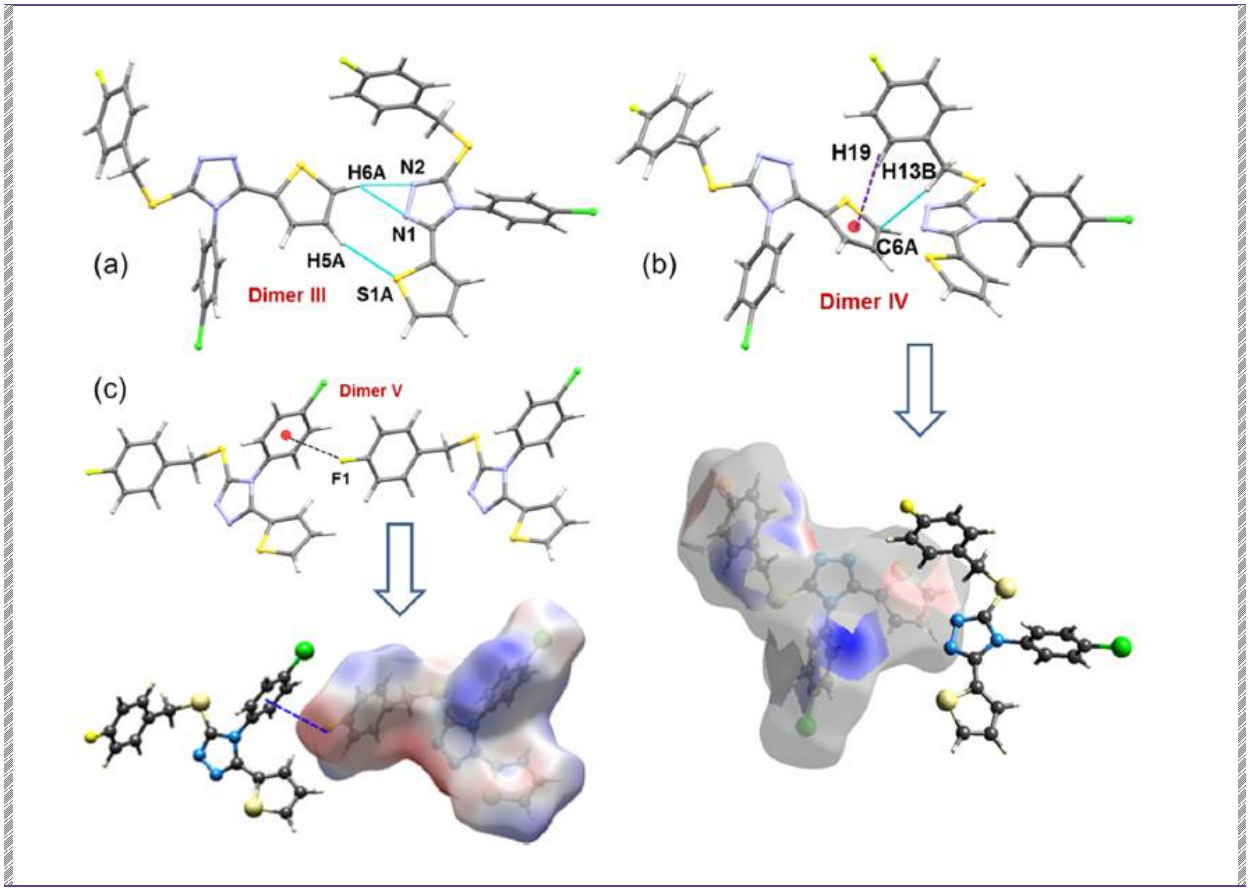
Hirshfeld surfaces

Short intercontacts

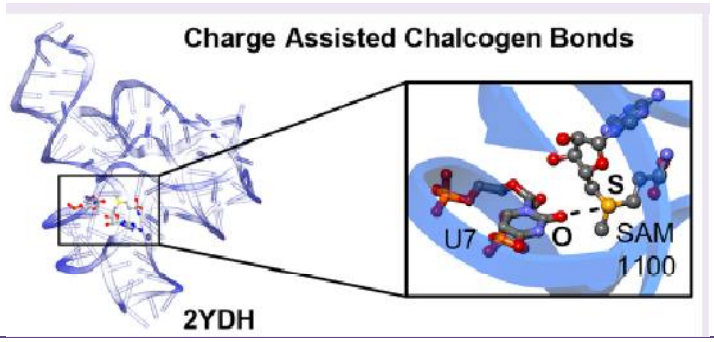


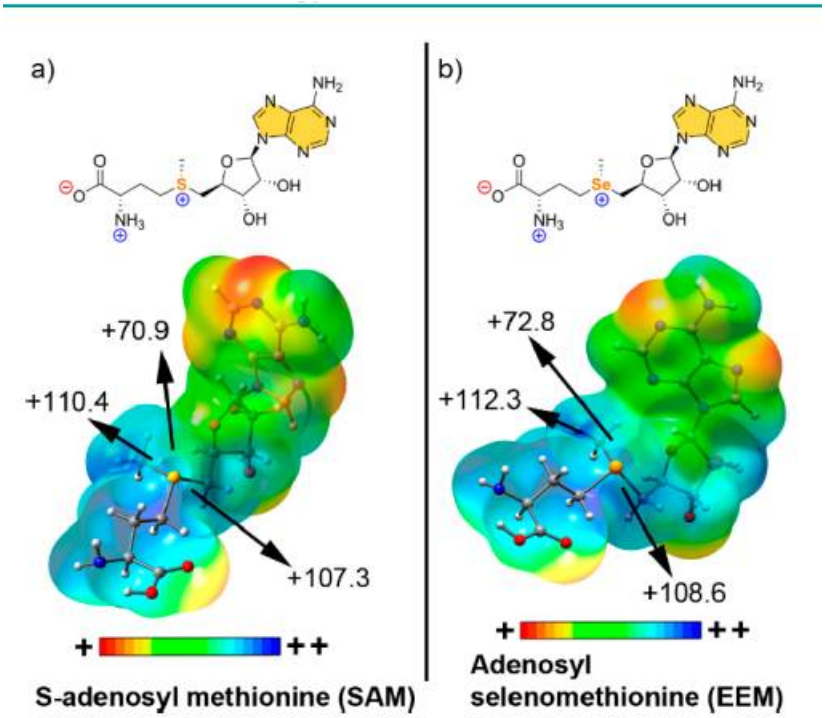
2D-fingerprint plots for selected inter-contacts

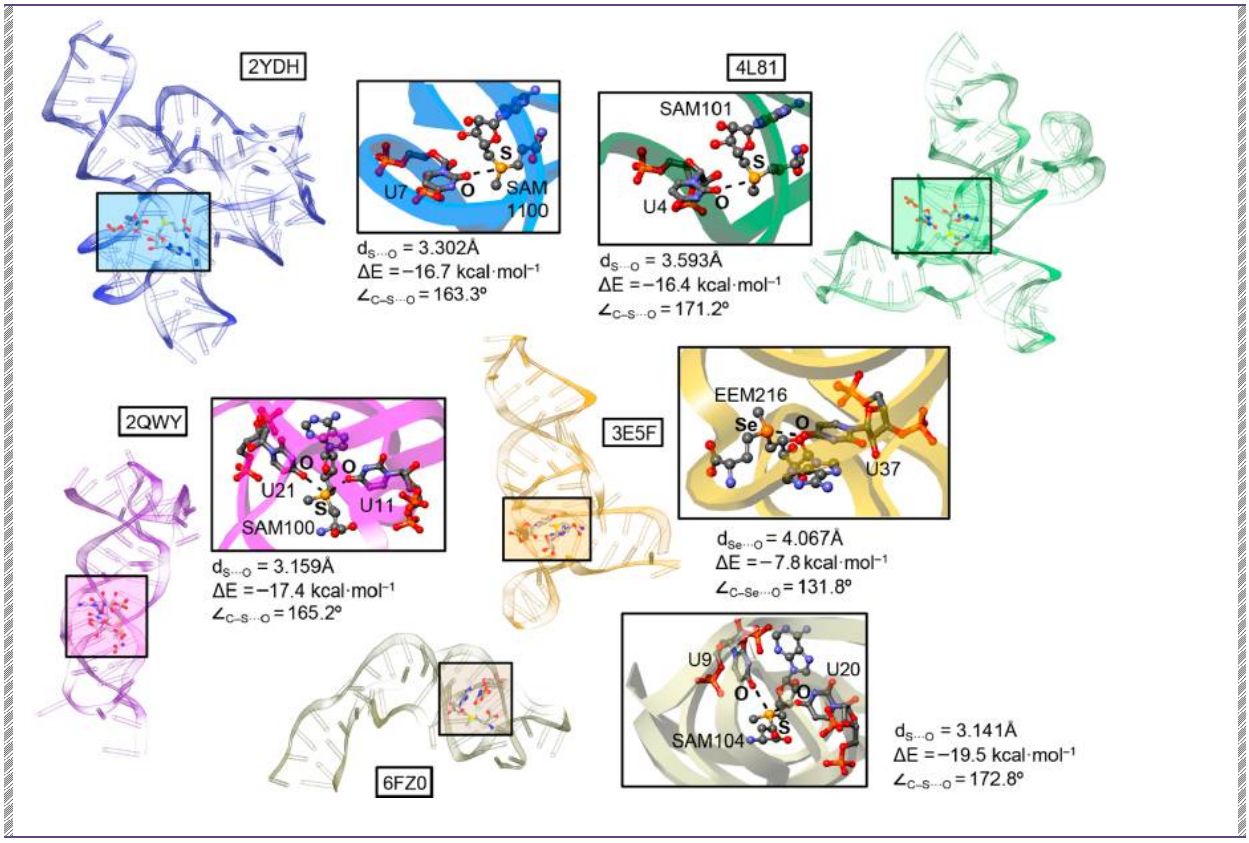

(a)
C1
S1A
H8
Dimer I
(b)
(c)
Cl1
S2
Dimer II
(d)
Dimer II
(e)
S2
Cl1
Dimer II


(a)
H6A
N2
N1
H5A
Dimer III
S1A
(b)
H19
H13B
C6A
Dimer IV
(c)
Dimer V
F1

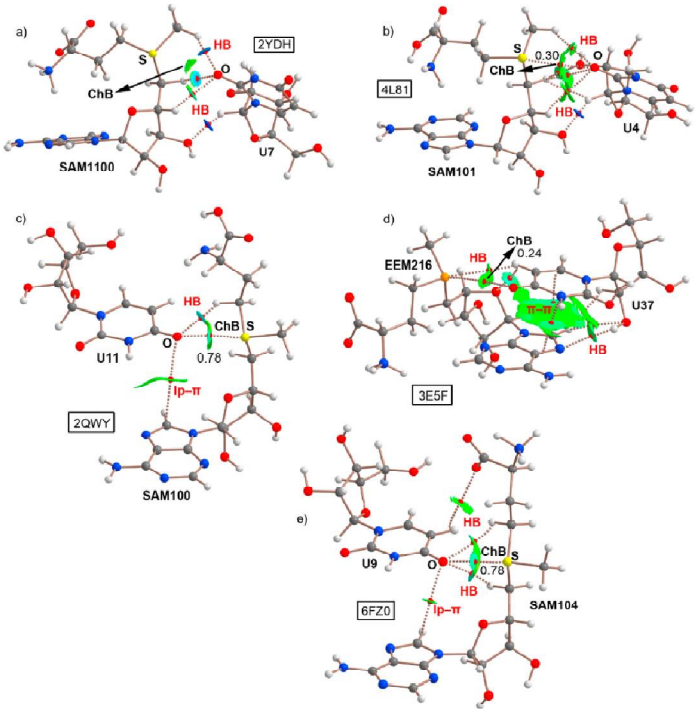
PDP


Charge Assisted Chalcogen Bonds
S
U7
O
SAM
1100
2YDH


a)
b)
+70.9
+110.4
+107.3
+72.8
+112.3
+108.6
S-adenosyl methionine (SAM)
Adenosyl
selenomethionine (EEM)

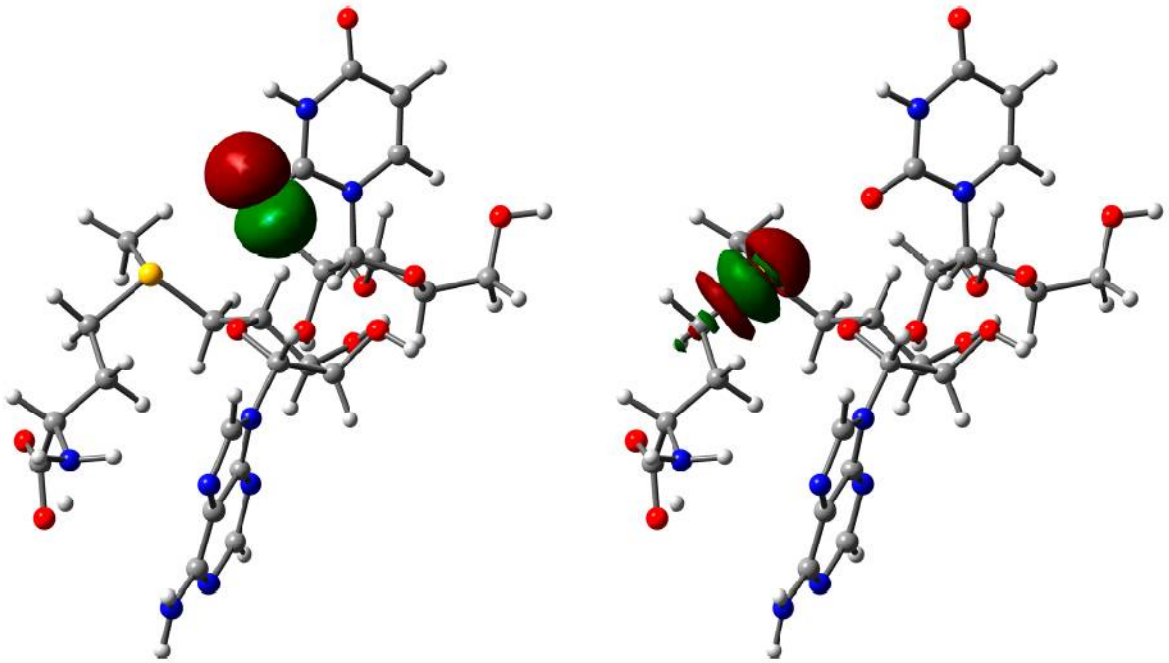


NCI plot analysis and AIM distribution of intermolecular bond critical points

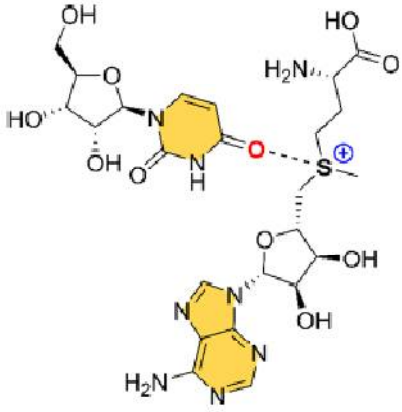


ChB interaction of 2YDH structure

NBO plots of donor (LP O, left) and acceptor (BD* S–C, right) orbitals

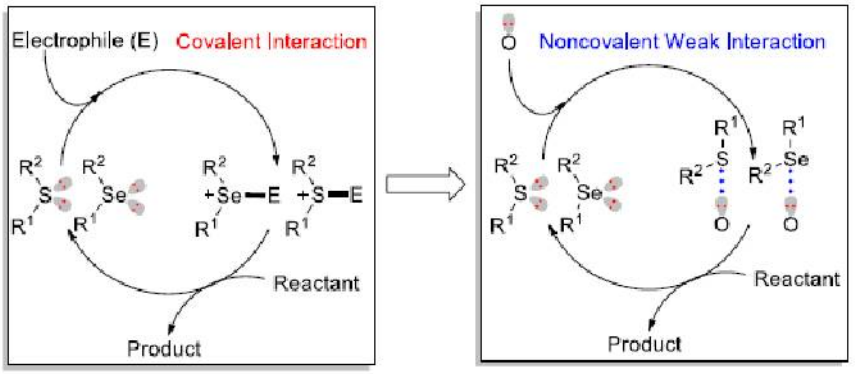


Charge assisted ChB energies



catalysis

Chalcogen Bond (S ; Se)		ChB.	ACS.	**45**
Covalent Lewis-base catalysis		Noncovalent Ch-Ch Bonding catalysis		



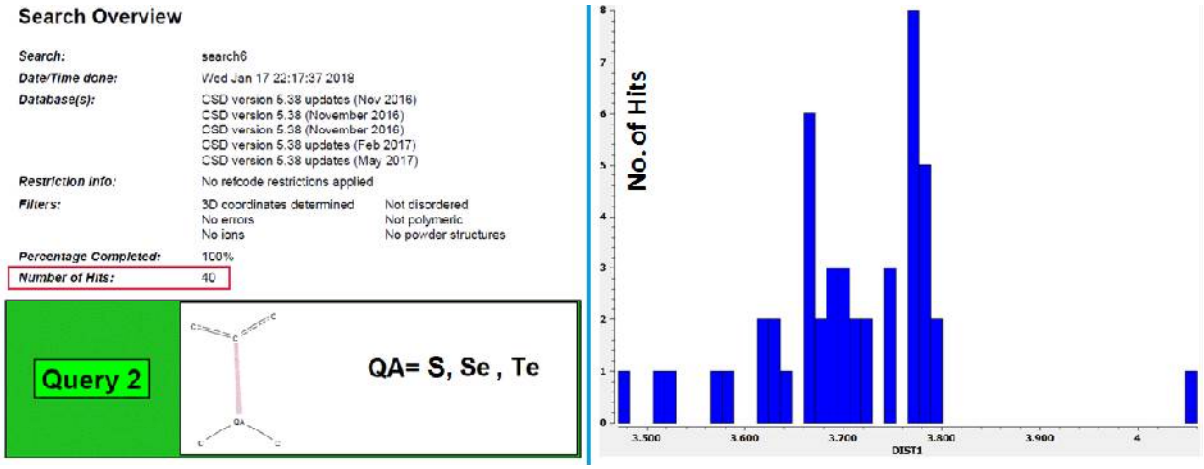
Fundamental Concept:
Covalent Lewis-Base Catalysis

Unknown Chemistry:
Chalcogen-Chalcogen Bonding Catalysis

CSD

Chalcogen Bond [S Se Te]	CSD	ChB.	ACS.	54

CSD Survey



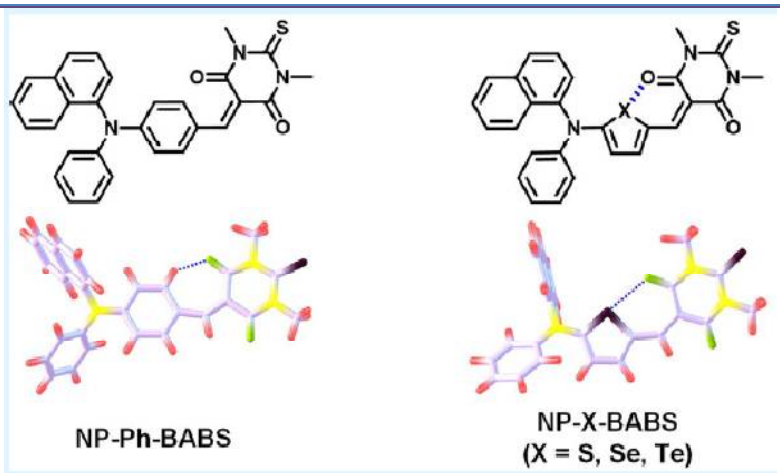
- ✓ Key words :divalent S, Se, and Te interacts with the aromatic rings
- ✓ No of hits: 40

Chalcogen Bond		ChB.	ACS.	05

Experimental	Computational Science

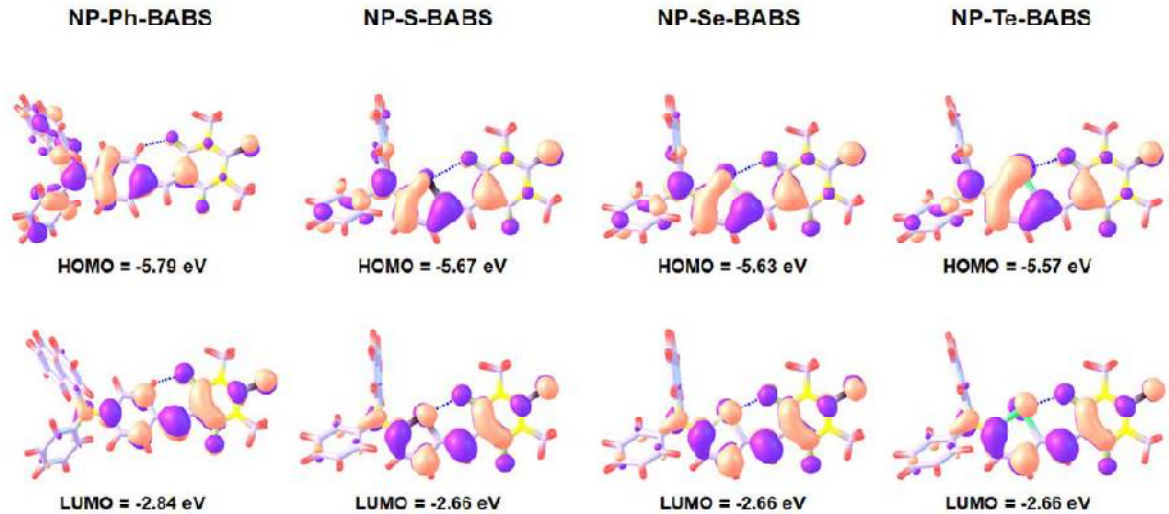
Synthesis	Spectroscopy NMR o 13C NMR; 1H o 13C CP-MAS solid-state NMR o 1H MAS solid-state NMR
	o FT-IR
	o UV-vis
	o Out-of-plane XRD patterns
	Thermal analysis o DSC curves

Comp Quan Chem (CQC)	
DFT	Level of theory
B3LYP	Functional
DGDZVP	Basis set



Energy minimized structures

Frontier molecular orbitals

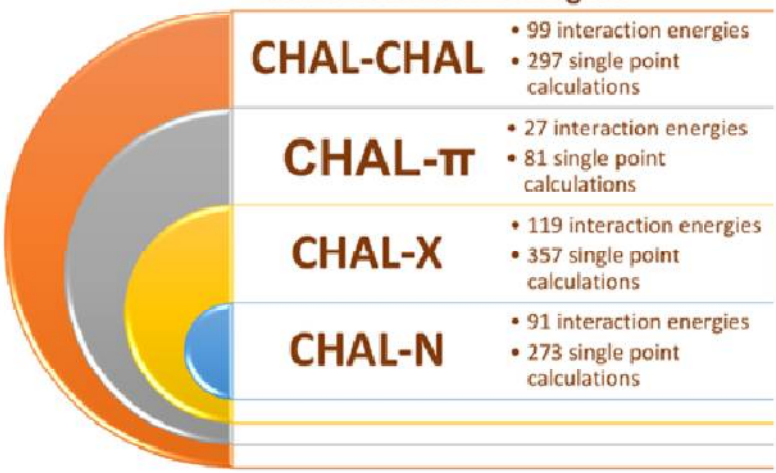


NP-Ph-BABS, NP-S-BABS, NP-Se-BABS, and NP-Te-BABS

Chal336: Bench mark set

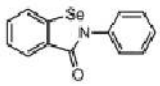
CHAL336 Benchmark Set

1008 single point calculations
336 interaction energies



Lewis structures of Se1–Se7 from CHAL–N subsets

Se1



2-phenylbenzo[*d*][1,2]selenazol-3(2*H*)-one

Se2

1,2-selenazol-3(2*H*)-one

Se3

selenophen-3(2*H*)-one

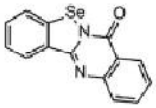
Se4

selenophene

Se5

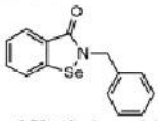
1,2-selenazole

Se6



7*H*-benzo[4,5][1,2]selenazolo[3,2-*b*]quinazolin-7-one

Se7



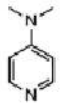
2-benzylbenzo[*d*][1,2]selenazol-3(2*H*)-one

Large nitrogenous bases (N1–N4) used in the CHAL–N subset

N1

pyridine

N2



N,*N*-dimethylpyridin-4-amine

N3

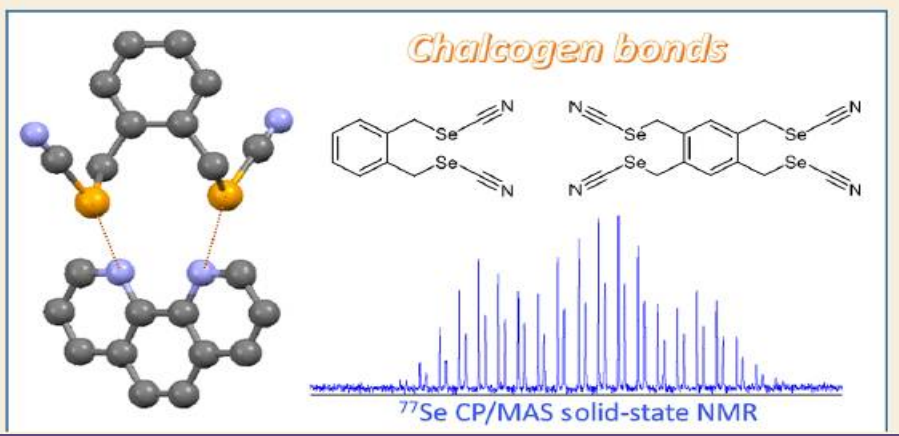
quinuclidine

N4

1,4-diazabicyclo[2.2.2]octane

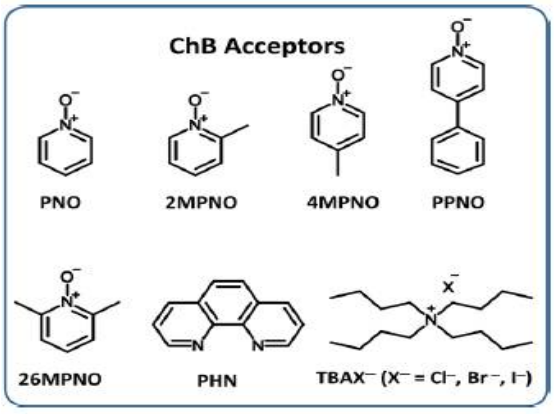
Cocrystals

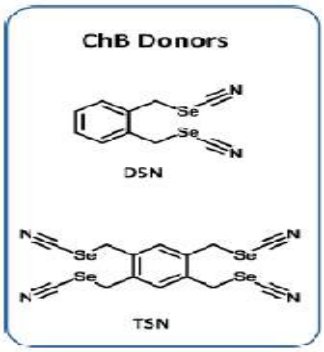
Chalcogen Bond (Se)		ChB.	ACS.	11



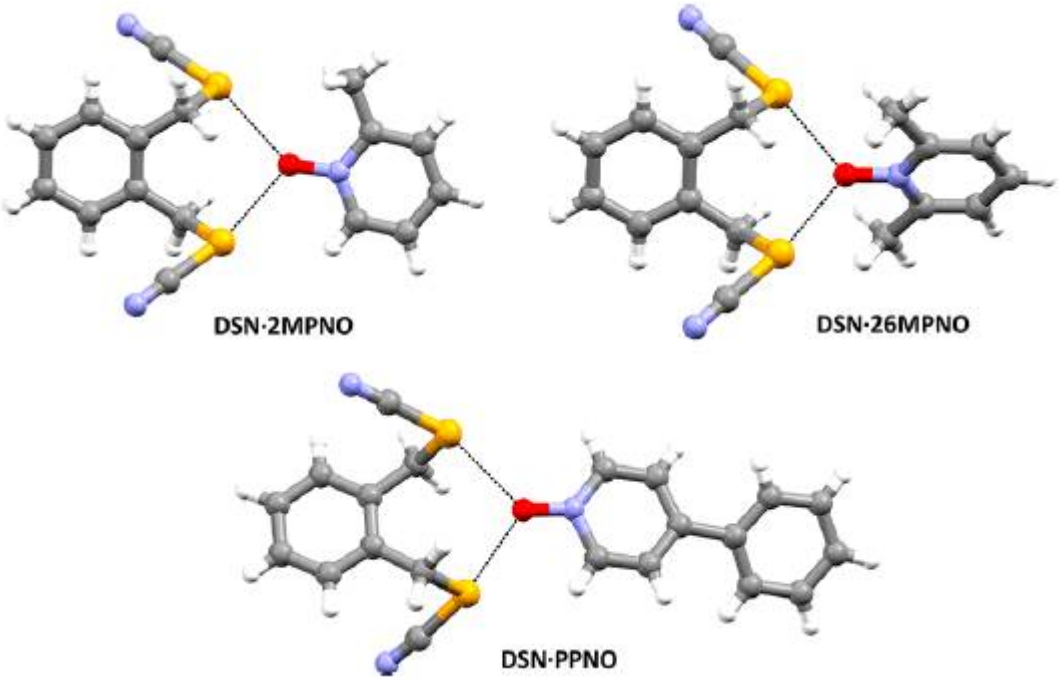
Experimental	
Synthesis	**Spectroscopy**
Preparation of Cocrystals	NMR o ^{77}Se solid-state o ^{77}Se CP/MAS solid-state
	Single-crystal X-ray diffraction

LA	Lewis bases	Complex
+ 1,2-bis (selenocyanatomethyl) benzene (DSN) + 1,2,4,5-tetrakis (selenocyanatomethyl)-benzene (TSN)	o Onium halides o N-oxides o Pyridine-containing heterocycles	ChB



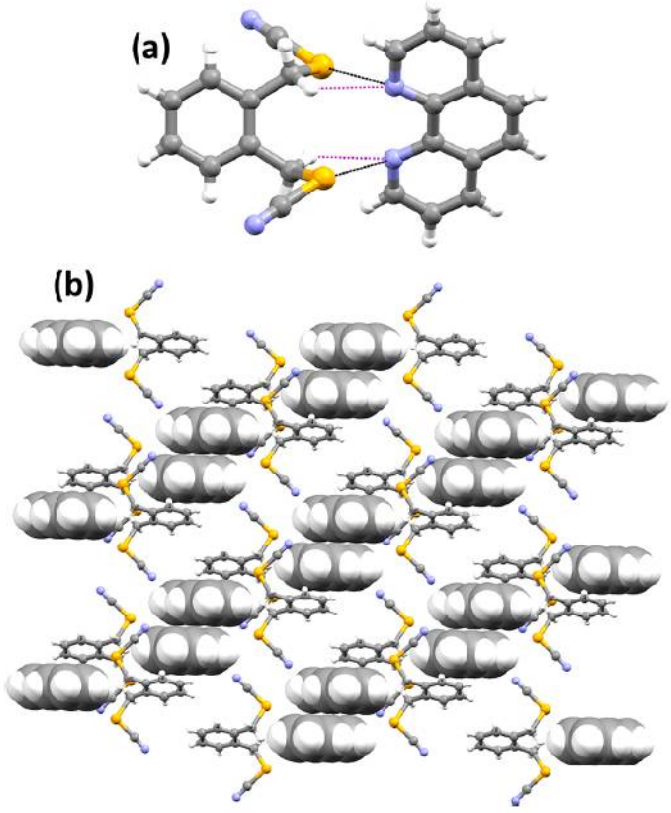


Cocrystals with ChB



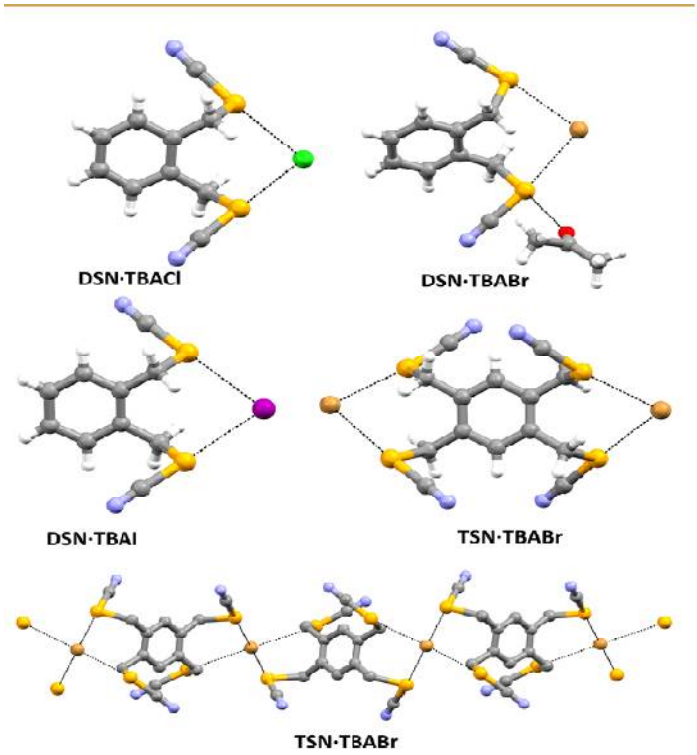
Software: Mercury 4.10.3

Cocrystal(DSN·PHN) with ChB



(b) Infinite chains

Cocrystal(DSN·PHN) with ChB



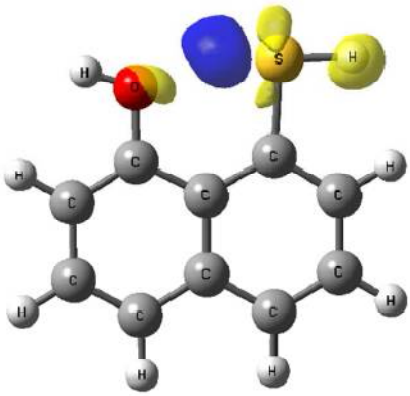
SB ; SeB ; TeB

Sulphur bonds

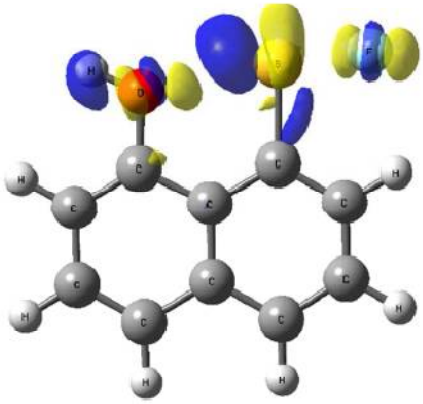
Chalcogen Bond (S)		ChB.	ACS.	57

Electron density shift maps

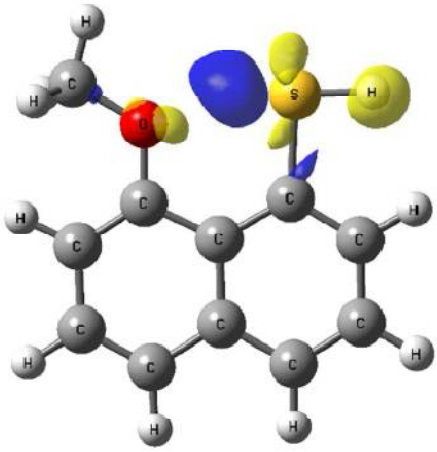
(MP2/jul-cc-pVDZ)



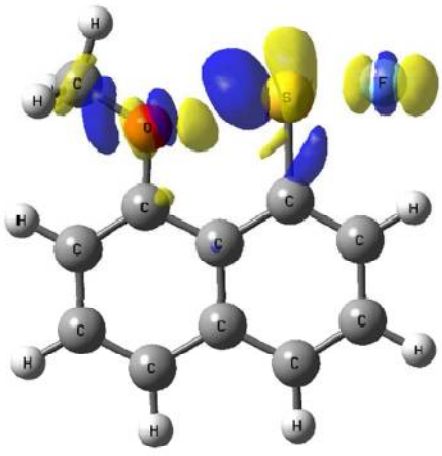
a) $O^{H}S^{H}$



c) $O^{H}S^{F}$



b) $O^{Me}S^{H}$

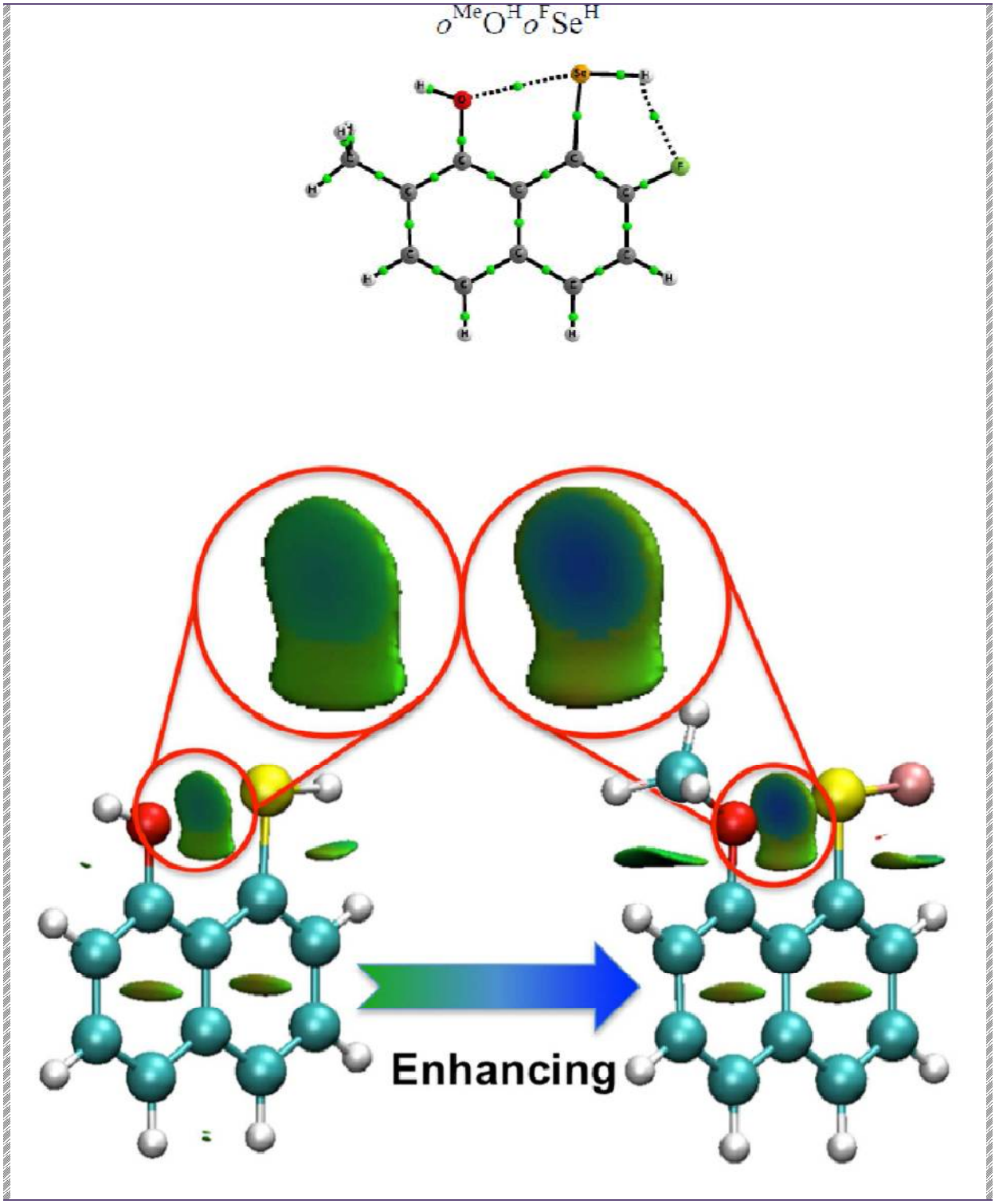


d) $O^{Me}S^{F}$

Electron density properties at

bond critical point

between O and T interacting atoms


$o^{Me}O^{H}o^{F}Se^{H}$
Enhancing

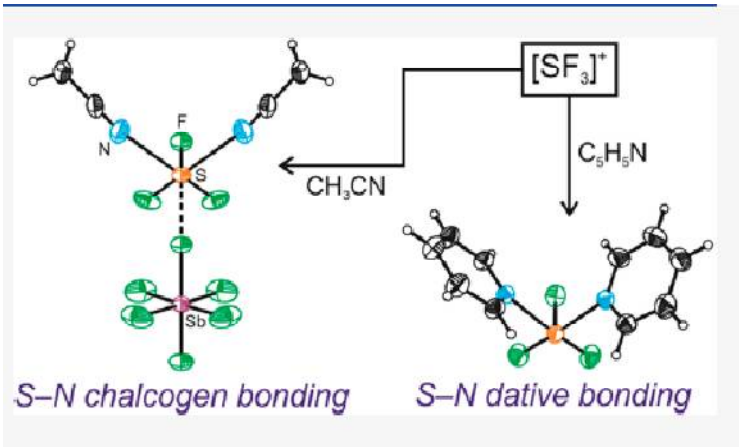
Synthesis

Instrument

➔ ^{19}F NMR

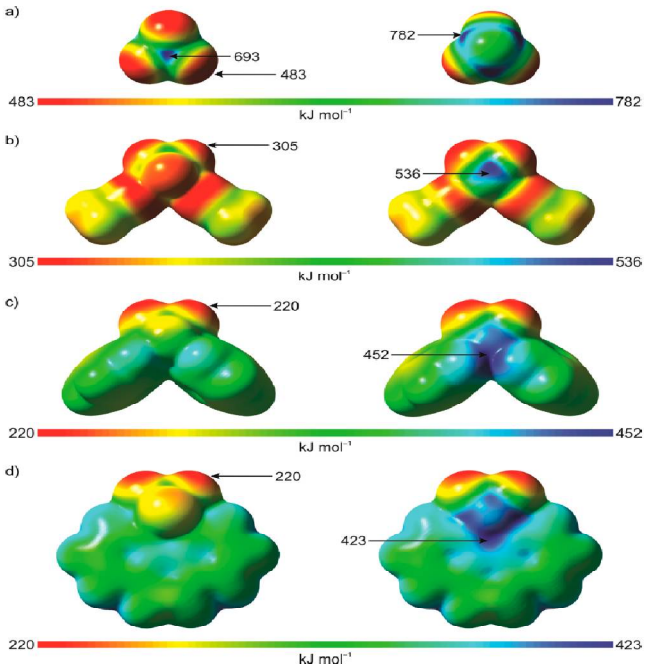
o Geom. Opt. o Natural Population Analysis	Gaussian 09 (rev. D.01)
➔ NBO analyses	NBO (ver. 6.0)
▪ Vibrational modes ✓ Visualization ✓ Assignment	GaussView (ver. 6.0)

Method	Tools
DFT	Level of theory
B3LYP	Functionals
aug-cc-pVTZ	Basis set



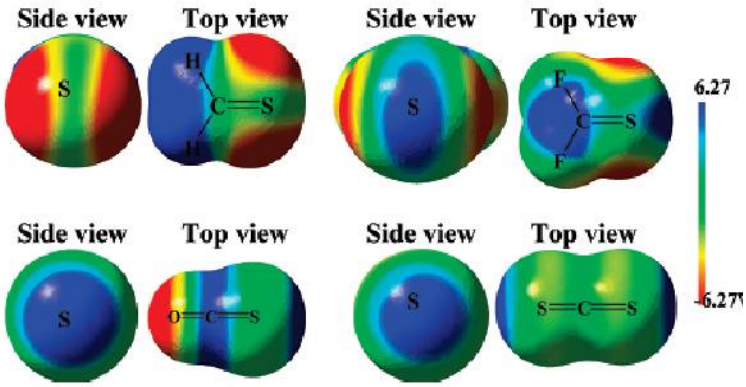
ESP

(a) [SF3]+, (b) [SF3(NCCH3)2]+, (c) [SF3(NC5H5)2]+, and (d) [SF3(phen)]+

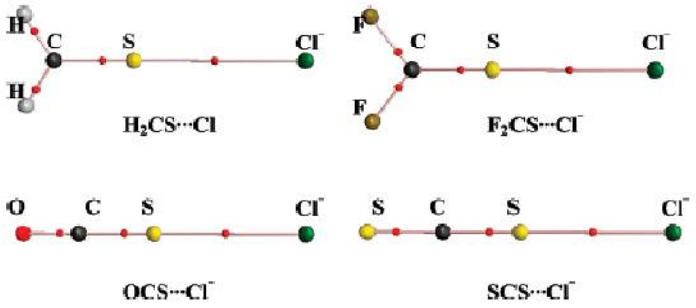


Opposite (left) and along (right) the lone pair on sulfur

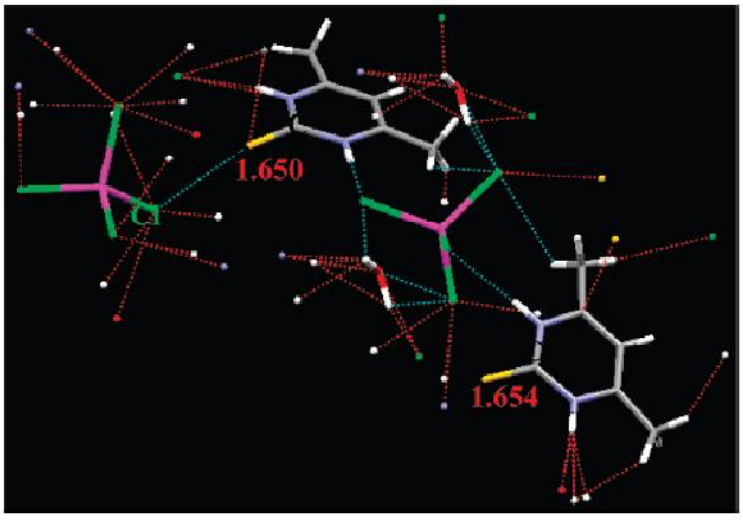
ESP H2CS, F2CS, OCS, and SCS
MP2/aug-cc-pVTZ



Structures of chalcogen-bonded complexes



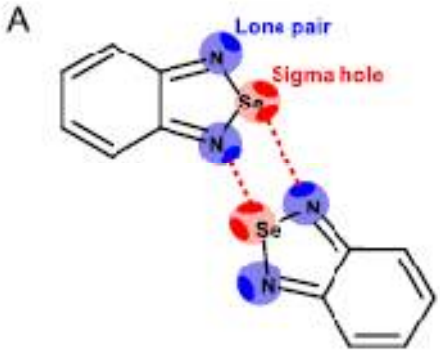
Crystal structure of bis(4,6-dimethyl-2-thiopyrimidinium) tetrachlorozincatum(II) monohydrate



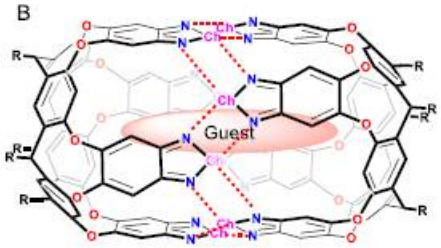
Chalcogen-bonded supra-Molecular capsules		Cavitand with 2,1,3-benzo-Selenadiazole	
Expt	o Single-crystal X-ray in solid state o High-resolution NMR ; o DOSY in solution	**Comp. Chem**	o CQC
Inference		✓ ChB persists in water in competition with the forces of HB	

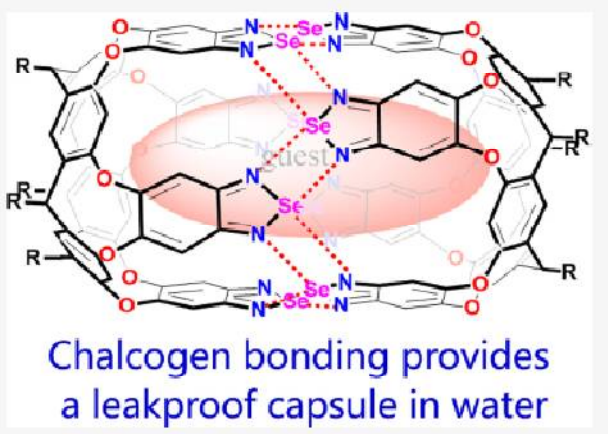
Chalcogen bonding between Se···N in 2,1,3-benzoselenadiazoles

A

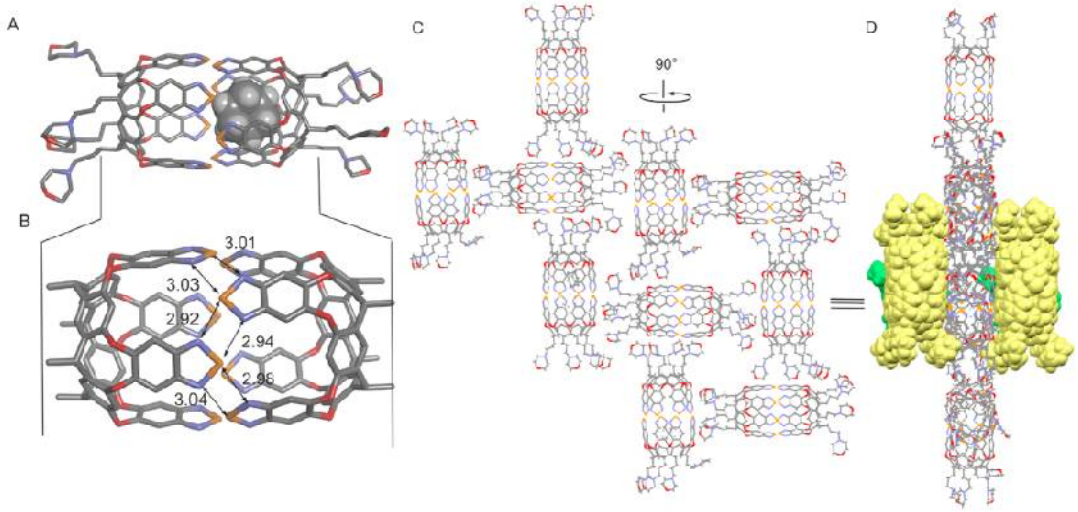


B



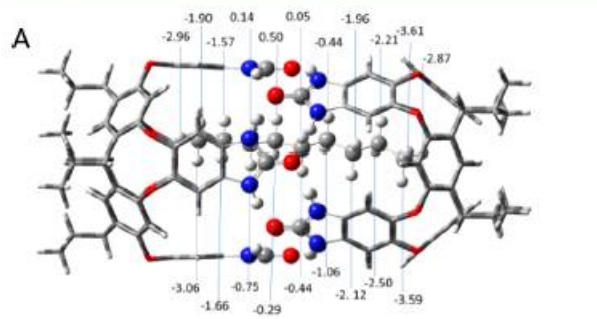


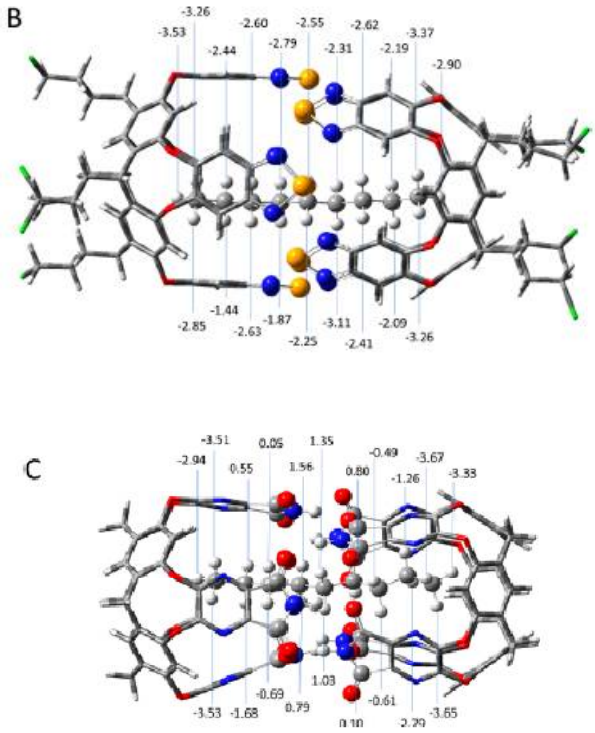
Single-crystal X-ray structure of 3



(A) Dimeric capsule containing one cyclohexane molecule
(B) Close-up of circular array of chalcogen bonds stabilizing capsular dimer with distances in angstroms
(C) Packing of perpendicularly oriented dimeric capsules into rods, which further assemble into layers
(D) Planar layer rotated 90° and sandwiched between two rods

Spectra.CQC		
NMR	1H	chemical shifts
PBE0		functionals
/6-31G(d,p))		basis set

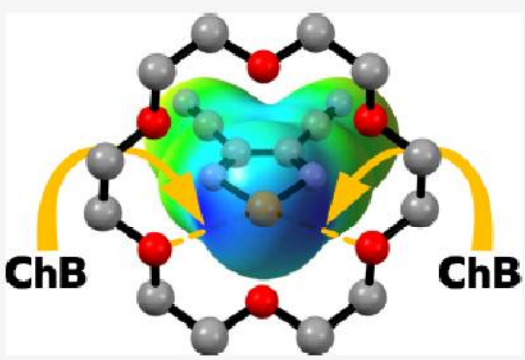




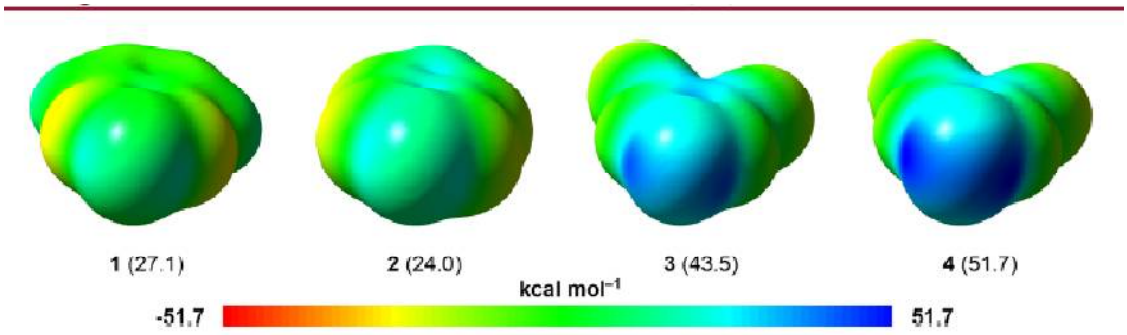
(A) benzimidazolone
(B) benzoselenadiazole
(C) pyrazine-imide walls

Chalcogen Bond (Se)		ChB.	ACS.	**33**

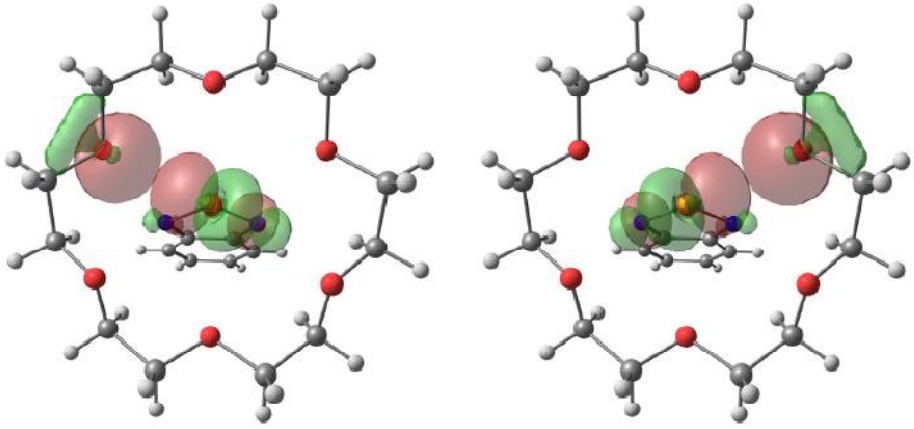
Experimental		Computational Science
Synthesis	Spectroscopy X-ray	Comp Quan Chem (CQC) NBO
	Thermal TG/DSC	



MEPs	
σ– holes	|e|·VS,max,
B3LYP/def2-tzvp	Functionals
ECP for Te	Basis set



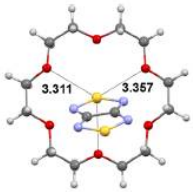
complex [18-c-6]



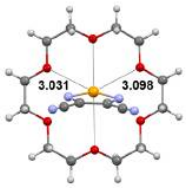
- ✓ Pairs of most strongly interacting localized orbitals
  - o including ELP of the O-atom of 18-c-6
- ✓ σ*-orbitals of the S– N

Shortened E···O contacts
XRD structures

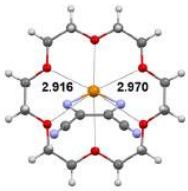
[18-c-6][1]



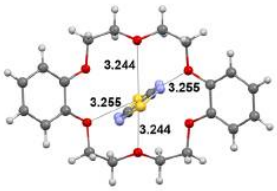
[18-c-6][2]



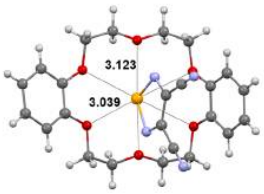
[18-c-6][3]



[18-c-6][4]

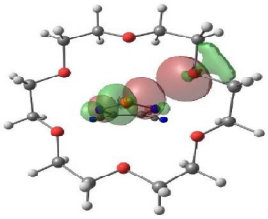


[db-18-c-6][2]

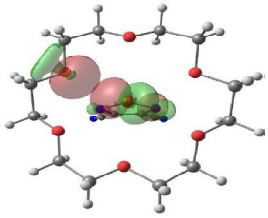


[db-18-c-6][3]

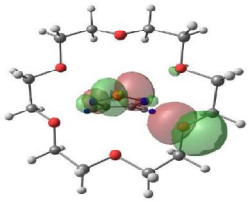
[18-c-6][3] with 18-c-6 as D $$$



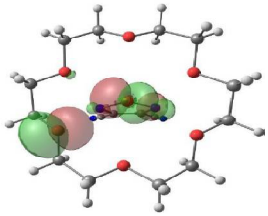
ELP O10 ↔ BD* Se1–N3



ELP O32 ↔ BD* Se1–N2



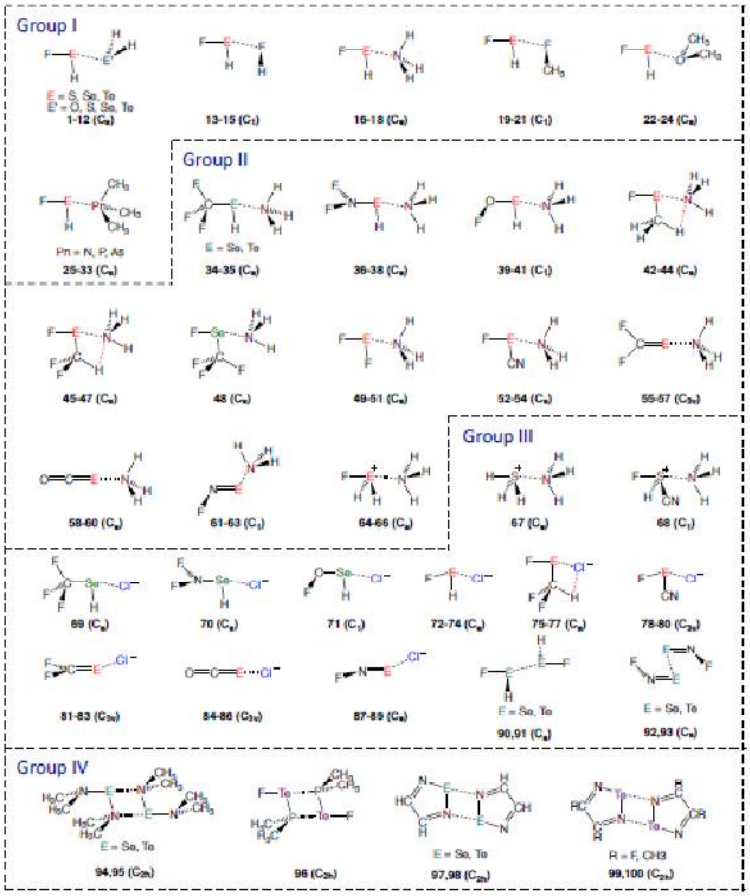
ELP O11 ‹ › BD* Se1–N3

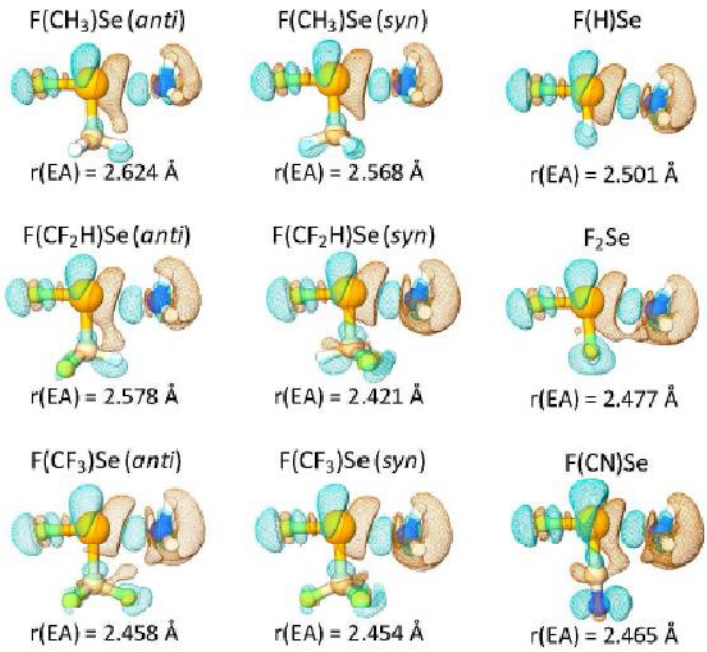


ELP O31 ‹ › BD* Se1–N2

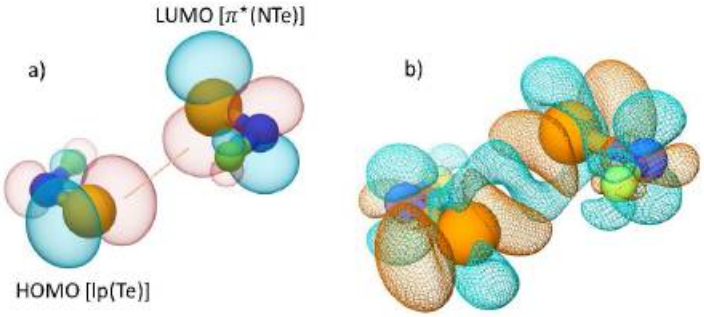
Interacting localized orbitals with high interaction energies

Structures of complexes 1 – 100

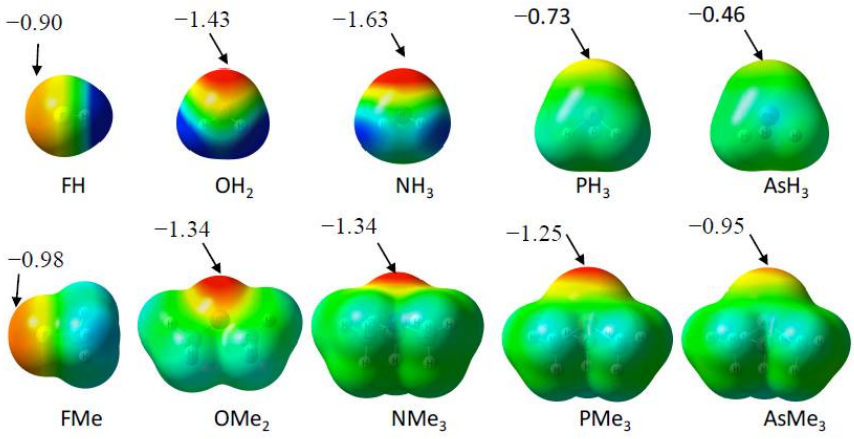




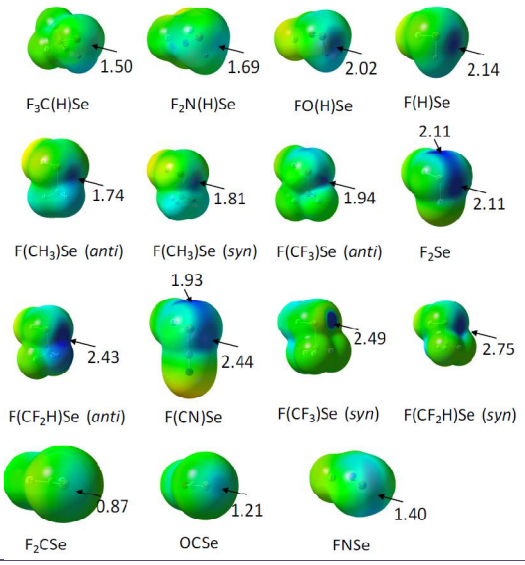
Electron difference density distributions



Frontier molecular orbitals of $FNTe_2$

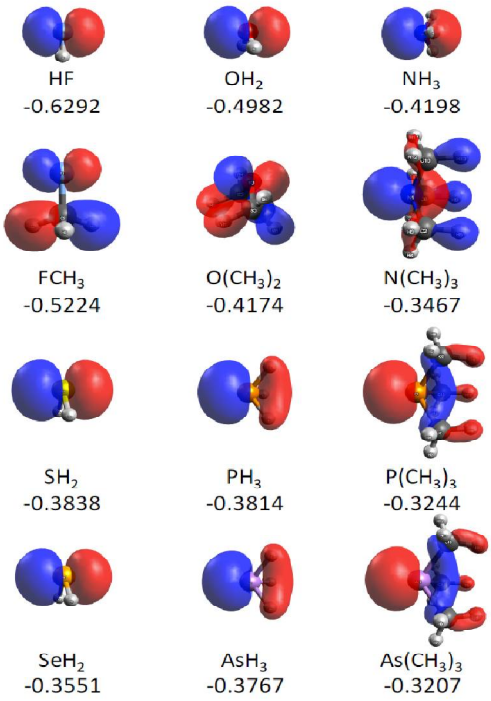


ESP (minimum) of chalcogen acceptors



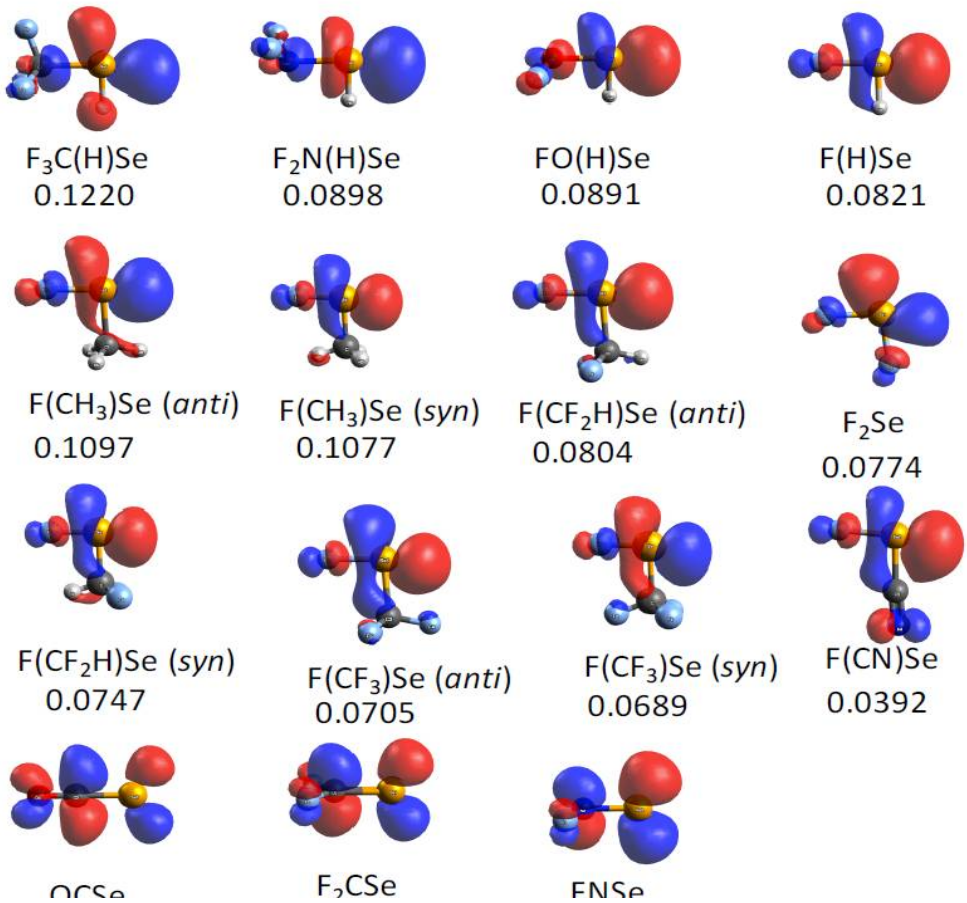
ESP (maximum) of chalcogen donors

HF/6-31g(d)



HOMO of chalcogen acceptor (energy in Hartree)

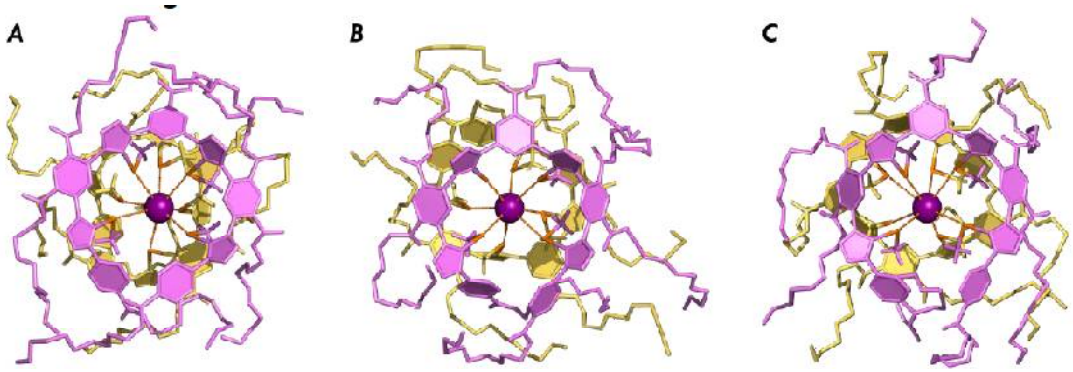
HF/6-31g(d)



LUMO of the chalcogen donors (energy in Hartree)

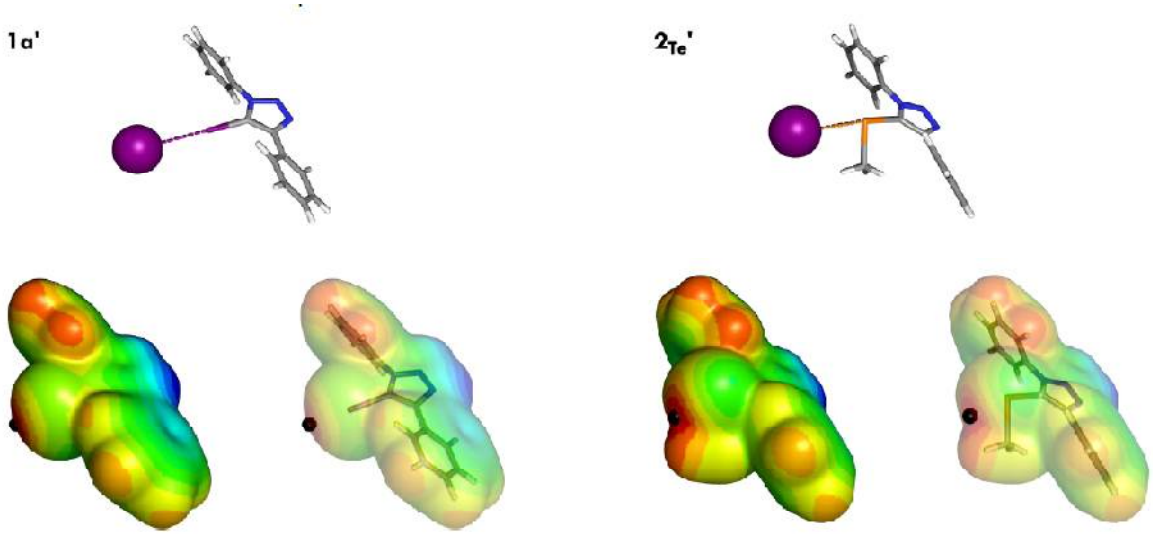
Comp Quan Chem (CQC)	
CQC	Gaussian 09
Molecular Mechanics (MM) energy minimisations classical force field calculations	AMBER 2016
Molecular Dynamics (MD) simulations	

MM structures of the 2:1 host-guest complexes of 2Te
ChB interactions in orange dashed lines



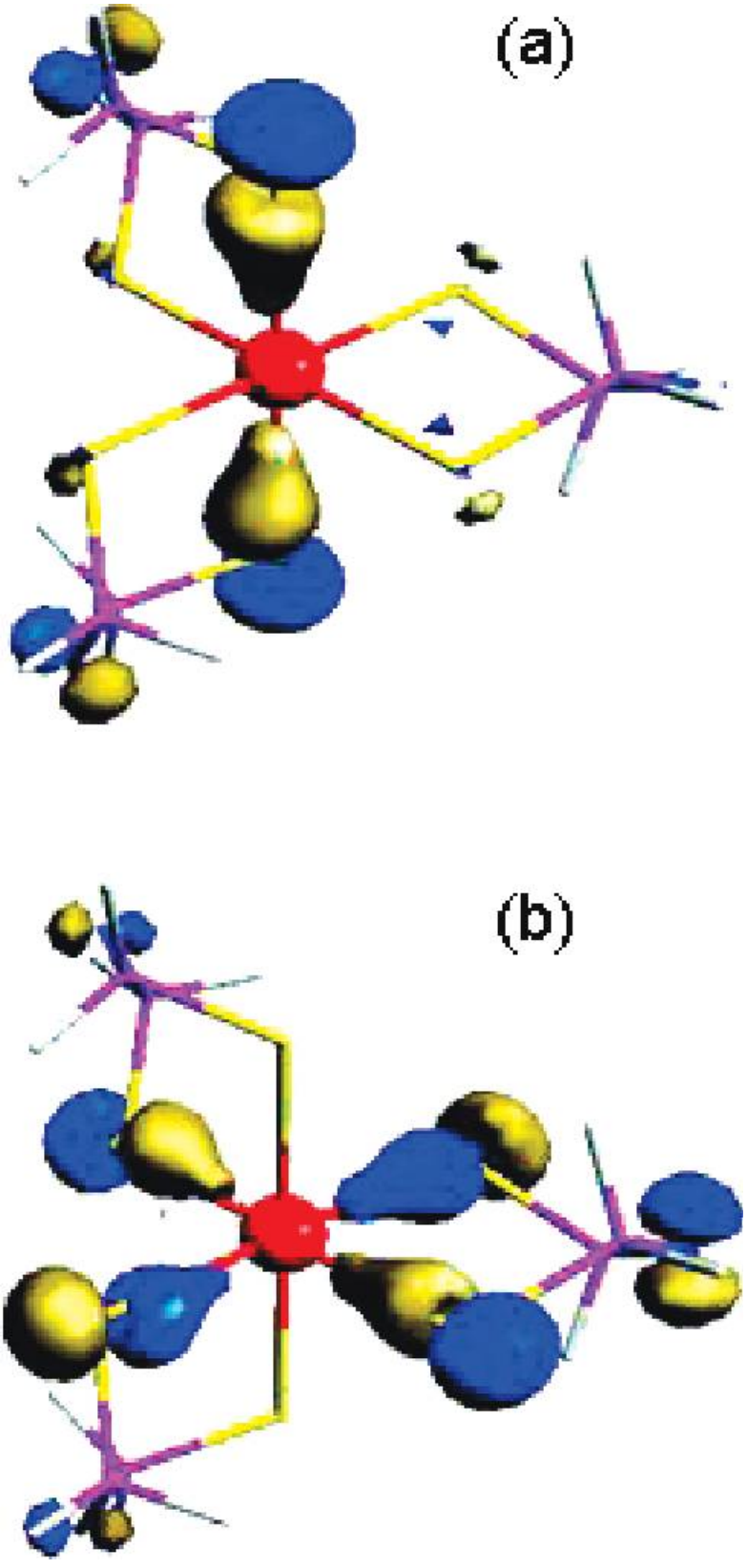
MD Movie	Movie of a selected MD run of the 2:1 host-guest iodide complex of **1a** in binding arrangement *C* (between the 51st and 80th ns), showing how the flexible PEG-side chains (shown as space filling) open/close the equatorial (left view) and axial (right view) holes of the dimeric capsule, thus limiting the access of the water molecules to the centre of the binding cavity

DFT Optimised structures of iodide model complexes of 1a' and 2Te'

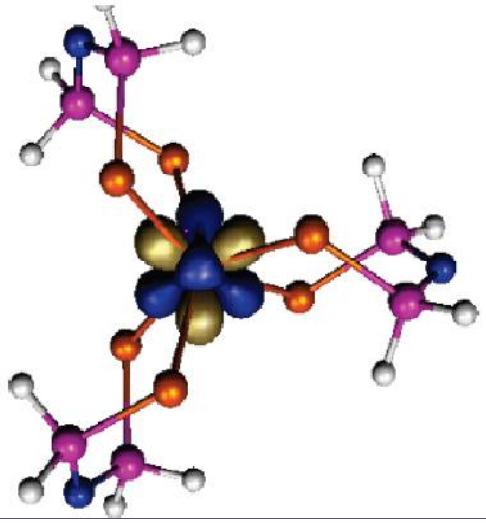


ESO f1a' and 2Te', after removal of the iodide
Dashed lines -- Purple: halogen Bonds; orange: chalcogen bonds

Am[N(SPH2)2]3
orbitals 39 and 40



f Element (Am)-Chalcogen Bond
Orbital 39 in six-coordinate Am[N(TePH2)2]3

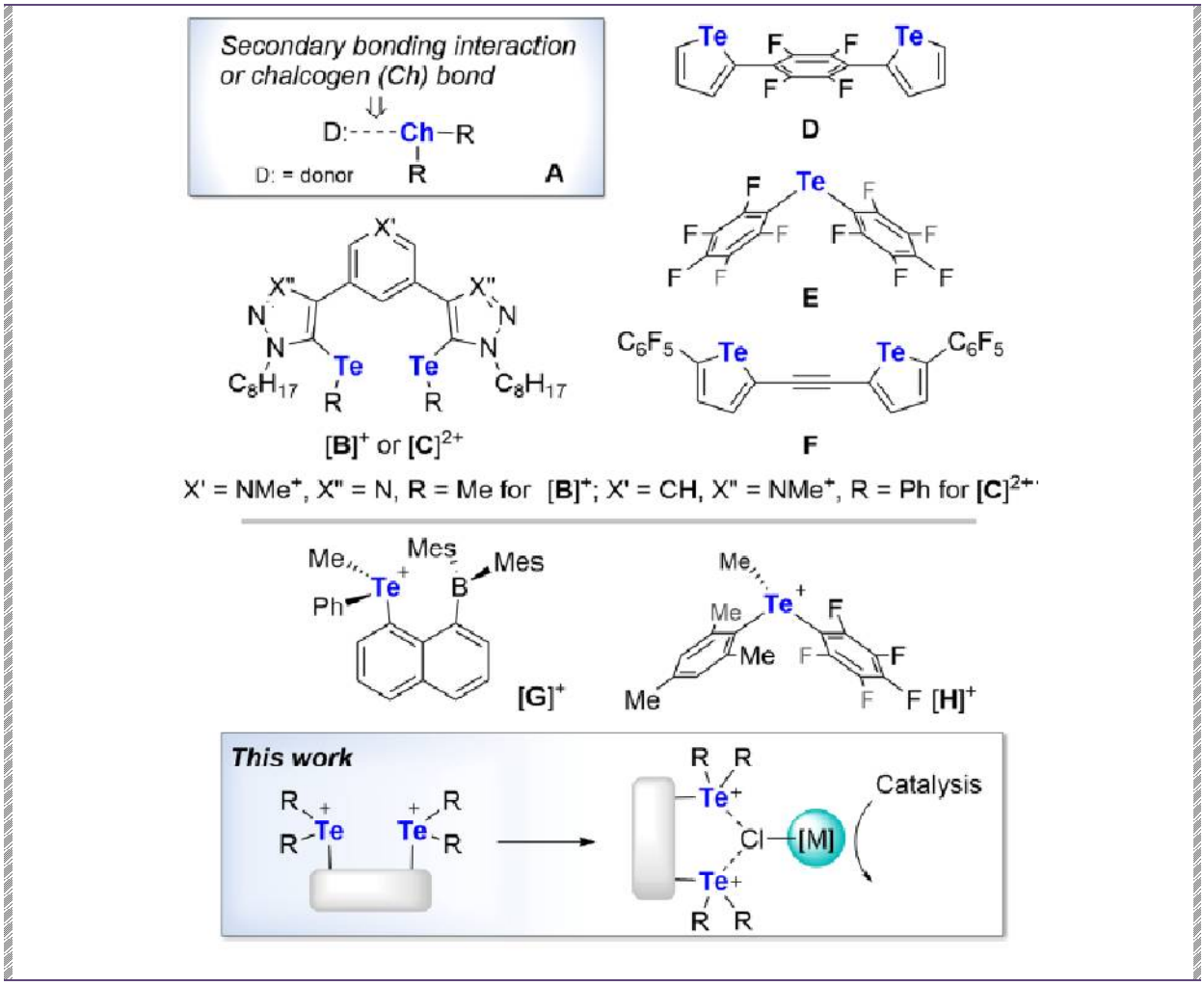


Te(IV)B ; Te(II)B

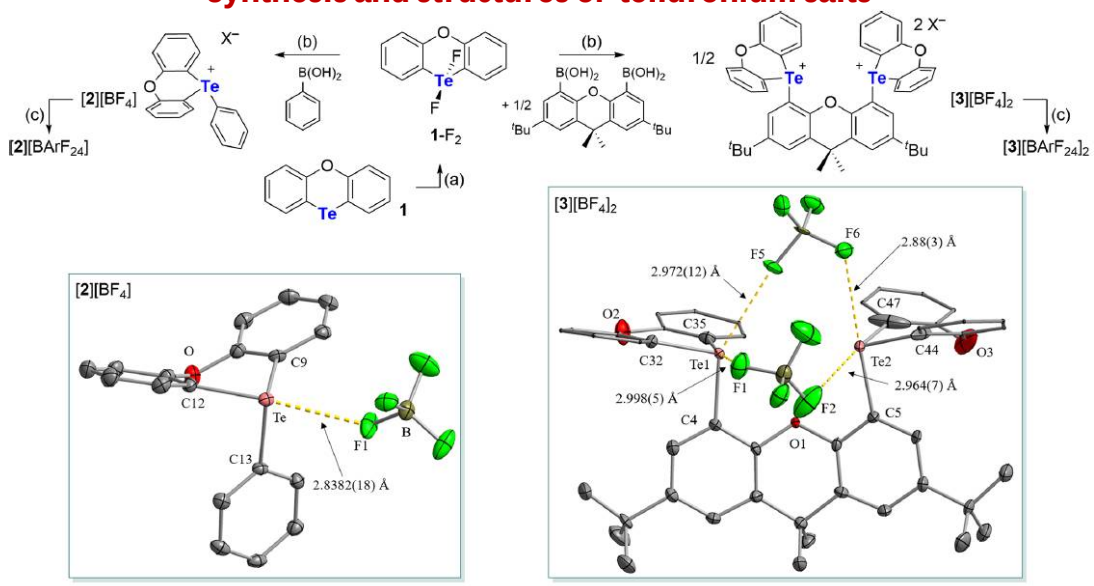
Chalcogen Bond **[Te(II) ; Te(IV)]**		ChB.	ACS.	**18**

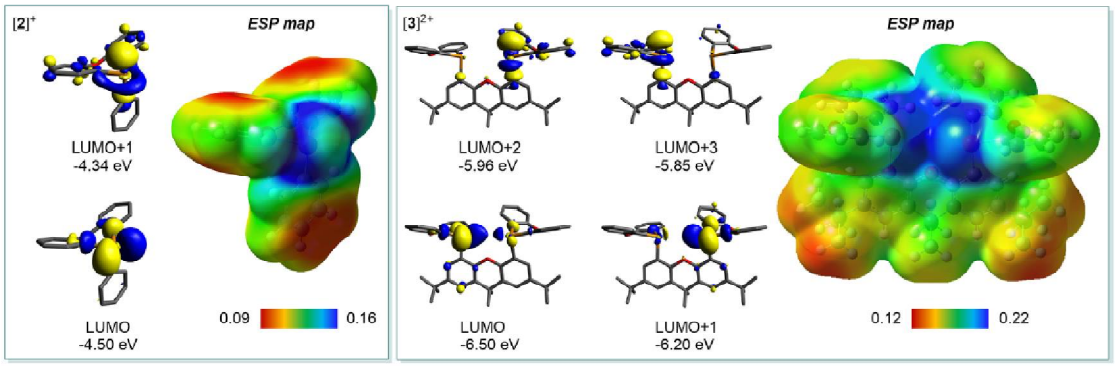
Experimental	
Synthesis	**Spectroscopy**
	➔ NMR o 13C o 19F o 1H o ^{125}Te
	➔ UV-Vis

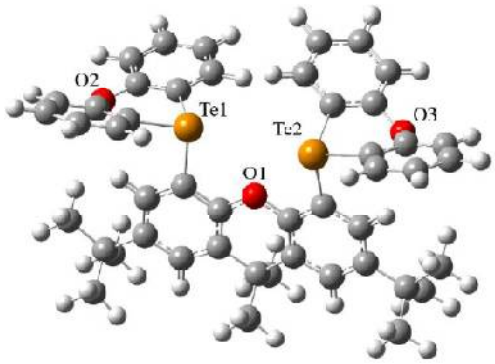
Chalcogen Bonding Concept
ChA: [Te(II) ; Te(IV)]



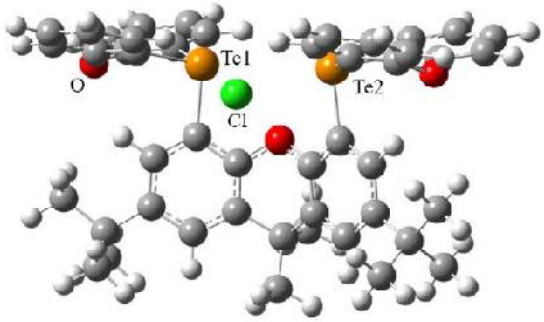
Synthesis and structures of telluronium salts







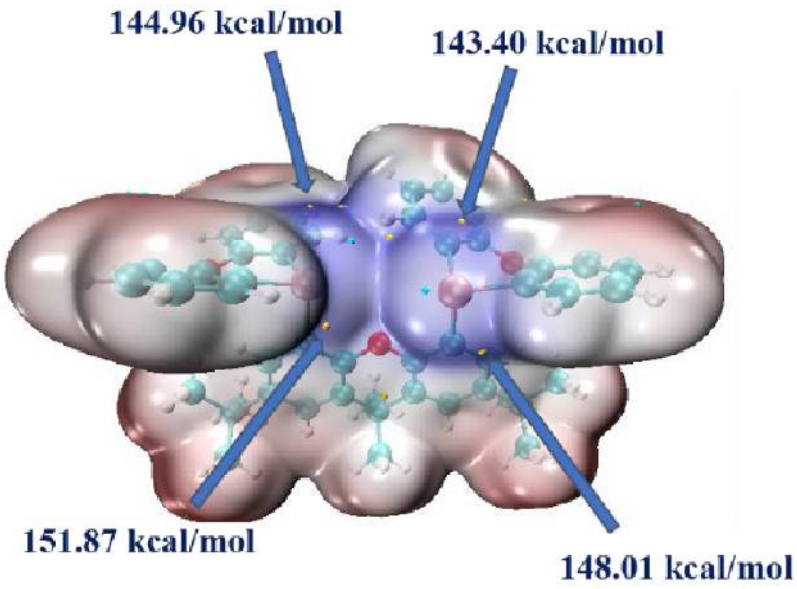
Optimized structure of $[3]^{2+}$



Optimized structure of $[3\text{-}Cl]^{+}$.

ESP

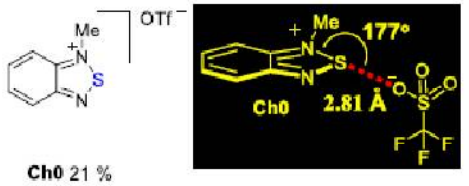
Software : Multiwfn12 and VMD



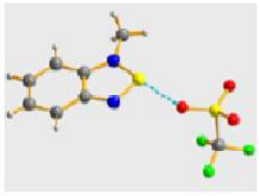
Chalcogen Bond (S ; Se)		ChB.	ACS.	**45**

Noncovalent

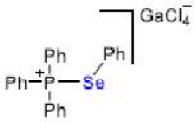
Ch-Ch Bonding catalysis



Ch0 21 %

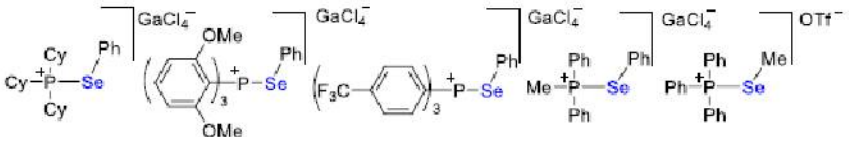


X-ray crystal structure of **Ch0**

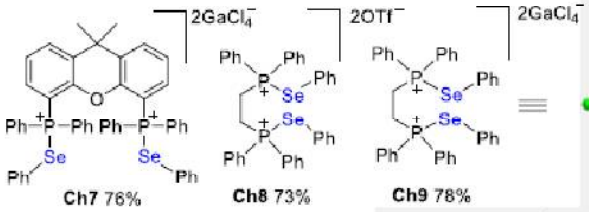


Ch1

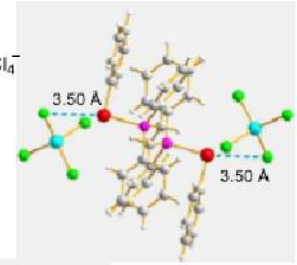
Ch1 (0 mol %), no reaction
Ch1 (15 mol %), 22%
Ch1 (15 mol %), $NaBF_4$ (30 mol %), 48%
Ch1 (15 mol %), $NaBF_4$ (30 mol %), Na_2SO_4 (0.5 g), 71%
Ch1 (15 mol %), $NaBAr^F_4$ (30 mol %), Na_2SO_4 (0.5 g), 52%
Ch1 (0 mol %), $NaBF_4$ (30 mol %), Na_2SO_4 (0.5 g), no reaction
$NaBF_4$ and Na_2SO_4 were used for catalysts **Ch0**-**Ch10**.

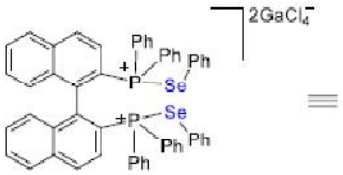


Ch2 34% **Ch3** 19% **Ch4** 57% **Ch5** 59% **Ch6** <5%

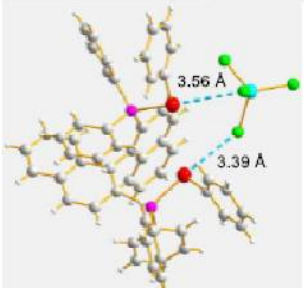


Ch7 76% **Ch8** 73% **Ch9** 78%

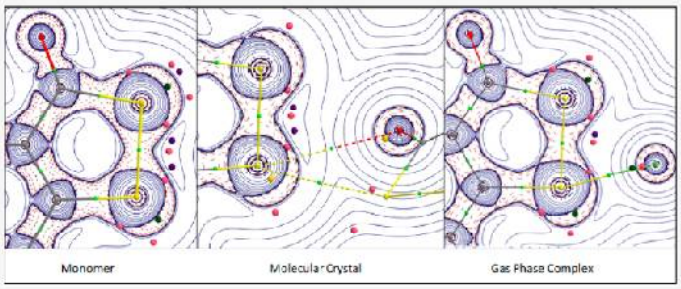




Ch10 65%

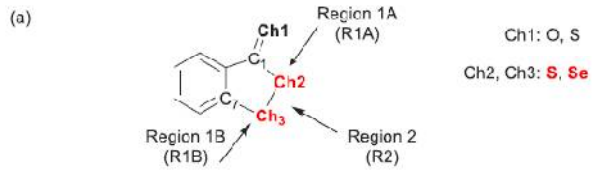


Chalcogen Bond (S ; Se)		ChB.	ACS.	**27**

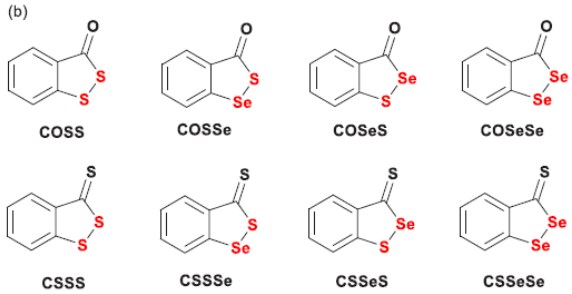


Electron density ρ(r)	Weak nature of the ch−ch bond
Topological properties of ρ(r)	Indicate strength of ChB
Σ-Hole and lone-pair regions	Charge depletion (CD) Charge concentration (CC) sites Found in the valence shell of chalcogen atoms
Topological critical points of l(r) = −∇2ρ(r)	CD and CC sites
L/ρ magnitudes	Electrophilic and nucleophilic powers
$[(L/\rho)_{CC} - (L/\rho)_{CD}]/d_{CC\cdots CD2}$.	Intensity of the electrophilic⋯ Nucleophilic interaction
Reactivity surfaces ∇2ρ(r) = 0,	Signature of the charge redistribution that involves the nucleophilic attack

1,2-Dichalcogenole Series

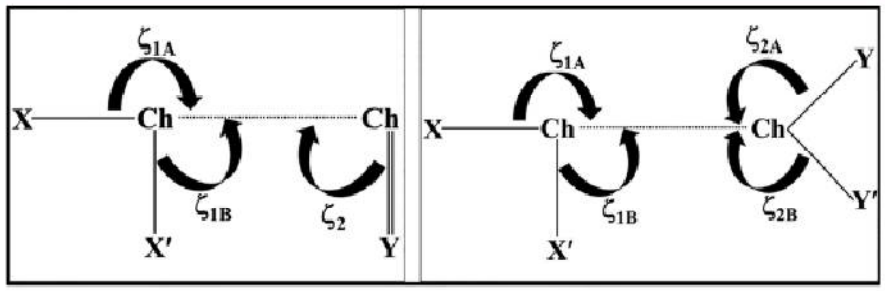


Examples

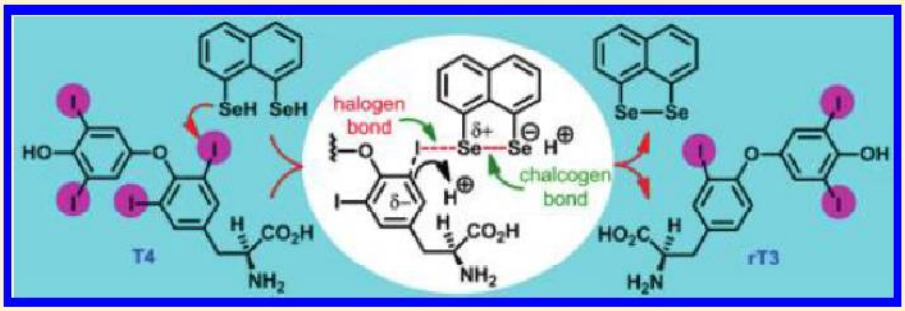


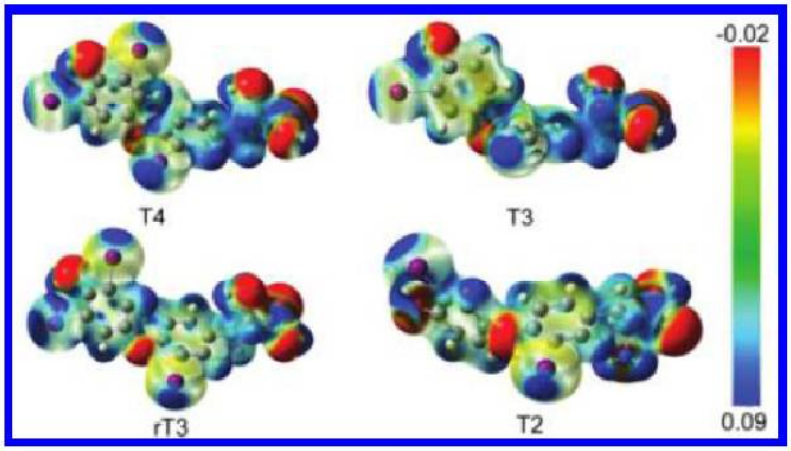
Possible σ-Hole Regions around Dichalcogenide Ch2 – Ch3 Bond

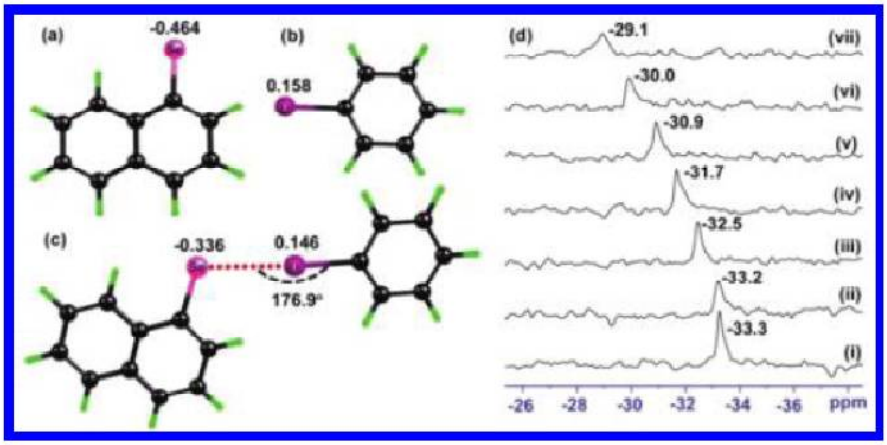
Synthesis	CQC Topological Analyses Geometrical Description of Chalcogen Bond

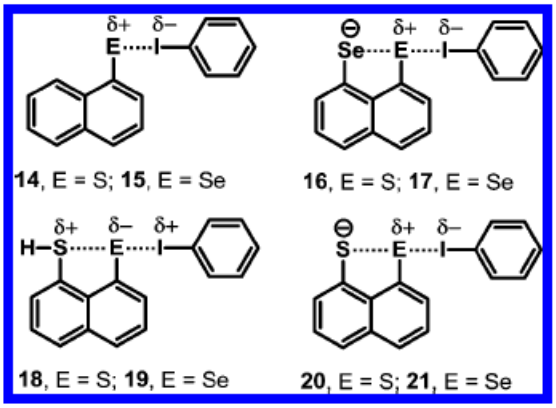


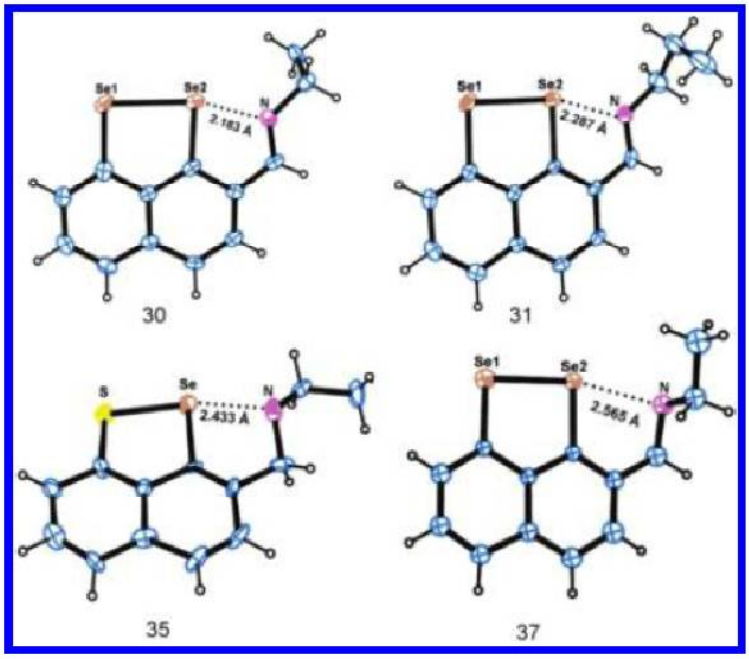
Chalcogen Bond [S ; Se]	HaB (I)	ChB.	ACS.	91

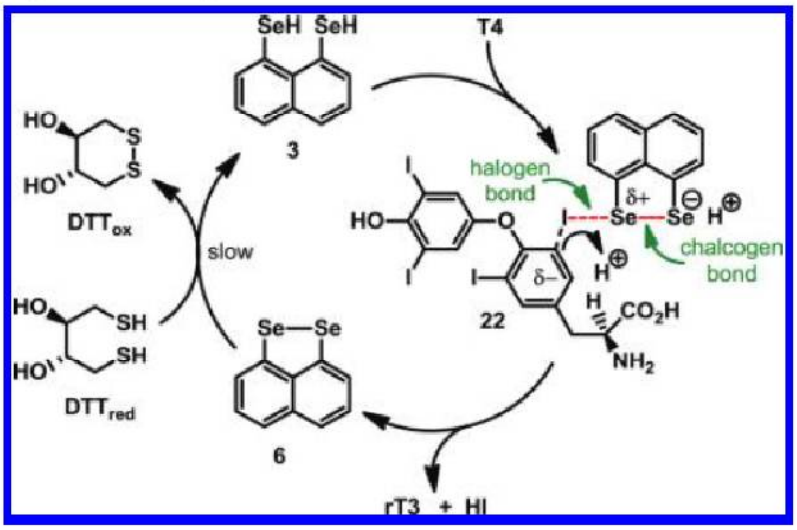





(a)
-0.464
(b)
0.158
(c)
-0.336
0.146
176.9°
(d)
-29.1
(vii)
-30.0
(vi)
-30.9
(v)
-31.7
(iv)
-32.5
(iii)
-33.2
(ii)
-33.3
(i)
-26
-28
-30
-32
-34
-36
ppm

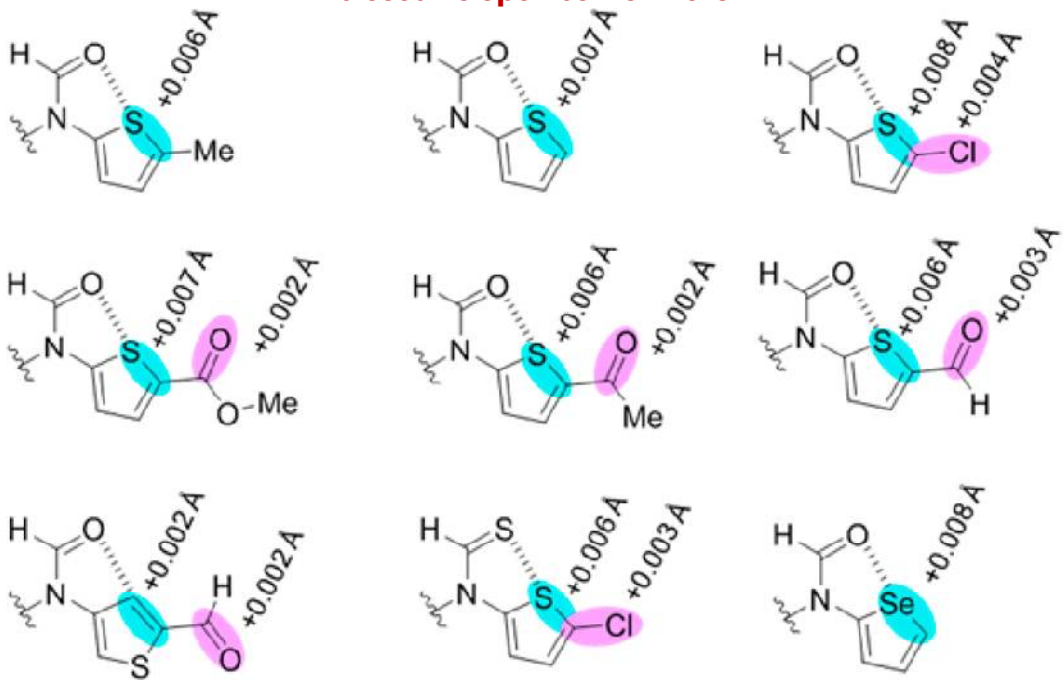

δ+ δ−
E····I
14, E = S; 15, E = Se
⊖ δ+ δ−
Se····E····I
16, E = S; 17, E = Se
δ+ δ− δ+
H–S····E····I
18, E = S; 19, E = Se
⊖ δ+ δ−
S····E····I
20, E = S; 21, E = Se


Se1
Se2
N
2.183 Å
30
2.287 Å
31
S
Se
2.433 Å
35
2.565 Å
37



Chalcogen Bond [S se]		ChB.	ACS.	59

Bond lengthening (B3LYP/6-311G*) in the closed vs open conformers

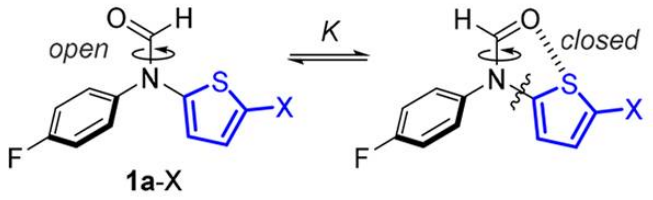


Chalcogen Bond [S se]		ChB.	ACS.	59

Molecular balances
Chalcogen-bonding interactions
^{13}C -NMR NOESY

FORMAMIDE BALANCES

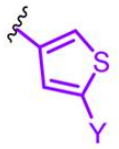
A α-thiophenes



1a-X

X = H, Me, Cl, COMe, CHO, COOMe

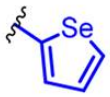
B β-thiophenes



1b-Y

Y = H, Me, CHO

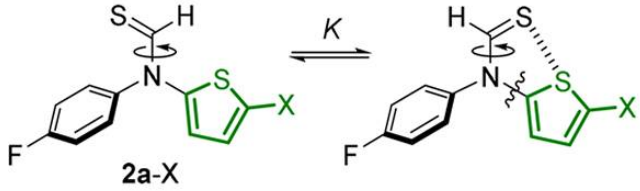
C selenophene



1c

THIOFORMAMIDE BALANCES

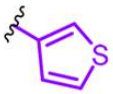
D α-thiophenes



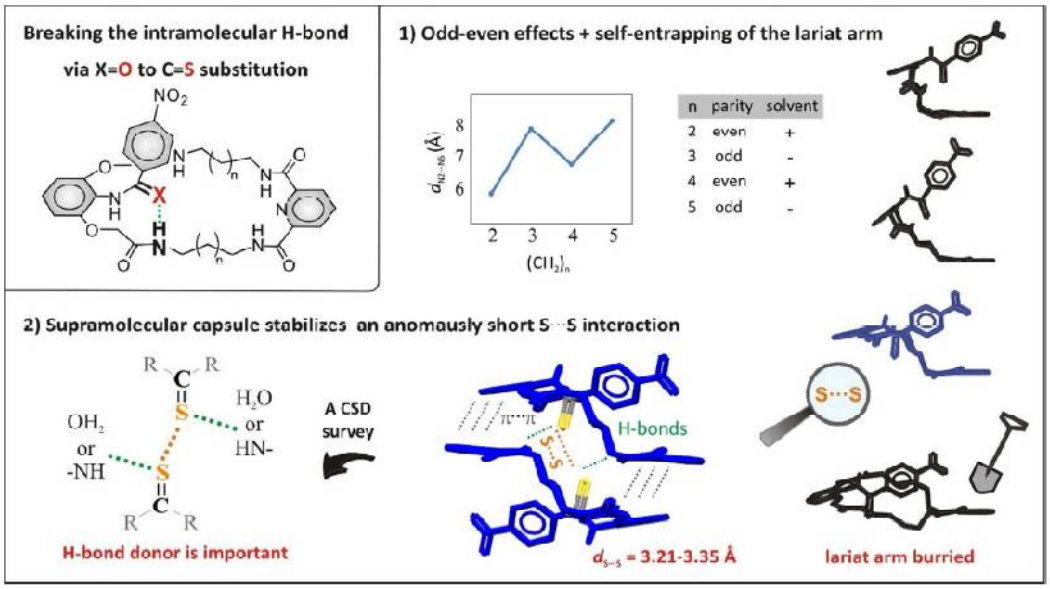
2a-X

X = H, Me, Cl

E β-thiophene

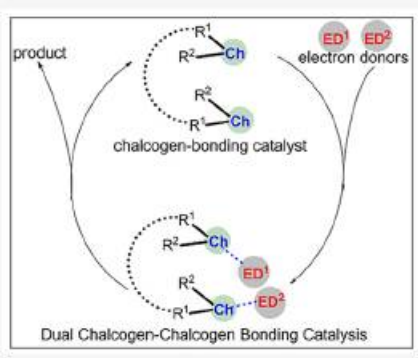


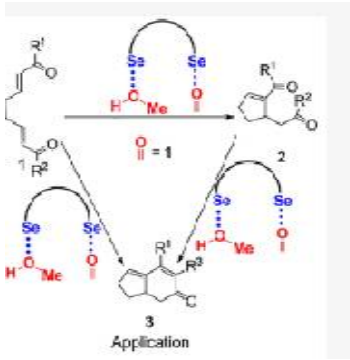
2b



Chalcogen Bond (S ; Se)

ChB. ACS. 39





Chalcogen Bond (S ; Se)

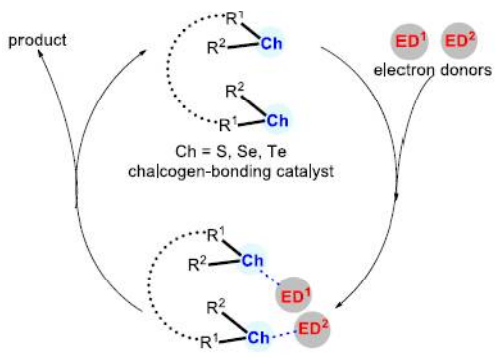
ChB. ACS. 39

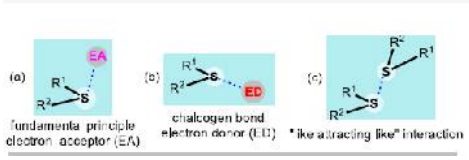
Ch-Ch bond formation		
Divalent selenium	presence of both the positive andnegative electrostatic potential sites	✓ CQC predicted ✓ Crystal structure demonstrated
Electron acceptor Se (Se2)	Approaches the electron donor selenium (Se1) from oblique direction of the molecular plane C1−Se1−P1	
Electron donor Se (Se1) interacts	With Se2 almost along the extension of the covalent C2−Se2 bond	
In Nature	! Noncovalent S···O bonding interaction is an evolutionary force + It has been smartly exploited by nature to modulate the conformational preferences of proteins	

Chalcogen Bond (S ; Se)

ChB. ACS. 39

Dual Ch-Ch Bonding catalysis





Experimental		Computational Science
Synthesis	**Instruments**	**CQC**
Chem.	Spectroscopy	**Static**
Preparation of Cocrystals	NMR	DFT
	X-ray diffraction	

Crystal structure

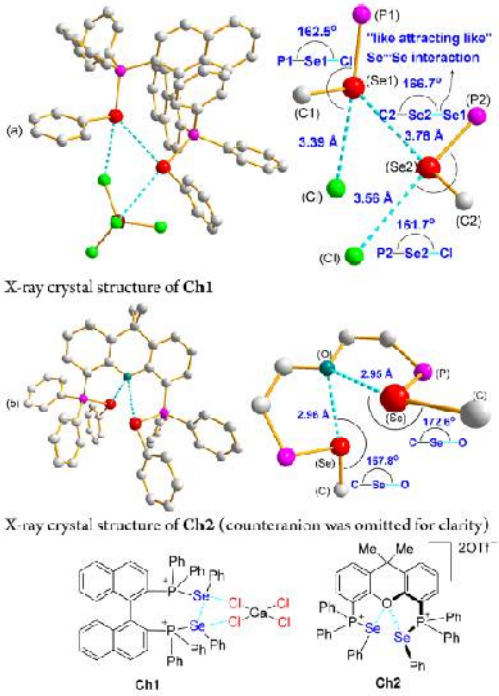
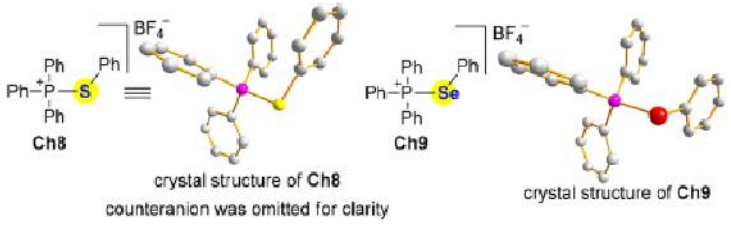
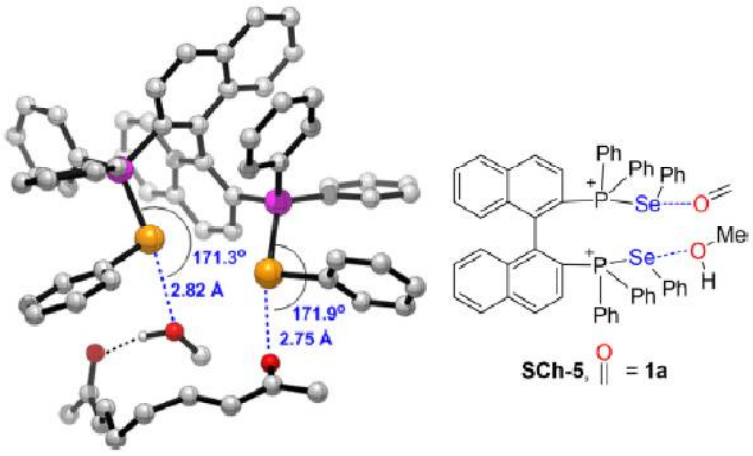


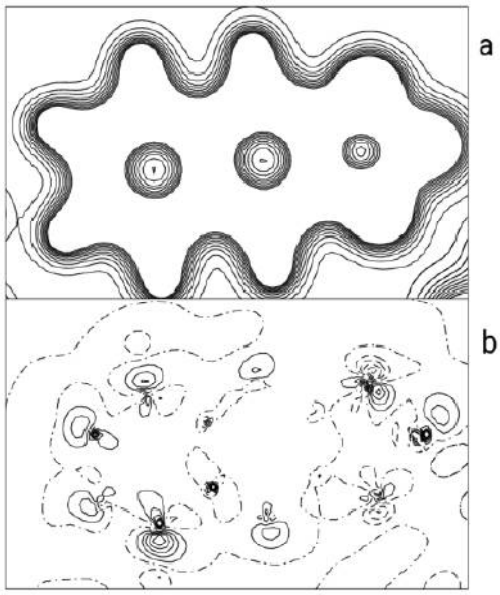
Figure 2. ~~Crystal structures~~



SCh-5—Opt Geom.

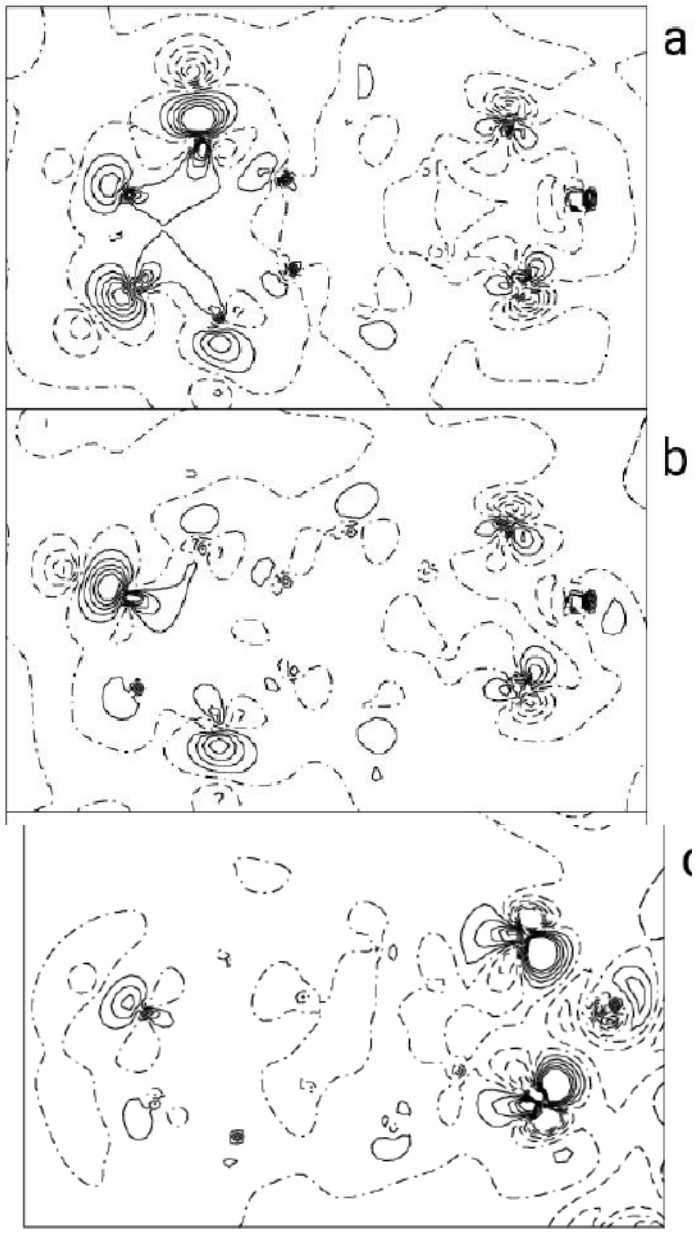


Total electronic density of 1
Continuous lines indicate positive difference



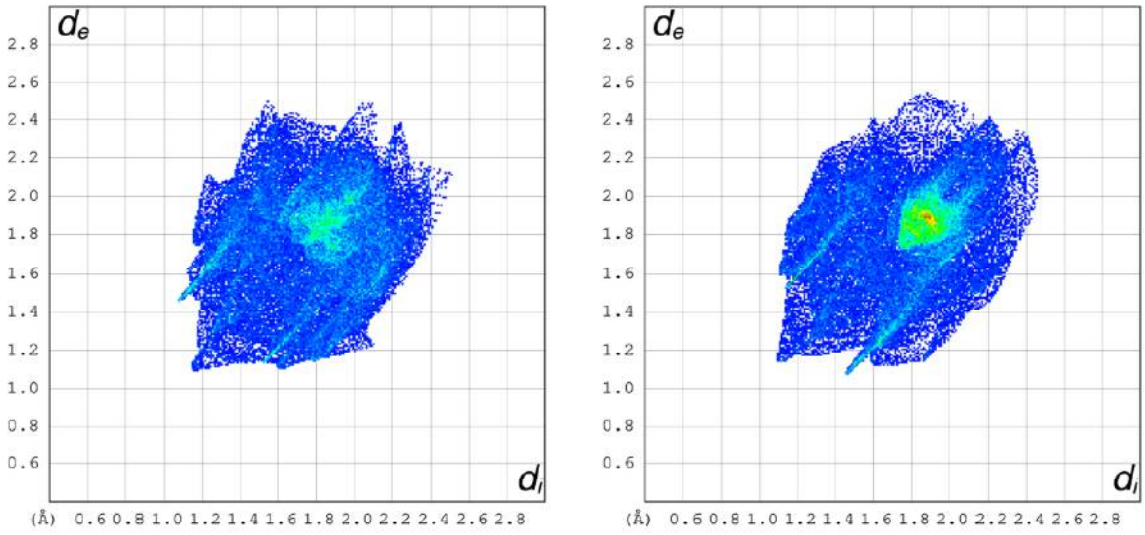
Deformation density (crystal minus insulated molecule)

Interaction differential density
(crystal minus isolated molecules)



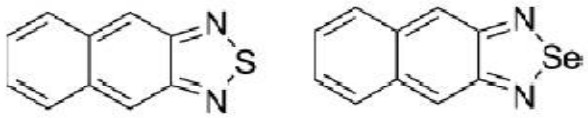
- ✓ (a) Polymorph II of 1; (b) polymorph III of 1; (c) crystal phase of 2
- ✓ Continuous lines: positive difference (crystal density higher that insulated molecule);
- ✓ Dashed line: negative difference
- ✓ Dot-dashed line: zero difference

Hirshfeldfingerprint plots



Chalcogen Bond (S ; Se)		ChB.	ACS.	**40**

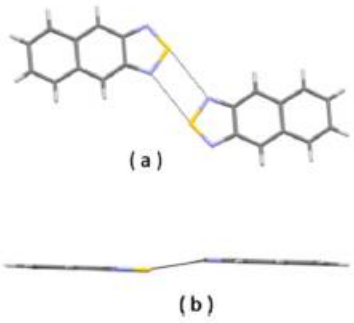
chalcogens



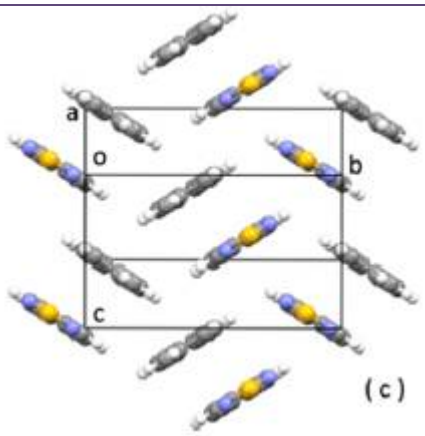
1 **2**

chalcogen-bonded dimer

(front view)

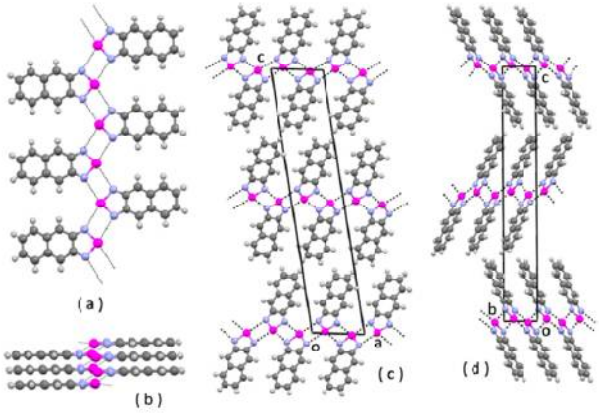


(Edge view)



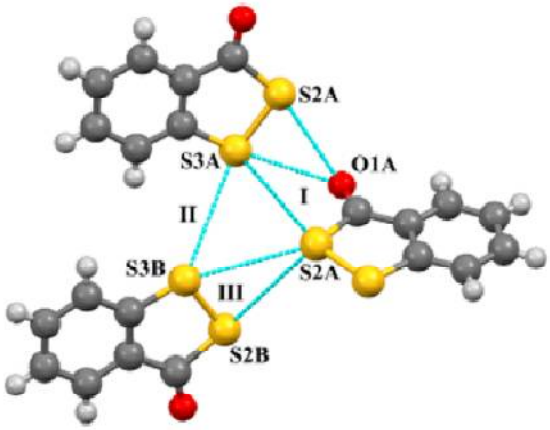
Packing viewed down a + c

Crystal packing of 2

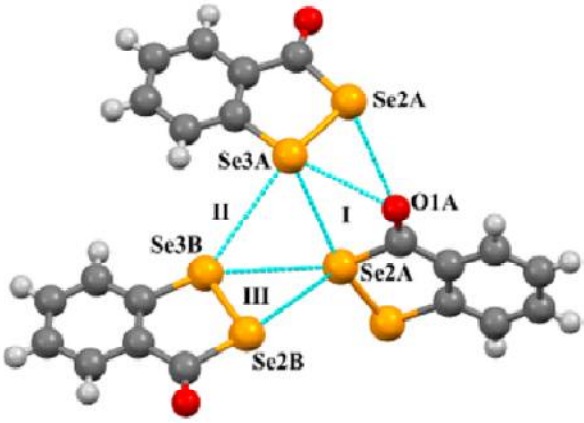


- (a) front view of a chalcogen-bonded ribbon;
- (b) edge view of a chalcogen-bonded ribbon;
- (c) packing viewed down b;
- (d) packing viewed down a

COSS



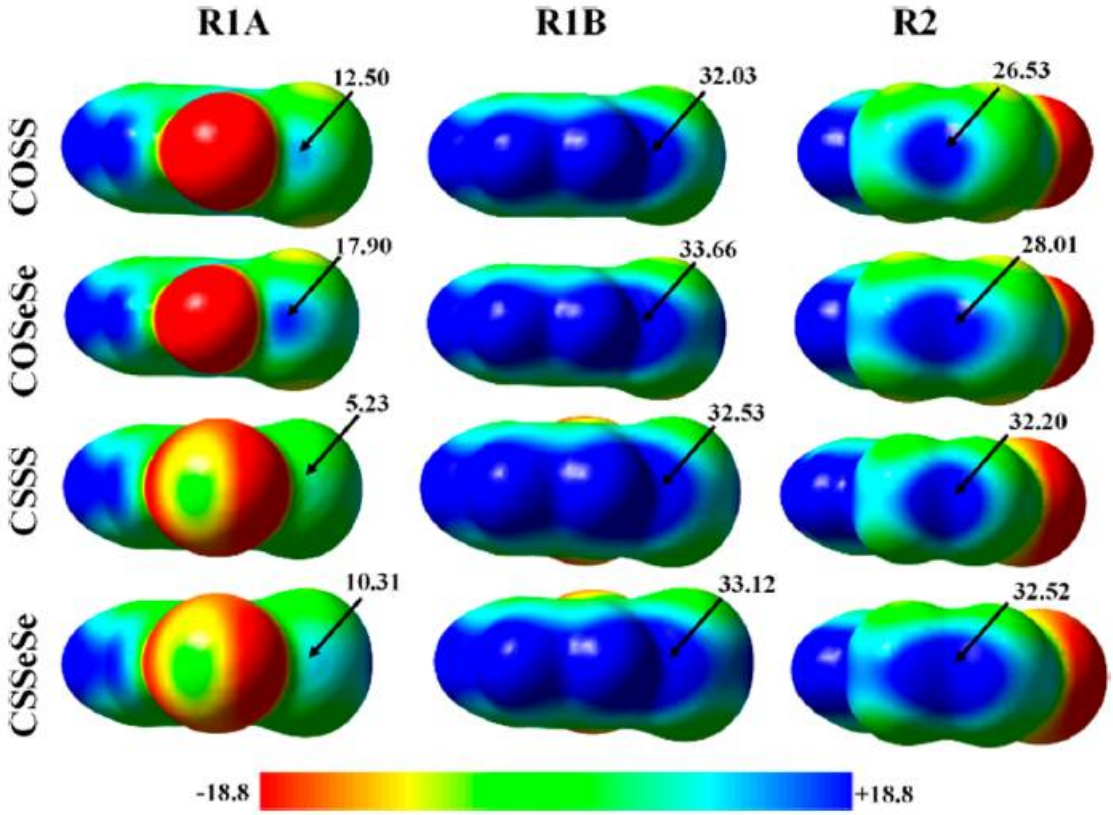
COSeSe



Labels A and B in atomic symbols point to the two molecules present in asymmetric unit

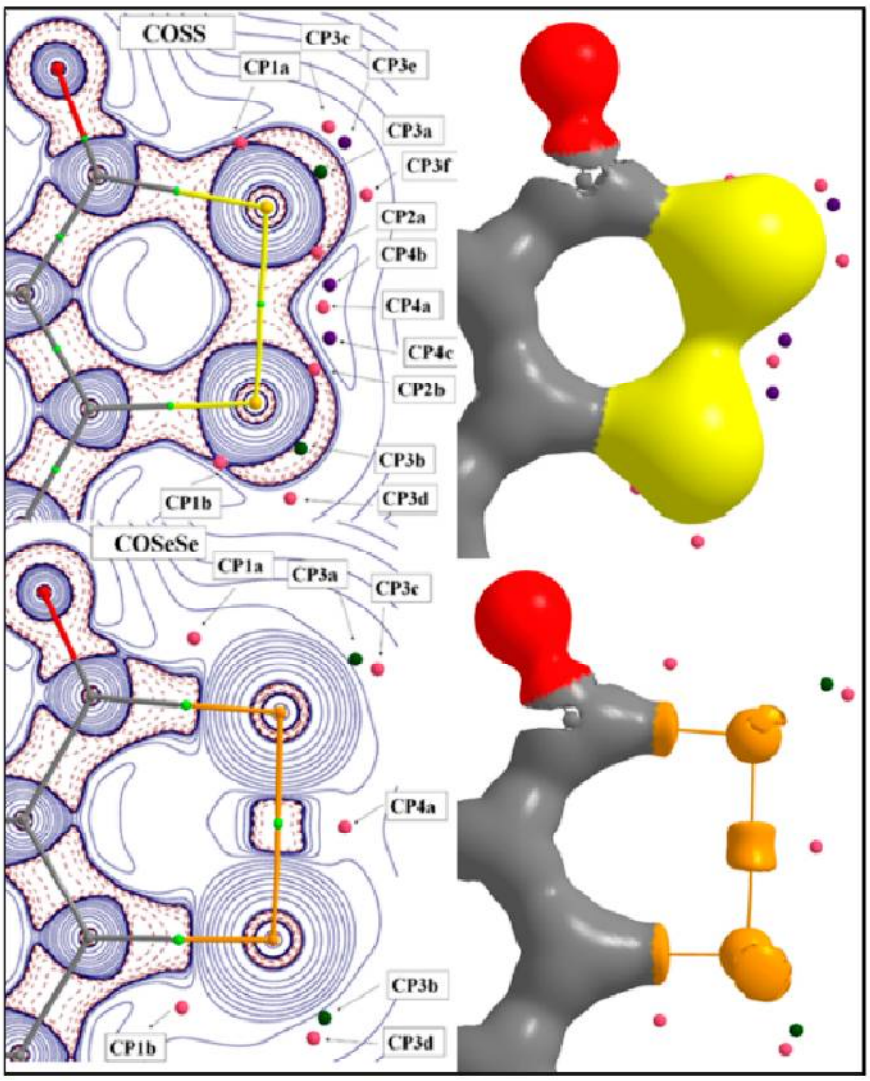
ESP maps

σ- hole along R1A, R1B, and R2A regions



Chalcogen Bond (S ; Se)		ChB.	ACS.	**27**

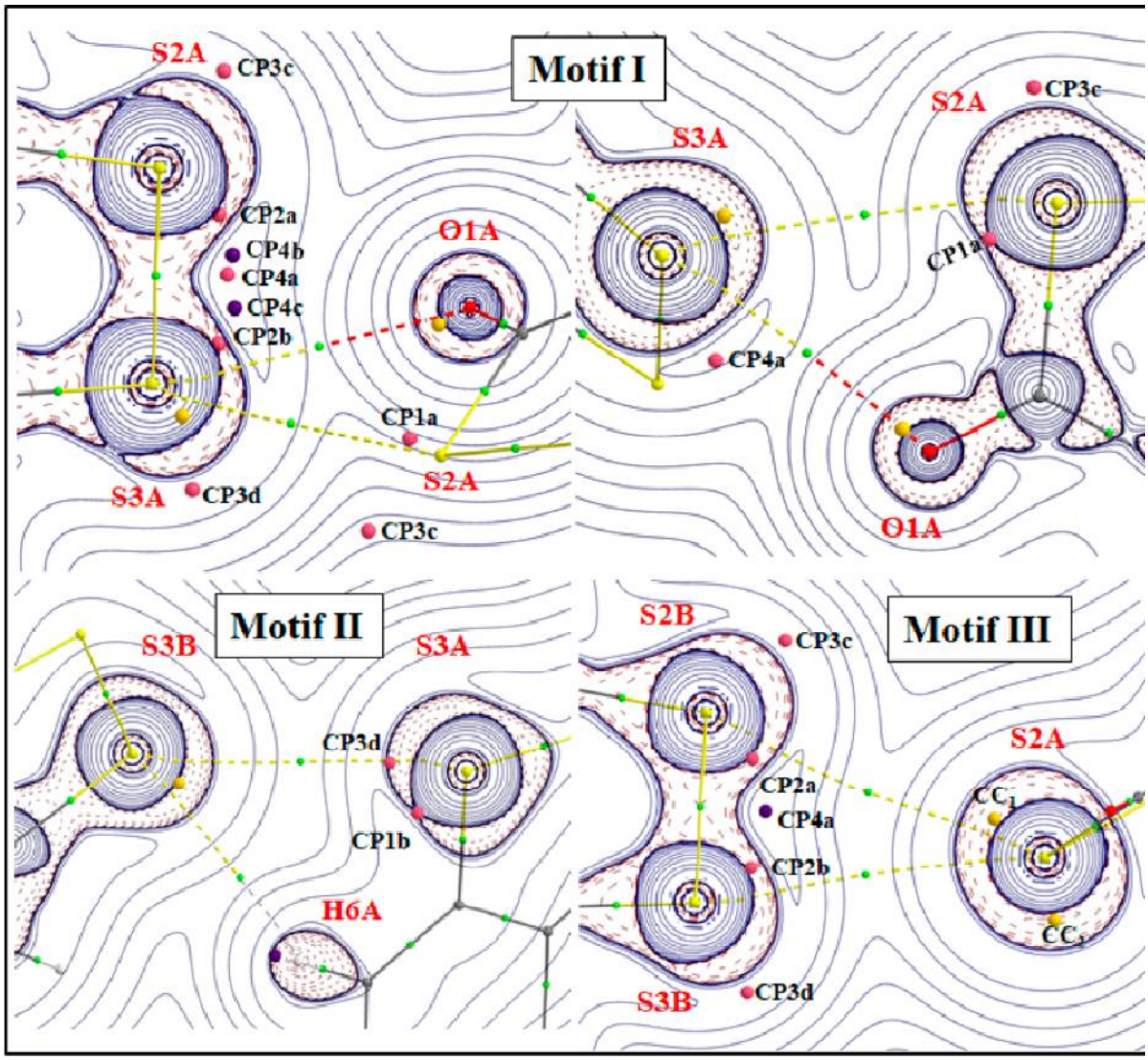
Left: L(r) = −∇2ρ(r) Right: The ∇2ρ(r) = 0



- COSS (top) ;COSeSe (bottom)
- CPs of L(r) in the valence shell of chalcogen atoms are denoted in maps as spheres [(3,−1) CPs are green, (3,+1) CPs are pink, and (3,+3) CPs are violet].
- (3,−3) CPs corresponding to lone pairs of Ch2 and Ch3 are out of plane in the left

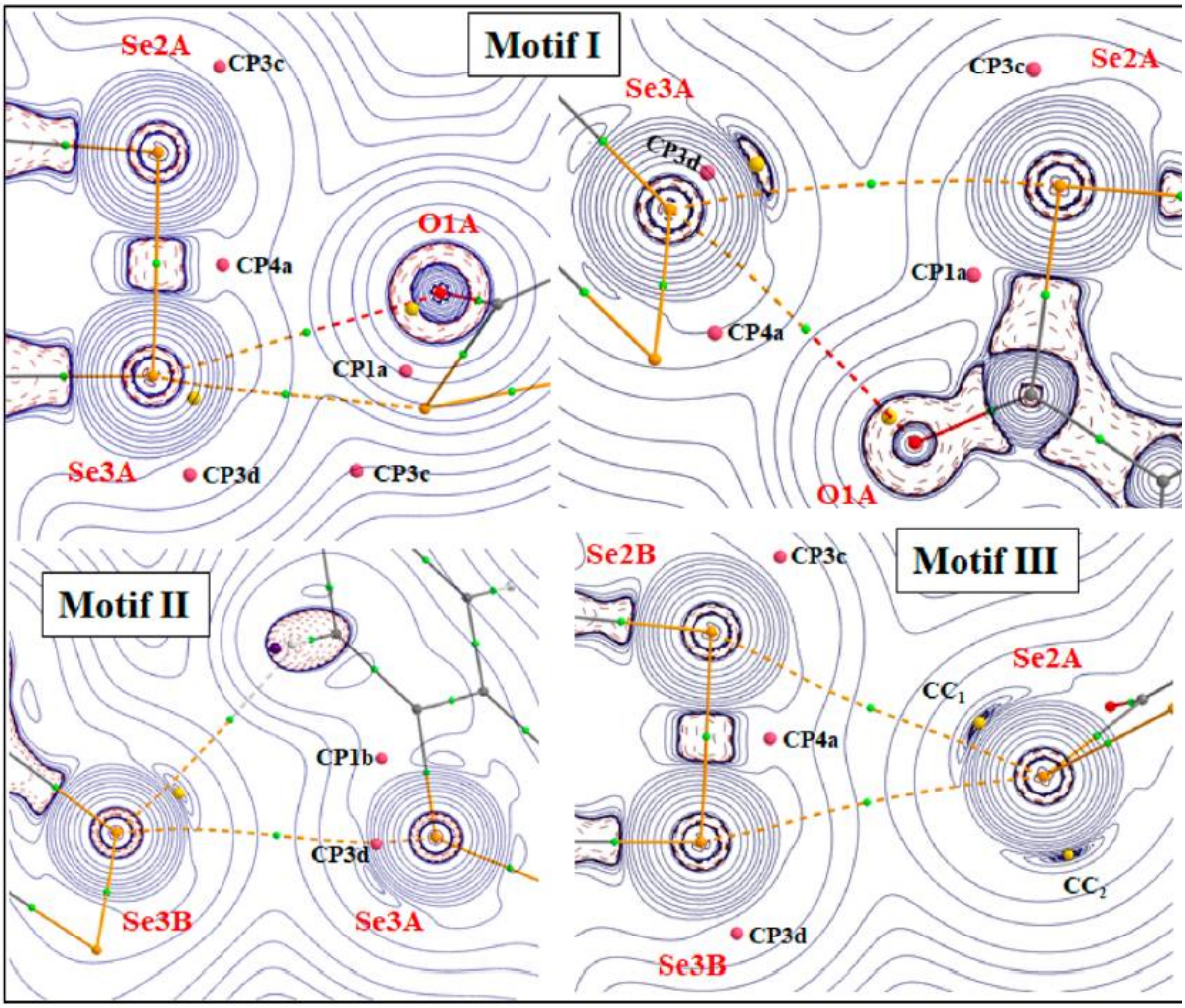
.

chalcogen (Sulphur) bonding interactions motifs I, II, and III

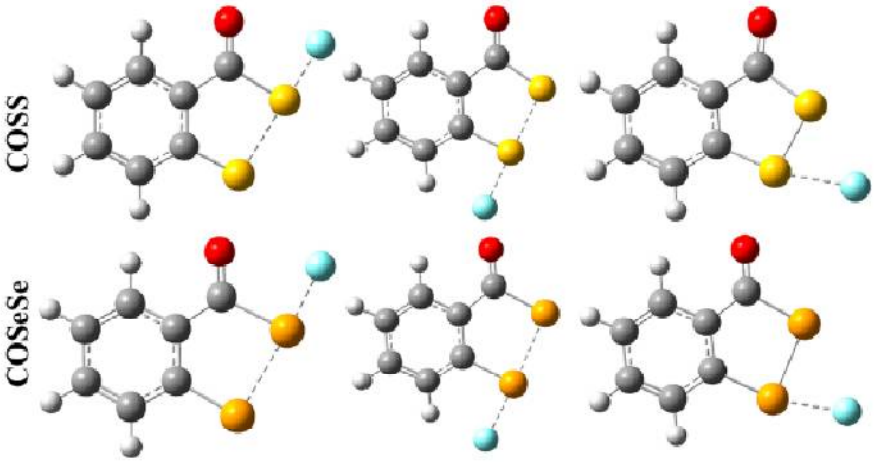


- Intermolecular bond critical points (BCPs, small green spheres),
- Intermolecular bond paths (dashed lines)
- Charge concentration and charge depletion (CC/CD) sites (yellow/pink/violet spheres)

Selenium bonding interactions

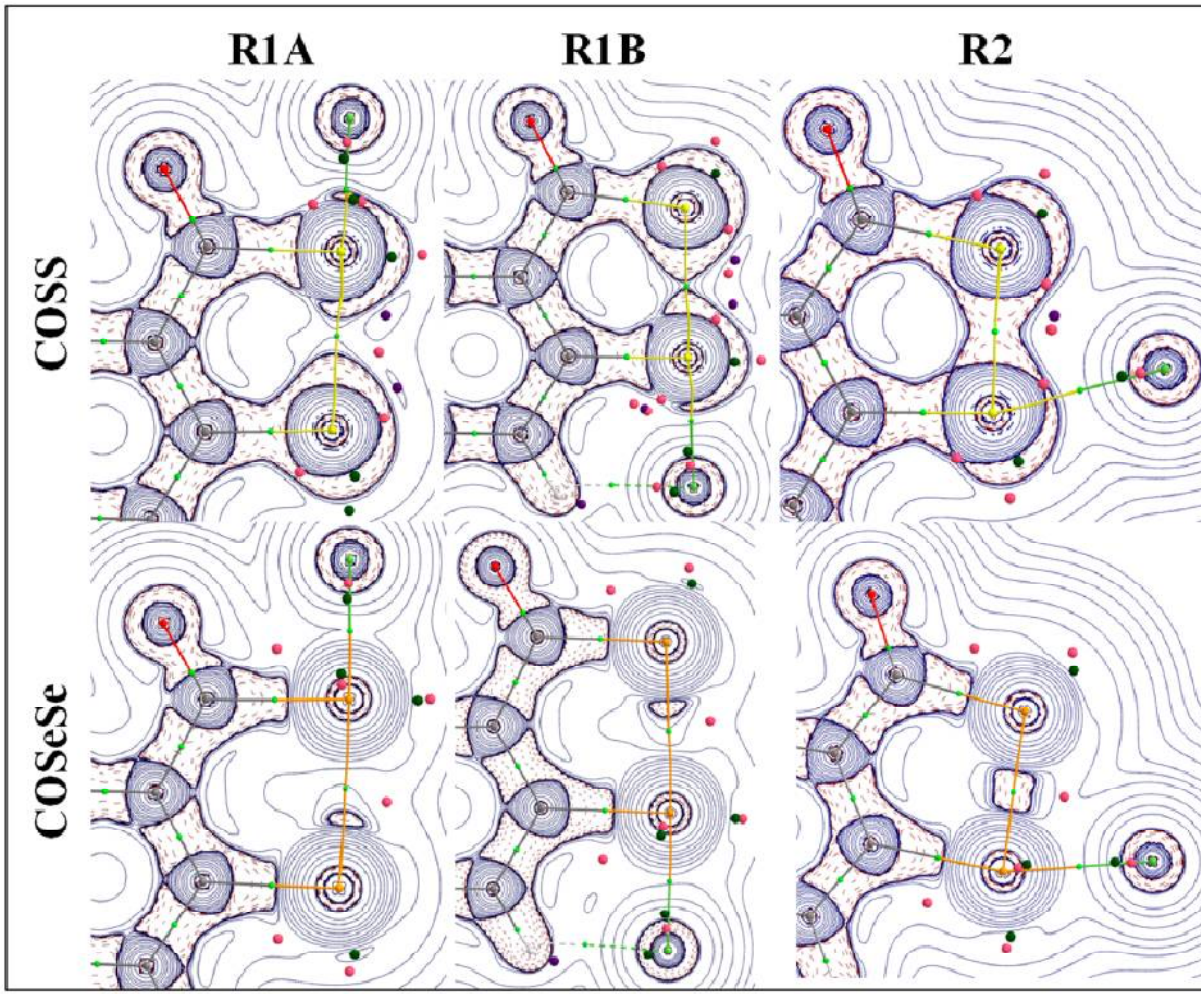


Fluoride adducts with COSS and COSeSe

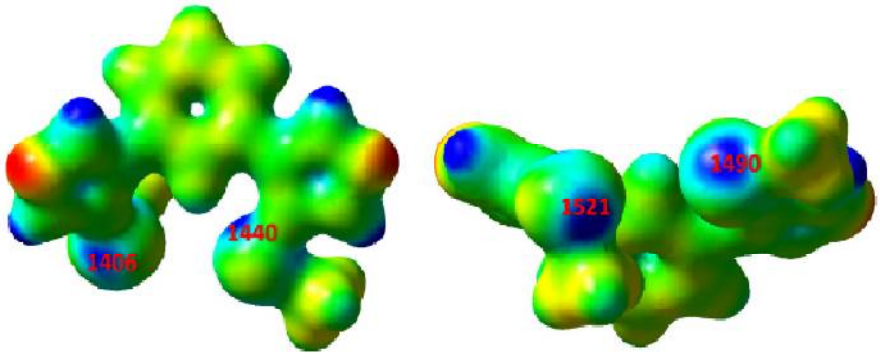


- ✓ Absence of covalent bonds between atoms should not be confused with the absence of a bonding interaction
- ✓ Ch···F and Ch···Ch bonding interactions (represented with dashed line) showing $1<|V|/G<2$
- ✓ Rest of bonds are covalent and exhibit $|V|/G>2$

L(r) maps
fluoride adducts of COSS ; COSeSe

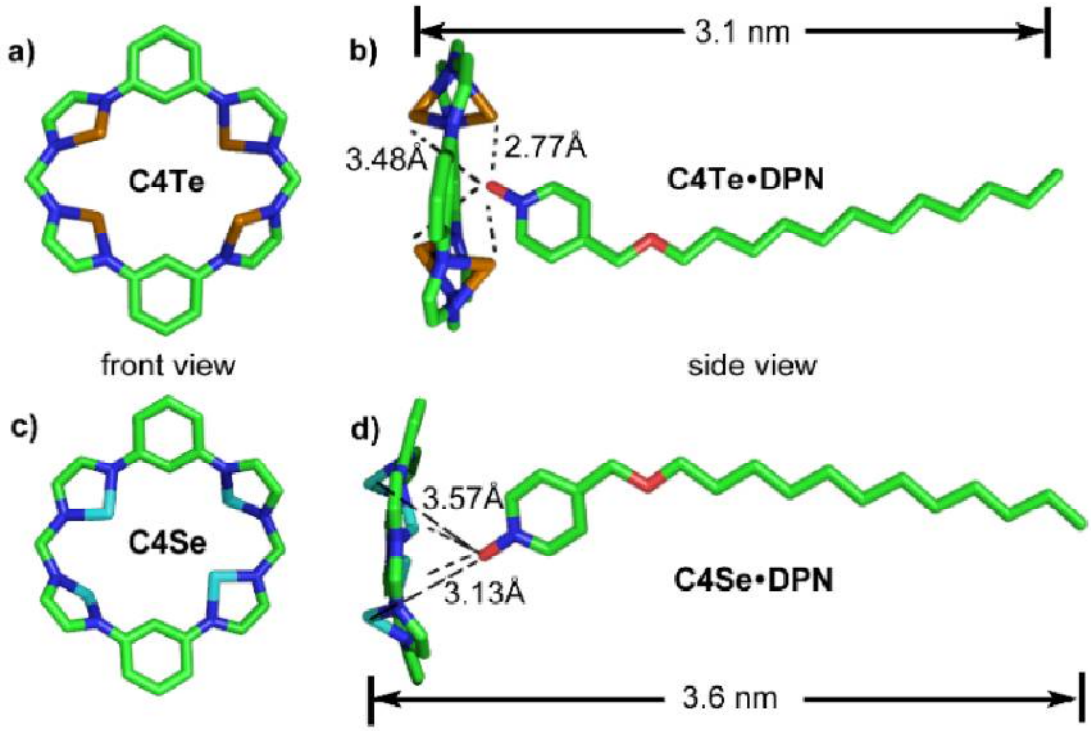


Two σ-holes at each Te atom of catalyst (complex I)
Maximum σ-hole ESPotentials



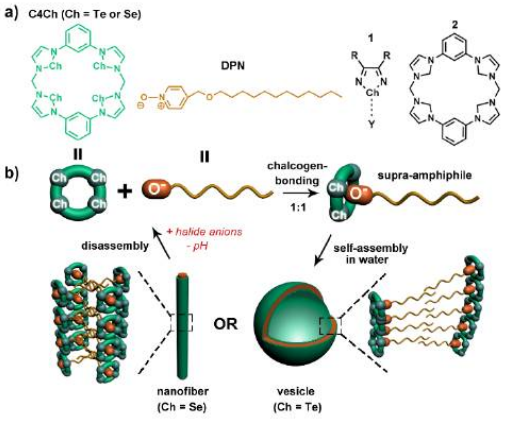
Stereochemical structures from DFT

(a) C4Te, (b) C4Te•DPN, (c) C4Se, (d) C4Te•DPN



Structures

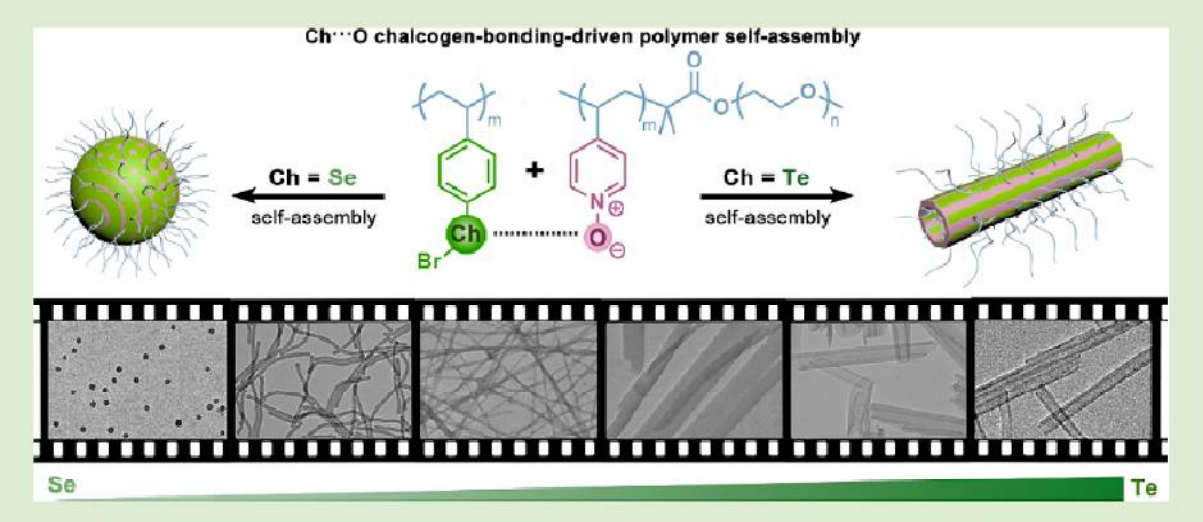
(a) C4Ch, Ch = (Te or Se), Surfactant (DPN), Control Compounds (1 and 2)



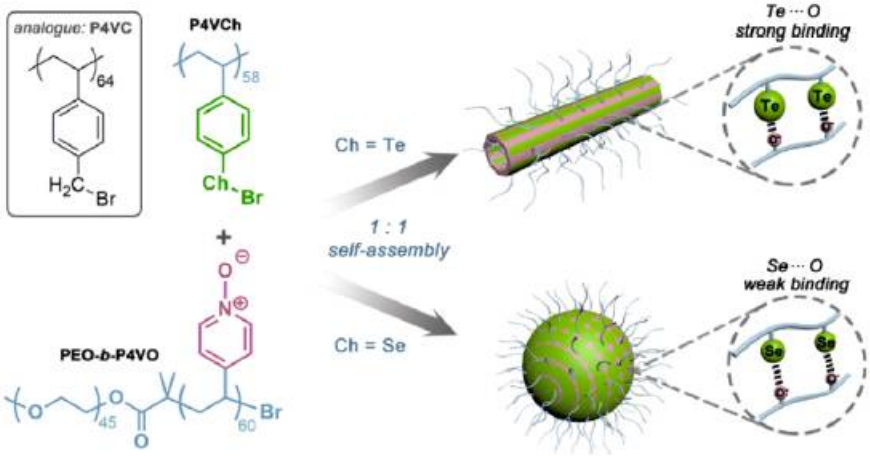
(b) Chalcogen-Bonding Interactions of C4Ch•DPN Supra-amphiphiles

- DPN:4-dodecyl-pyridine N-oxide

Chalcogen–Chalcogen Interactions
Strong Te···O
Weak Se···O

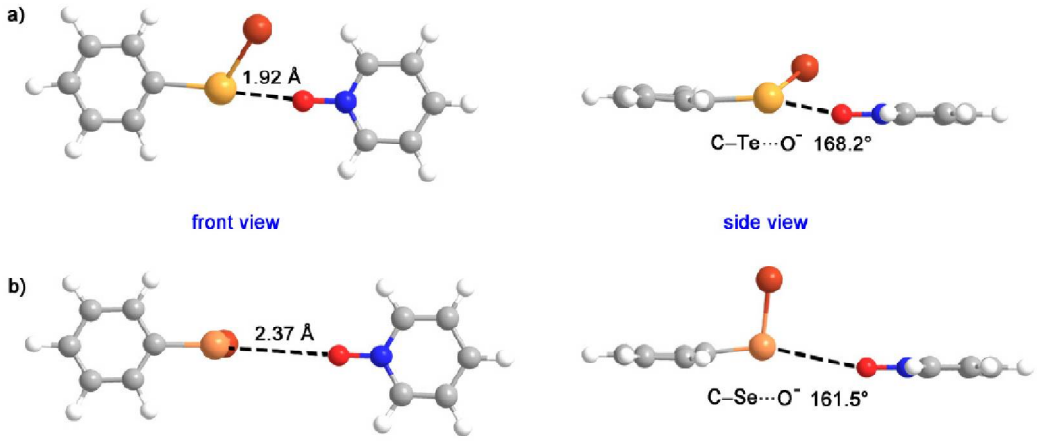


Noncovalent Complexation in	
Chalcogen Bond	
Donor (P4VCh, Ch = Te and Se)	Acceptor (PEO-b-P4VO)



Molecular simulation
DFT (B3LYP/6-31G) by the software Gaussian09

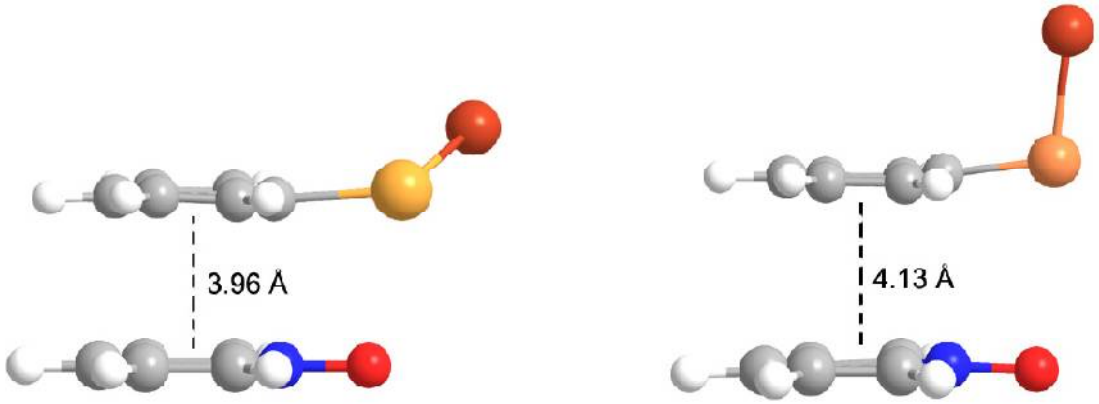
Chalcogen-chalcogen contact



Molecular simulation of π-stacking interaction

DFT (b97d/6- 31G)

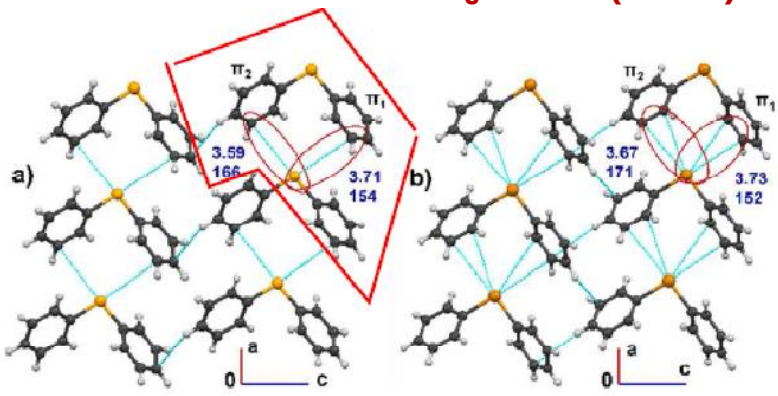
Benzene telluryl bromide and pyridine N-oxide	benzene selenyl bromide and pyridine N-oxide



Chalcogen Bond **[S Se Te]**	**CSD**	ChB.	ACS.	**54**

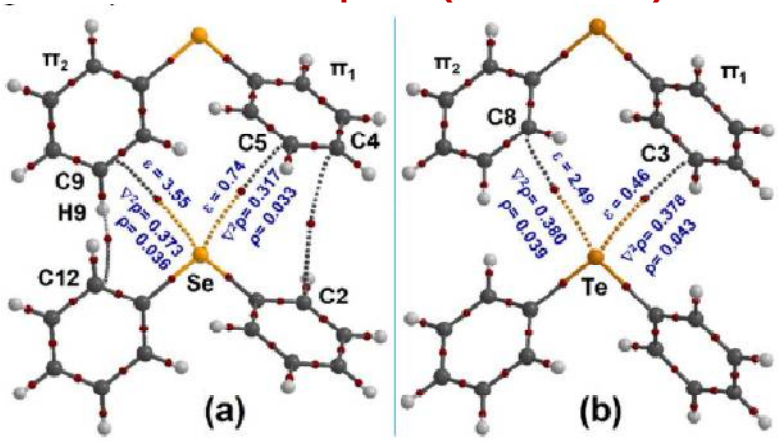
Double π2 · · · Se · · · π1

π2 · · · Te · · · π1 chalcogen Bond (in blue)



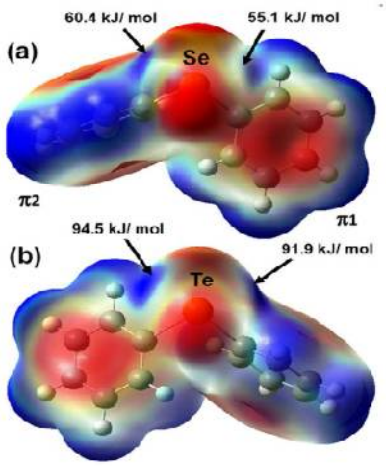
Ph2Se Ph2Te

Bond critical points (dark red dots)

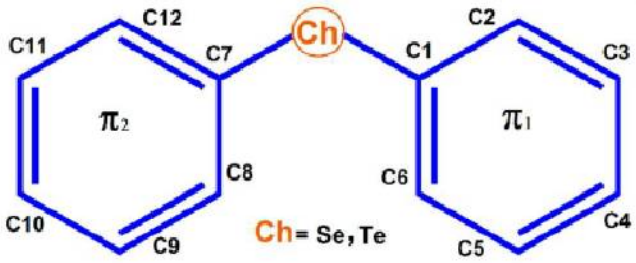


✓ Bond paths (a) Se··· π 1/ π 2 and (b) Te··· π 1/ π 2

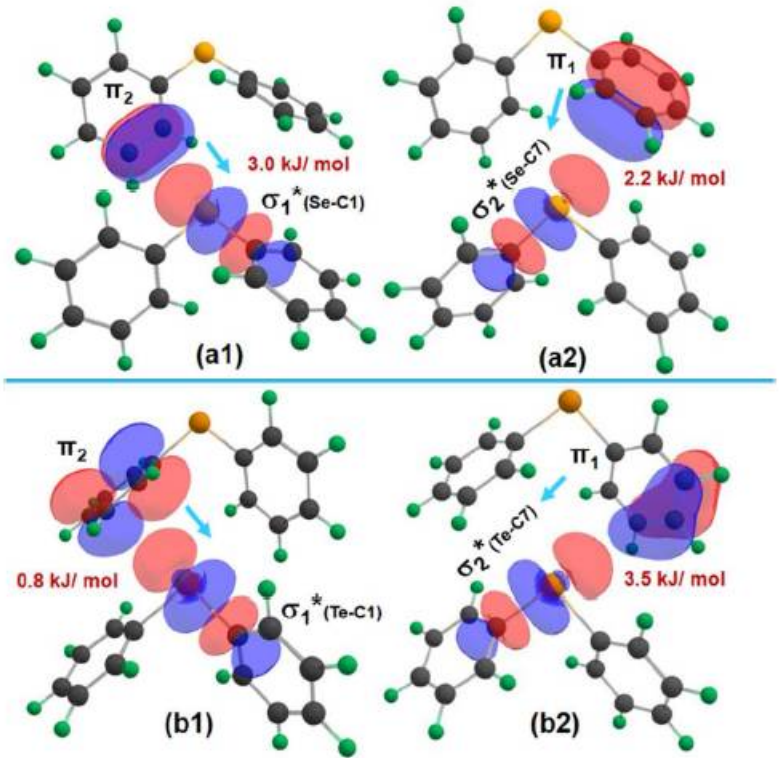
ESP of Ph2Se, Ph2Te



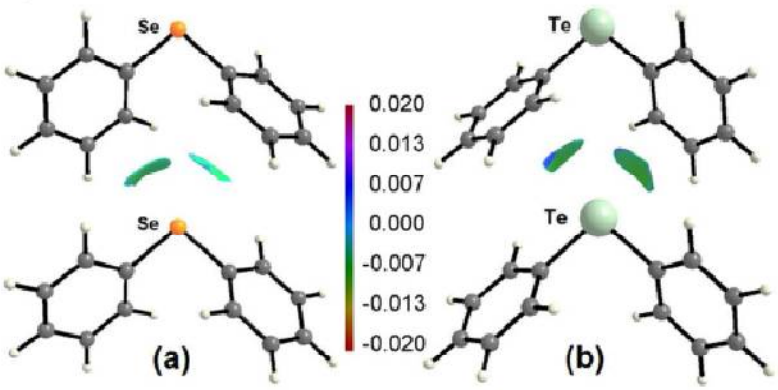
Atom-numbering scheme



NBO orbitals showing charge transfer

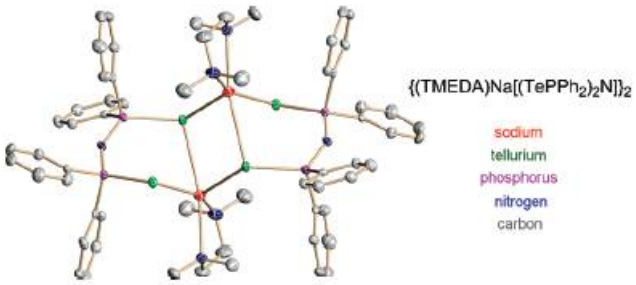


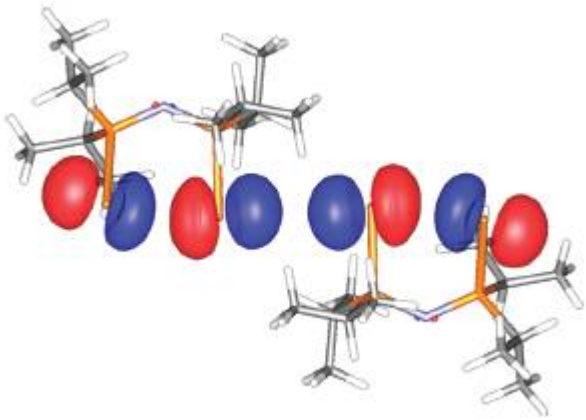
RDG isosurfaces



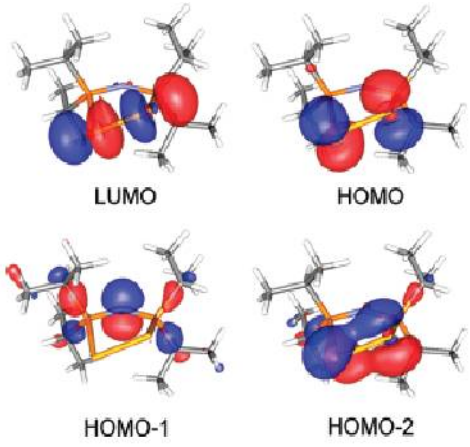
✓ (a)Se・・・π and (b) Te・・・π interactions

Experimental		Computational Science
Synthesis	Spectroscopy Solution NMR	Comp Quan Chem (CQC) DFT
	Redox behavior	





Bonding interaction between two [TePiPr2NiPr2Pte]



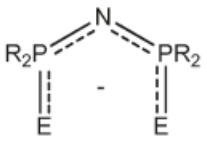
Frontier MOs of the cations [N(PiPr2E)2]+ (E) Se, Te).

Polymeric structure of [N(PiPr2E)2]I (E) Se, Te).

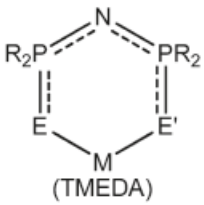
Experimental		Computational Science
Synthesis	Spectroscopy	
	o ^{31}P NMR	
	o X-ray	
	☞ Thermal ellipsoid	

Comp Quan Chem (CQC)	
DFT	Level of theory
✓ NPA Charges ✓ Wiberg Valences ✓ WBIs	

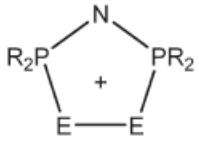
Structures



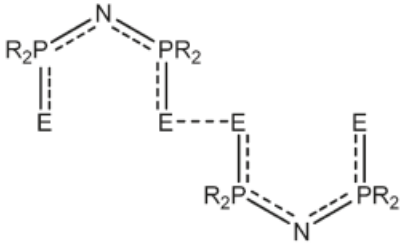
(1)



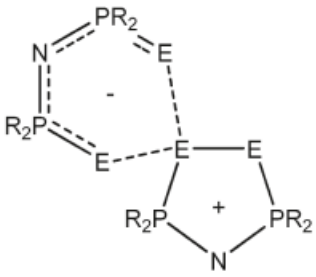
(2)



(3)

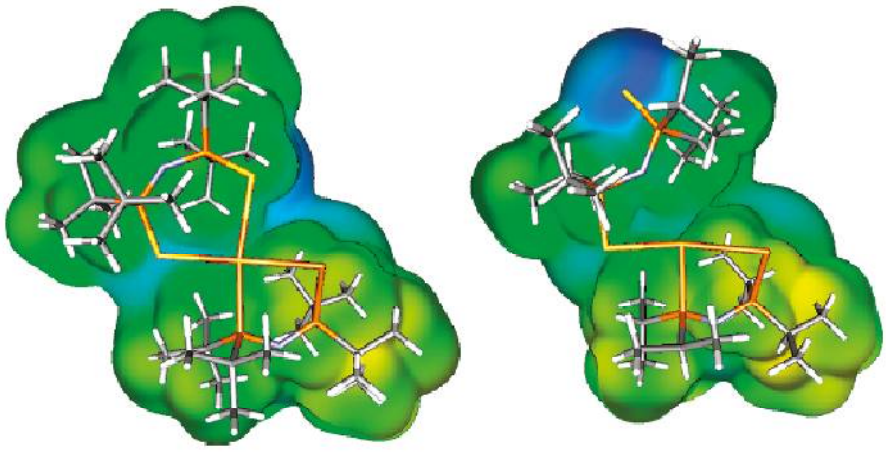


(4)

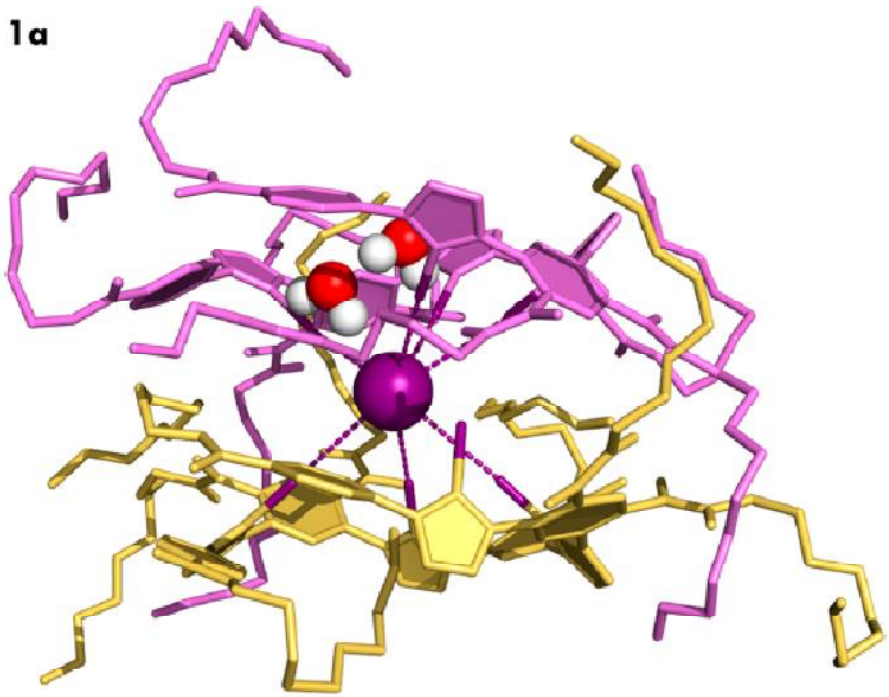


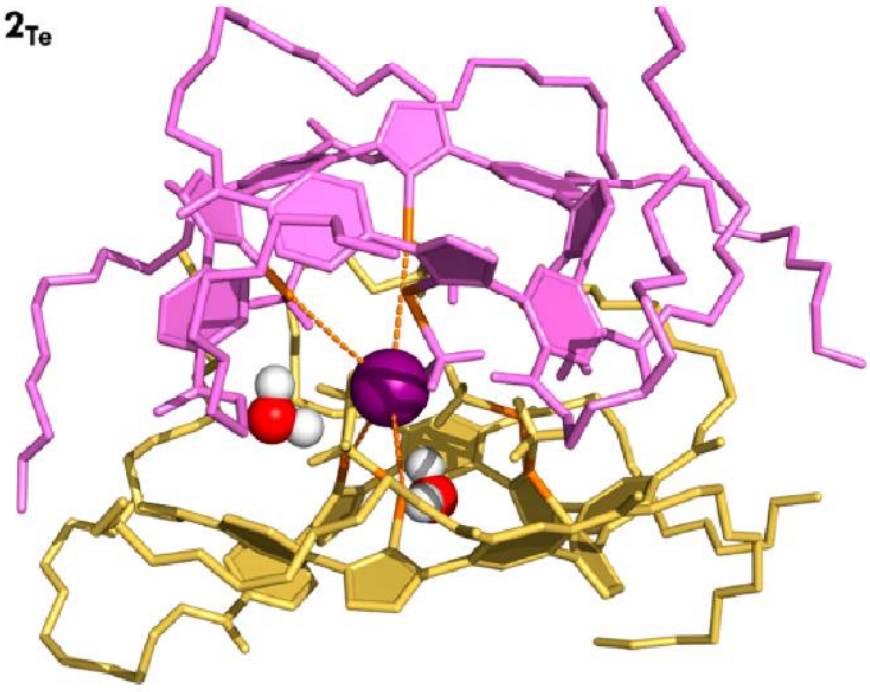
(5)

ESP



MD snapshots of dimeric capsules of 1a and 2Te

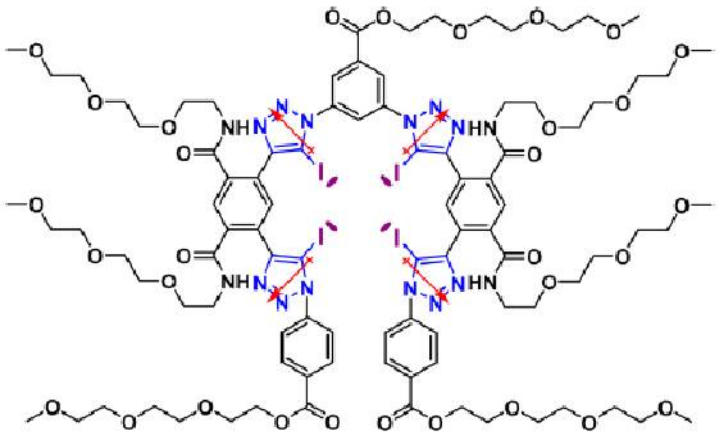




- ✓ Dashed lines: XB (purple) ; ChB (orange) interactions
- ✓ Two foldamer entities surrounded by a few water molecules

Comp Quan Chem (CQC)	
MD	✓ AMBER software package ✓ General AMBER Force Field (GAFF)

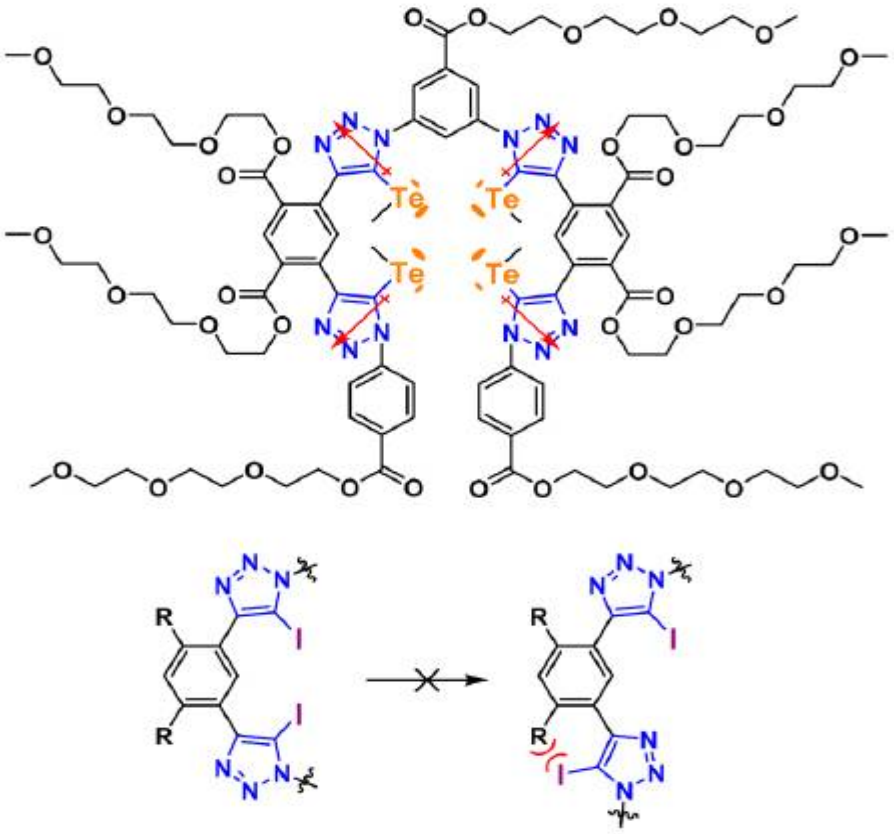
1a



XB and ChB anion receptors

Local dipoles of triazole units and positions of σ-holes highlighted

2_{Te}

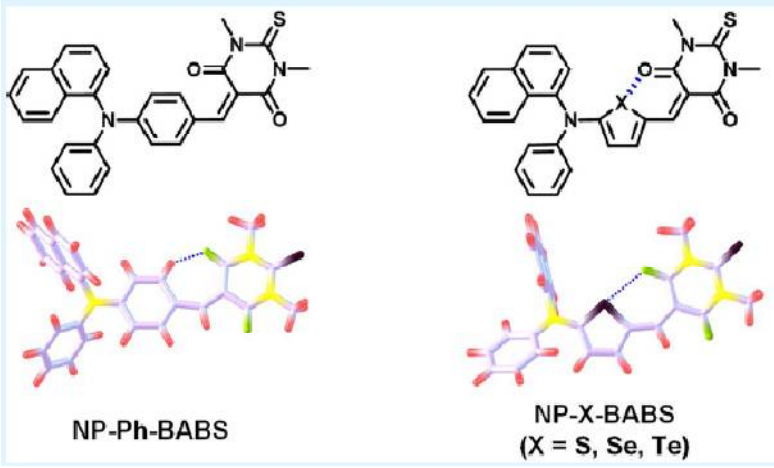


- Preorganization of receptor arms by restricted intramolecular rotation

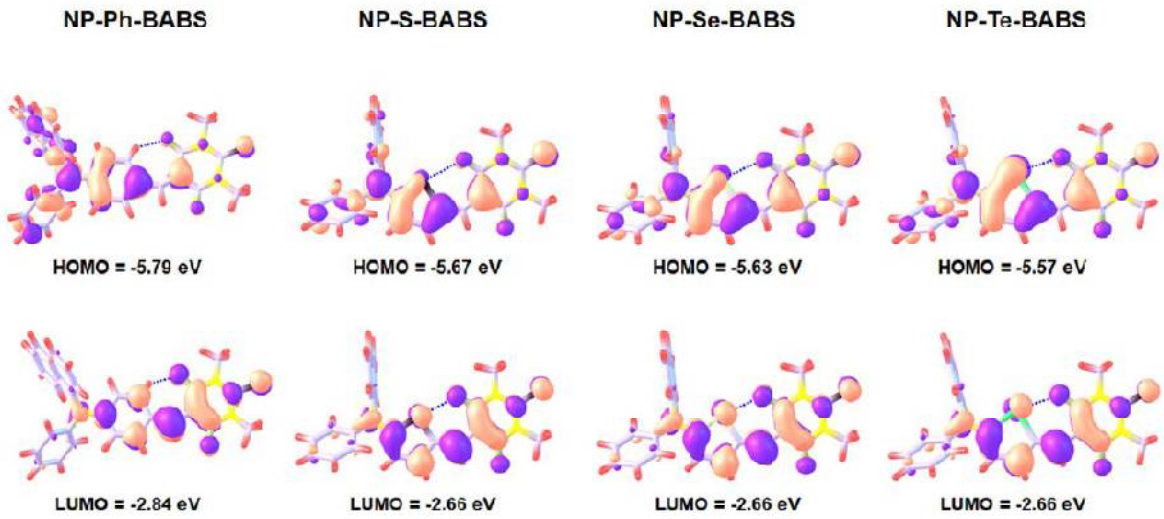
Experimental		Computational Science
Synthesis	**Spectroscopy** o NMR o 13C NMR 1H o 13C CP-MAS solid-state NMR o 1H MAS solid-state NMR	
	o FT-IR	
	o UV-vis	
	o Out-of-plane XRD patterns	
	Thermal analysis o DSC curves	

Comp Quan Chem (CQC)	
DFT	Level of theory
B3LYP	Functional
DGDZVP	Basis set

Energy minimized structures



Frontier molecular orbitals



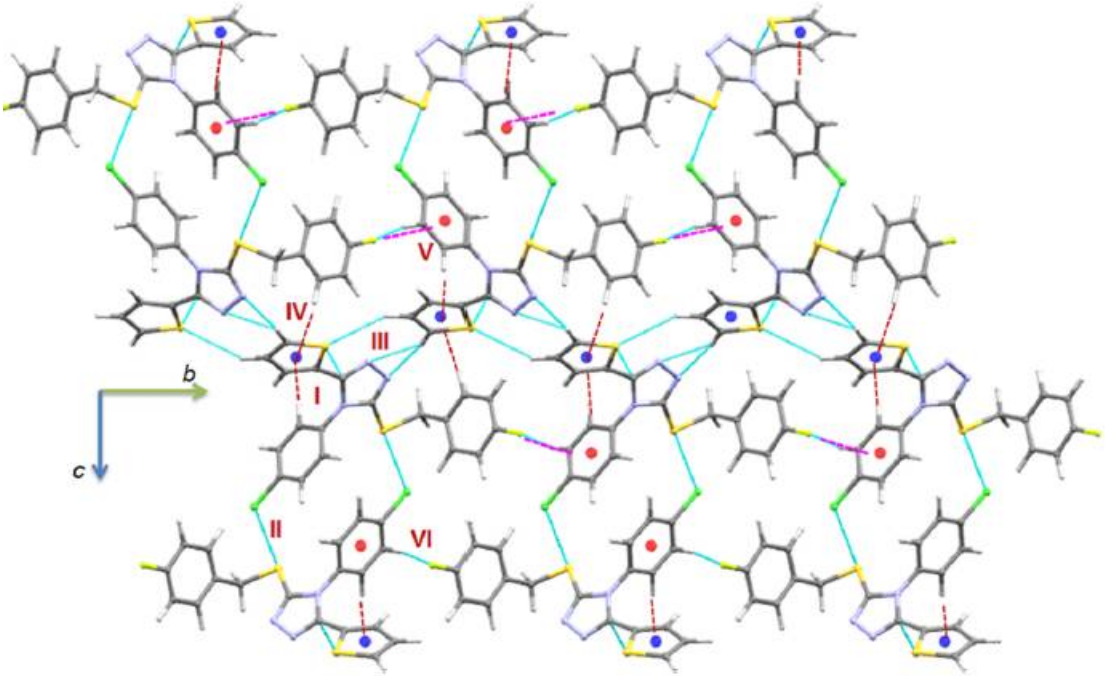
NP-Ph-BABS, NP-S-BABS, NP-Se-BABS, and NP-Te-BABS

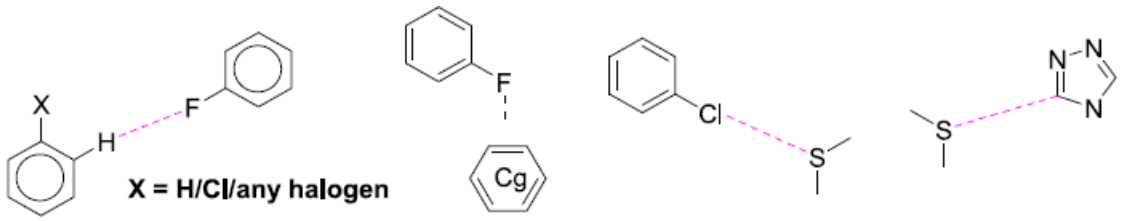
ChB + HB + unorthodox_Non_Cov_Int

Chalcogen Bond [S]	Cox-2	ChB.	ACS.	23

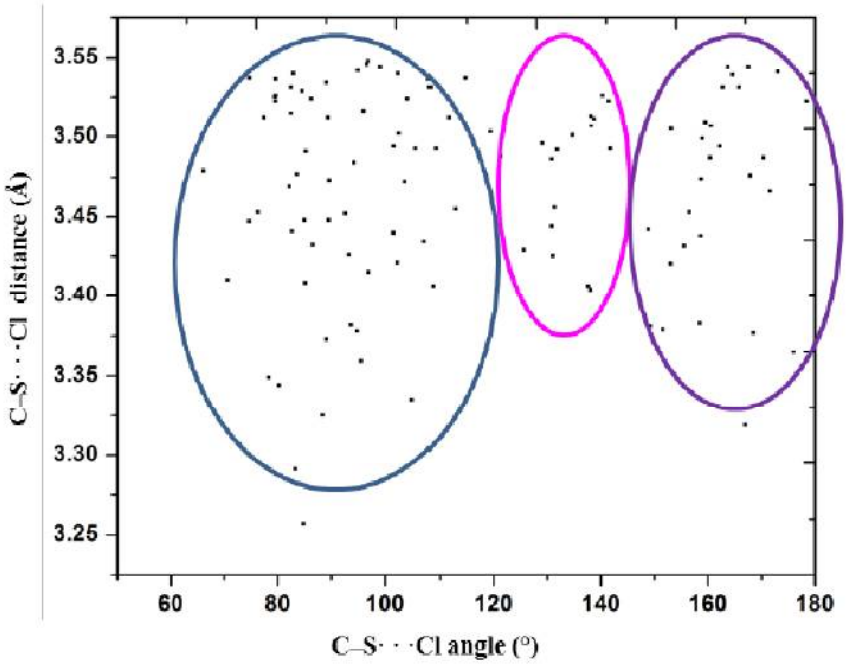
Chalcogen and hydrogen bonds in supramolecular sheet

Other unorthodox noncovalent interactions

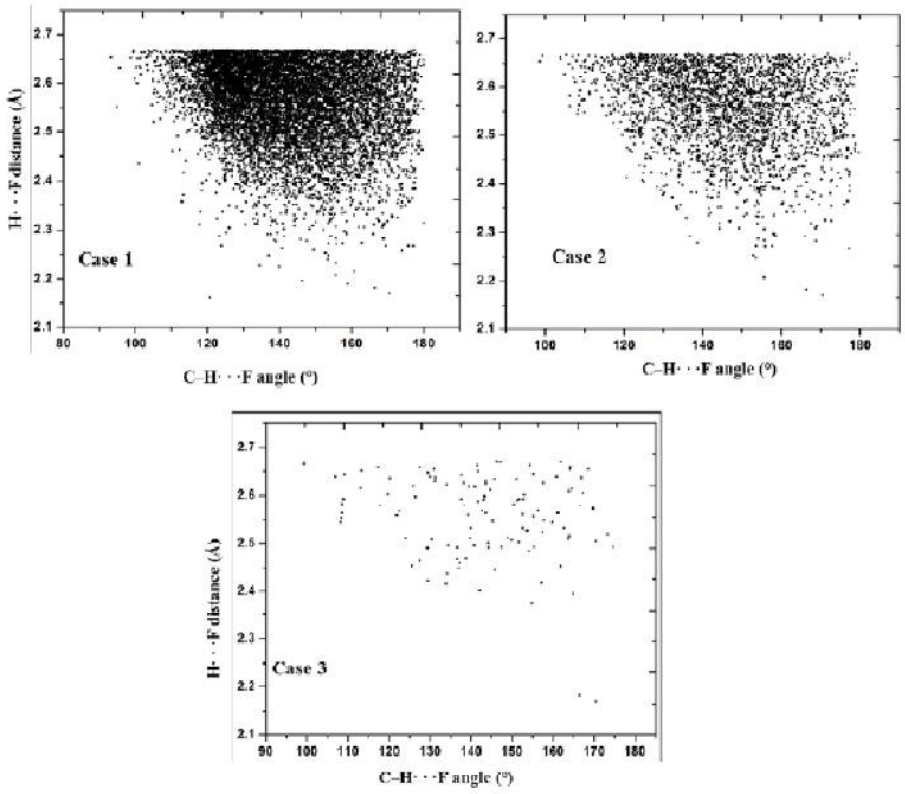




Distribution of C–S···Cl contacts 23



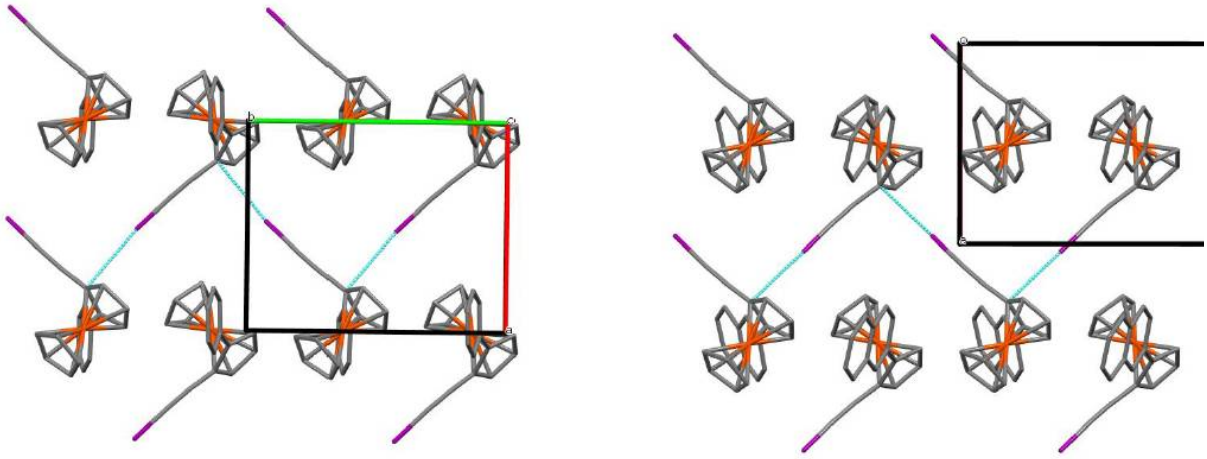
Distribution of C–H···F contacts

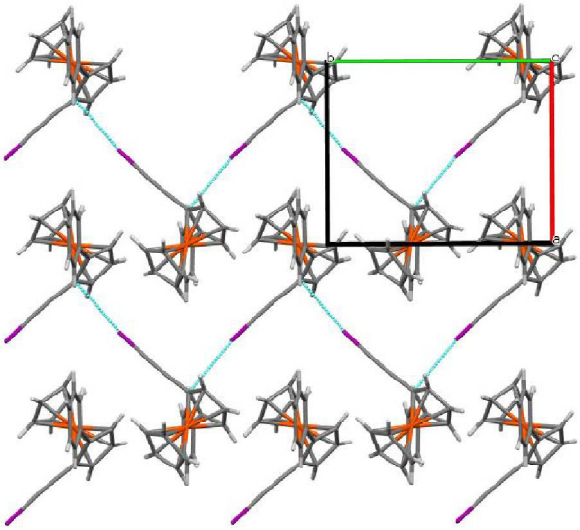


HaB

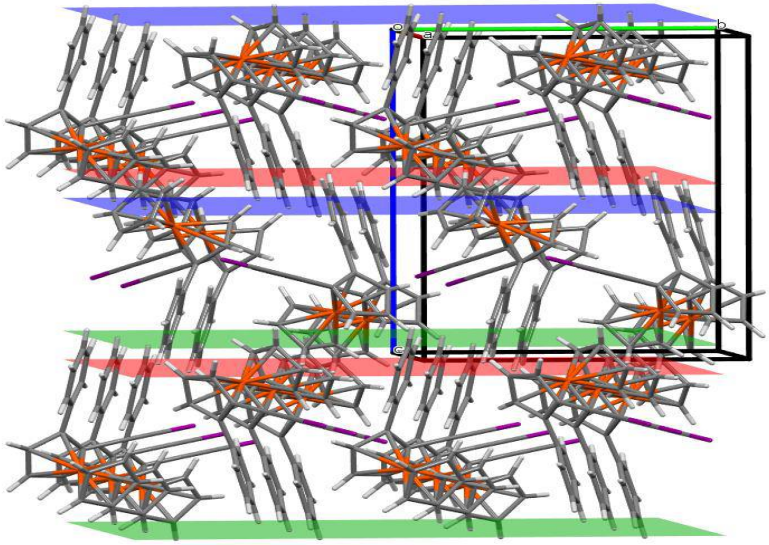
Halogen bonds		ChB.	ACS.	29

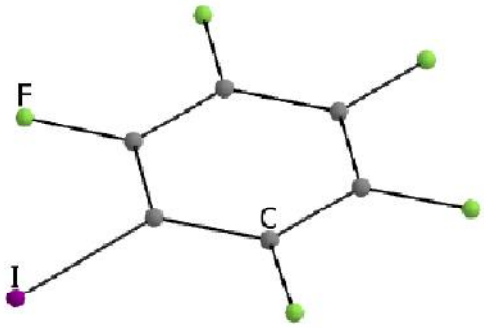
I···C halogen bonds (in cyan)
(001) plane containing the stacking of chains





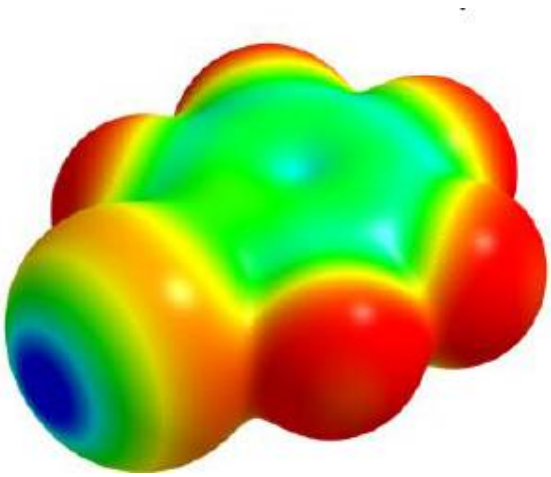
I···C halogen bonds
Display of three adjacent and interpenetrating (001) planes
(delimited by blue, red and green planes)



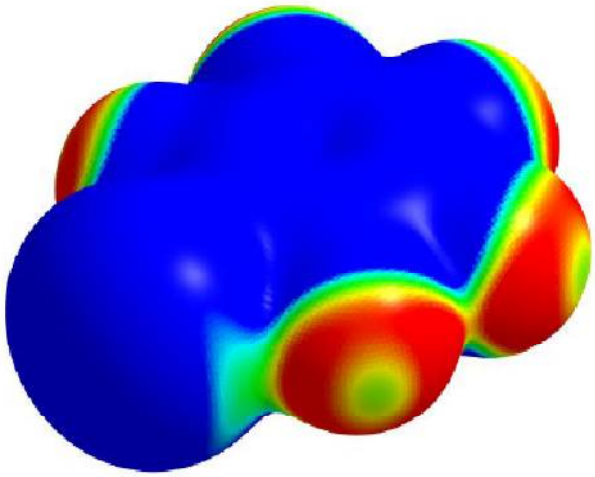


Pentafluorophenyl group

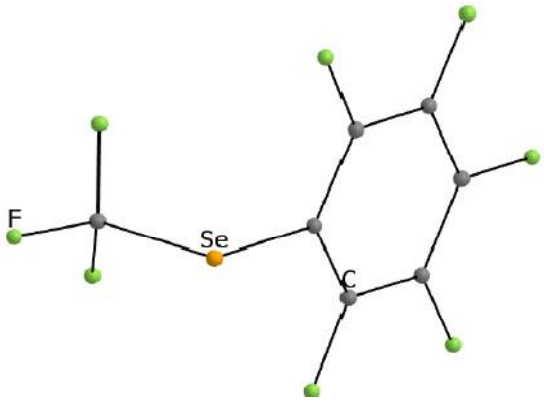
- Induces strong electron depletion on iodine



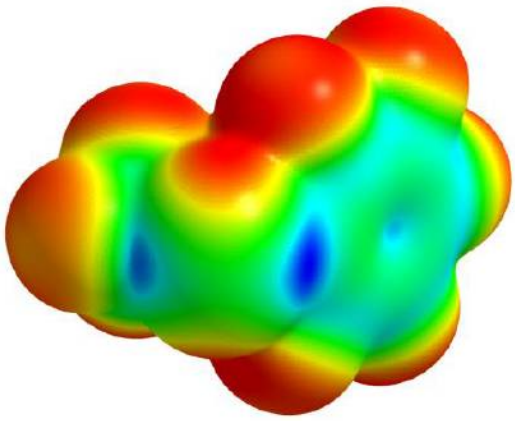
ESP
blue: 0.06a.u. / cyan: 0.0425 / green: 0.025 / yellow: 0.0075 / red: -0.1



Compound **18**



Compound **20**



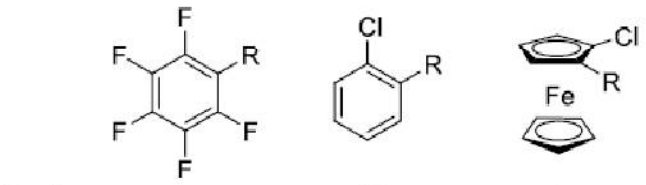
ESP
Blue: 0.06a.u. / cyan: 0.0425 / green: 0.025 / yellow: 0.0075 / red: -0.1

Halogen bonds in solution

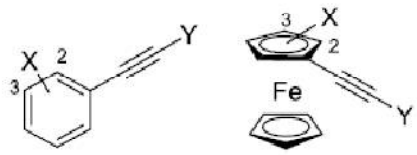
Halogen Bond		ChB.	ACS.	29
Expt	Computational Science Comp Quan Chem (CQC)			

	Task	Method--Tool	
Synthesis	Geom. Opt.	DFT	Level of theory
		B3LYP	Functionals
		Def2TZVPP	Basis set
Instrument			
NMR	Conformations search	Scanning corresponding degrees of freedom	
	True energy minima	Frequency calculations	
	ESP	Software o AIMAll77 o MultiWfn programs	

Holes (B3LYP-D3/Def2TZVPP)

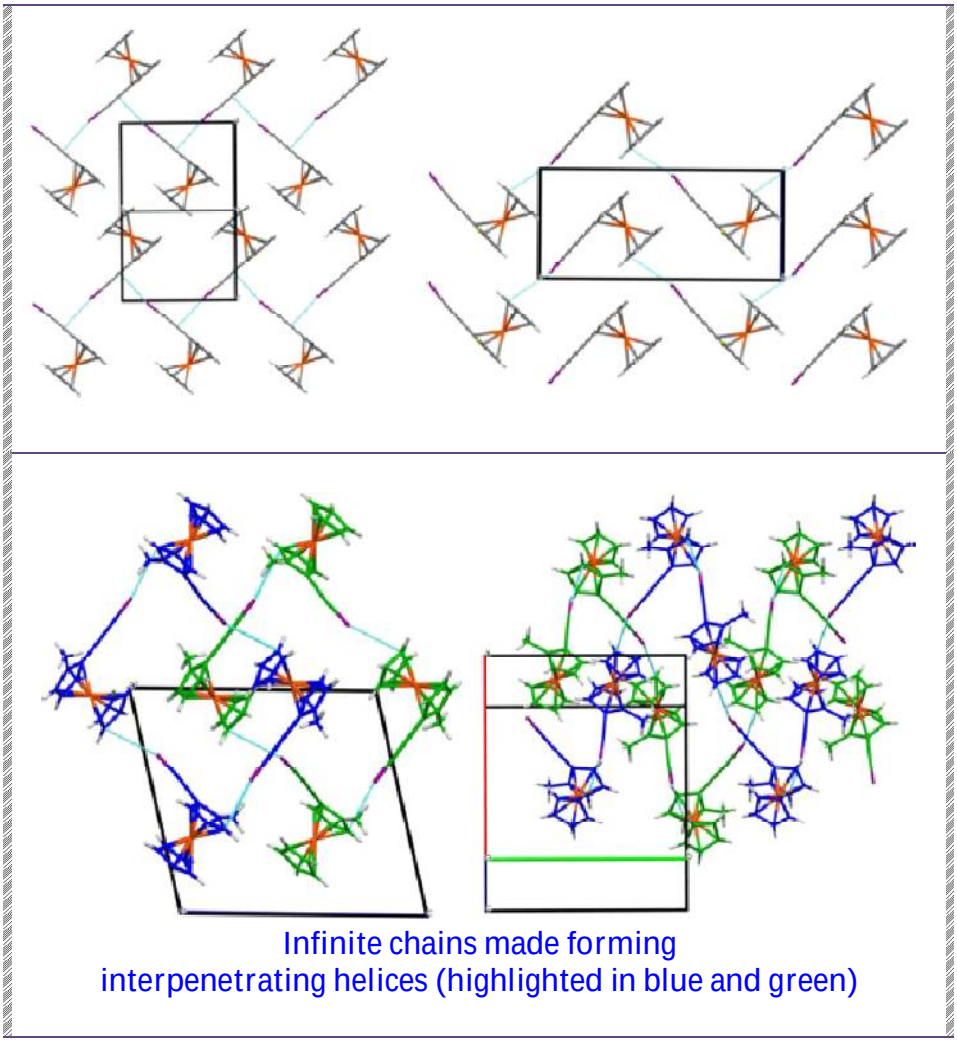


R = I	18	21	1b
R = SCF_3	19	22	3a
R = $SeCF_3$	20	23	3b



X = H, Y = I	24	31
X = 2-F, Y = I	25	9c
X = 2-Cl, Y = I	26	9b
X = 2-Br, Y = I	27	9a
X = 2-Cl, Y = SCF_3	28	16a
X = 2-Cl, Y = $SeCF_3$	29	17a
X = 3-Cl, Y = I	30	10b

I···C halogen bonds (dashed cyan)

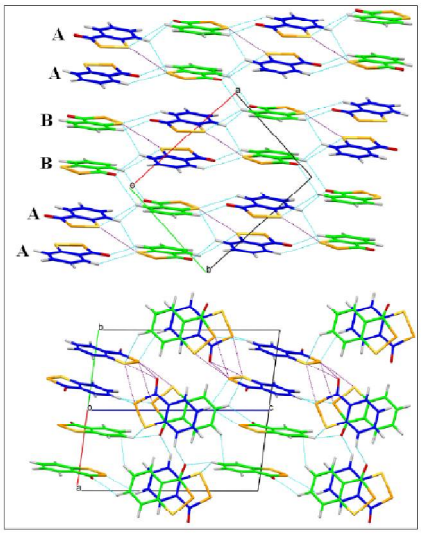


Infinite chains made forming
interpenetrating helices (highlighted in blue and green)

ChB + HB+

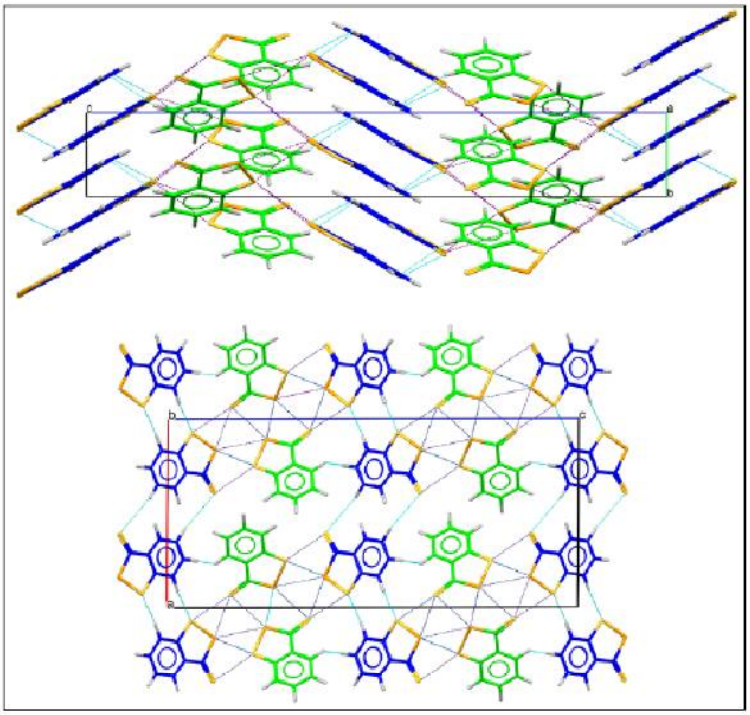
π stacking

Chalcogen Bond		ChB.	ACS.	31?
Crystal packing COSeS				



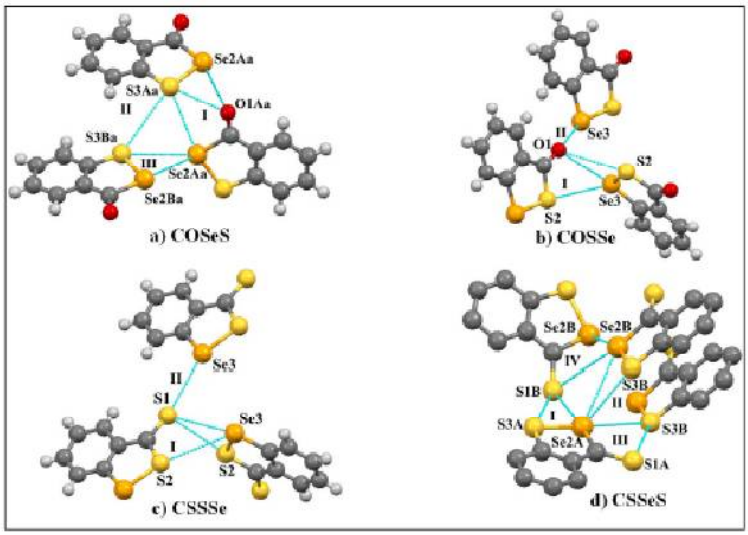
Chalcogen bonding (purple) ;Hbond (cyan)

CSSeS --- Crystal packing



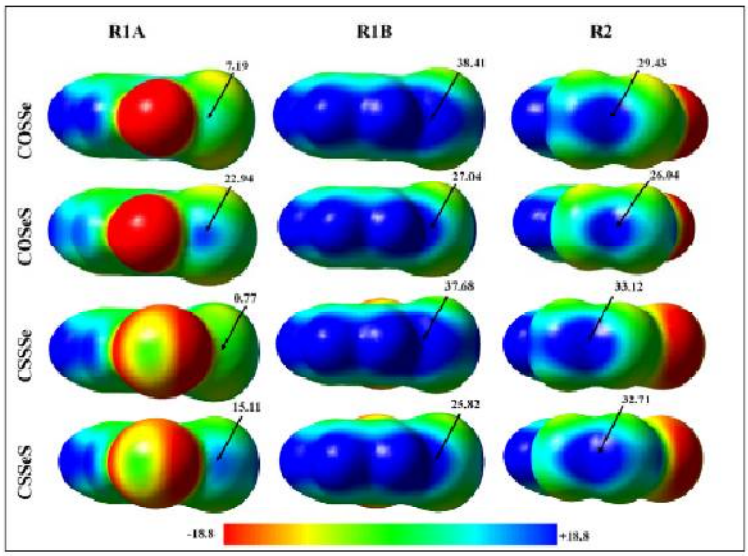
Chalcogen bonding (purple) ;Hbond (cyan) ; π stacking

ChB motifs



ESP

COSSe, COSeS, CSSSe and CSSeS

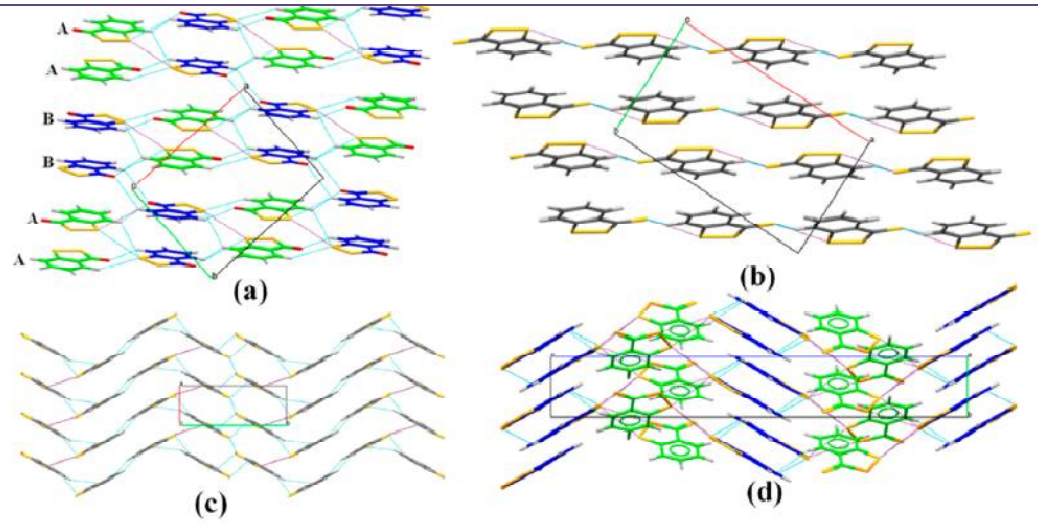


HB+

π stacking

Chalcogen Bond (S ; Se)	o H-bond o π-stacking	ChB.	ACS.	27

Interactions
π-stacking, hydrogen bonding (cyan)
chalcogen bonding (purple)

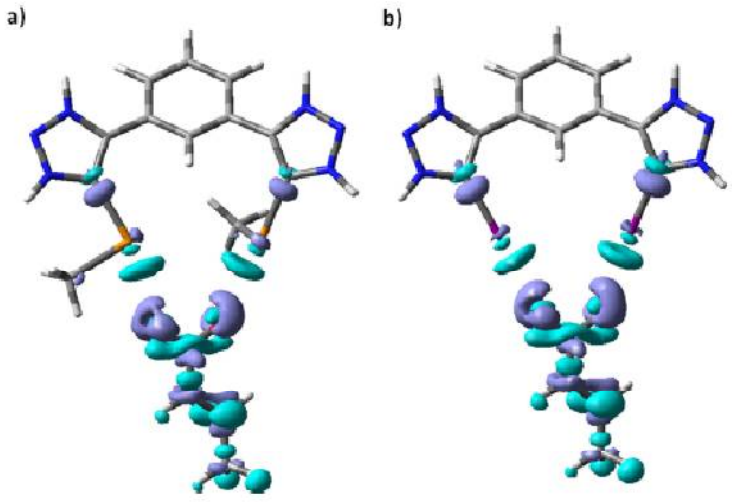


Crystal packing of (a) COSS, (b) CSSS (AYOZAR),
(c) CSSS polymorph (AYOZAR01), (d) CSSeS (CCDC code: NABQUC)

Chalcogen Bond (Te)		ChB.	ACS.	17

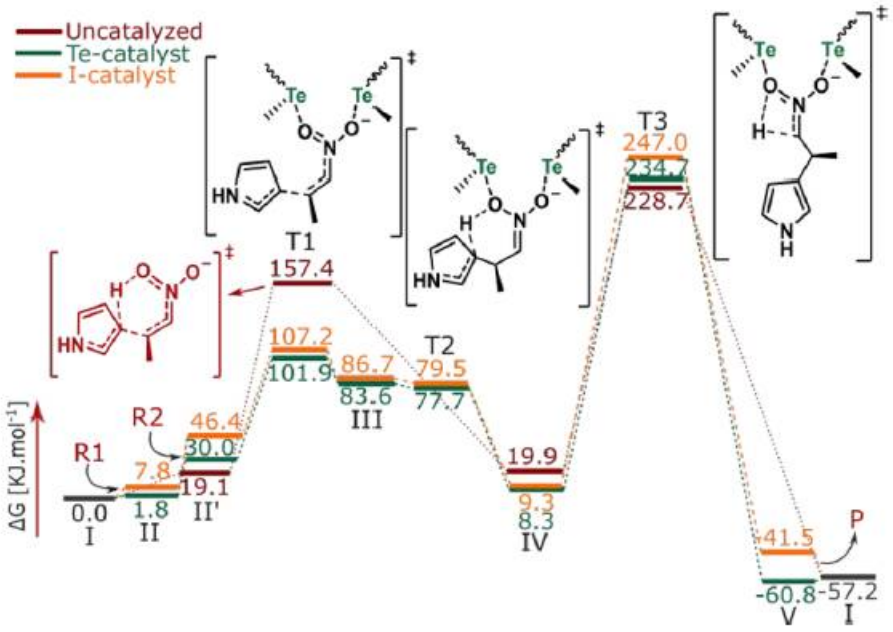
3D isodensity Electron density plots
Turquoise accumulation ; purple depletion

Halogen bond Chalcogen bond



charge displacement from nitrostyrene oxygens to (a) Te and (b) I σ-holes

Gibbs free energy profile -- nitro-Michael reactions
uncatalyzed, Te-catalyzed, and I-catalyzed



Gibbs free energy profile
uncatalyzed nitro-Michael reactions with
zero, one, two, three water molecular bridges