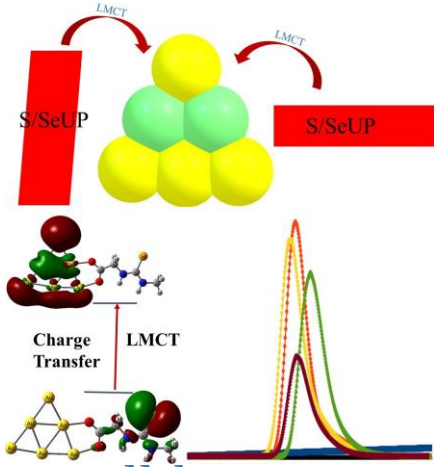
Computational Studies on Interface Structure and Charge Transfer Properties of Thio and Seleno-Ureidopeptide Functionalized Bimetallic Nanocluster

*Divya Maldepalli Govindachar, and Ganga Periyasamy**
Department of Chemistry, Bangalore University, Bengaluru-560056
divyamg03@gmail.com



- Peptides are building blocks of proteins and are found to play a major role in almost all bioactivity like catalysis, signal transduction, metabolism, etc.
- Many substituted peptides are reported with thio, seleno, ureido, thioureido, selenoureido, groups that are found to alter the backbone structure and their functions as in proteins or enzymes.
- These synthetic analogous are called peptidomimetics and used in the field of drug delivery, sensors, and molecular devices.
- The lower electronegativity and the greater polarizability of sulfur and selenium increase the reactivity of these moieties and inclined to display interesting physical, chemical, and biological activities when compared to regular peptides.
- The peptidomimetics units are anchored on metal clusters for drug delivery, photoswitches, and sensors, where the interface chemistry becomes an important control to tune towards the required application.

Theoretical Methodology

- DFT calculations in this work were performed using CAM-B3LYP and wB97XD hybrid functional with LANL2DZ pseudo potential basis set for Au, Ag, Pd, and Pt atoms, 6-31+G(d) and TZVP all-electron basis set for all other atoms as implemented in the Gaussian 09 package.
- An analysis of the vibrational normal modes in the ground state has been carried out in order to characterize the minima or maxima nature of the molecules at the potential energy surface.
- Time-dependent density functional theory (TDDFT) has been used to calculate the transition energy and wavelength in CAM-B3LYP functional.
- Natural population analysis (NPA) have been carried out to analyse the nature of charge distribution in metal nanocluster and functional moiety.
- BSSE corrections are carried out using the Boys and Bernardi counterpoise correction method as implemented in the Gaussian 09 package at the same level of theory.

$IE = (E_{(S/SeUP\text{-}Au4M2)} - [E_{(Au4M2)} + E_{(S/SeUP)}] + BSSE$ for neutral clusters and

$IE = E_{(S/SeUP\text{-}Au4M2)} - (E_{(Au4M2)}^{+} + E_{(S/SeUP)}^{-}) + BSSE$ for ionized clusters.

- Hole migration was examined via migration of a hole produced after vertical ionization of the neutral molecule at CAM-B3LYP functional.
- The hole migration occurs at Vertical ionization, before nuclear relaxation, or at frozen frame nuclei.

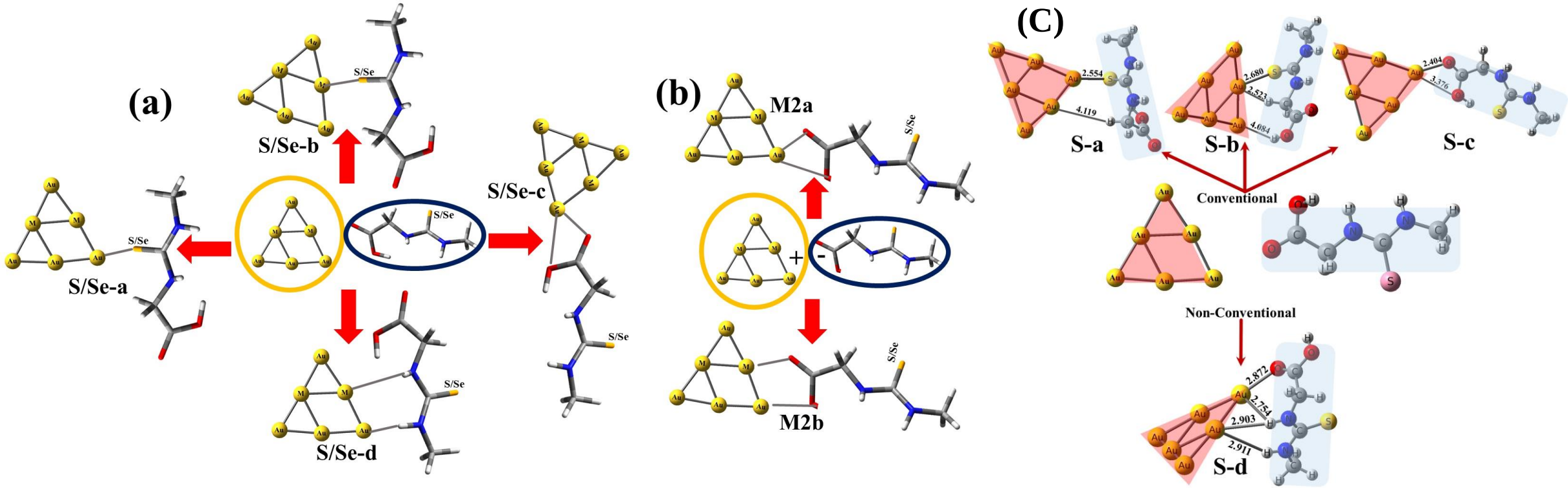
Structure and Interface

Peptides have the possibilities to interact with both edge and/or corner atoms in following manner,

(i) Conventional bond between S/Se atom of ureido end and metal clusters (Au-S/Se =2.554/2.636 Å).

(ii) Metal clusters form a strong bond with carboxylate unit (Au-O = 2.403- 3.370 Å).

(iii) Non-conventional H-bonding interaction between ureido end and metal cluster.



Govindachar, D. M., Periyasamy, G., *Journal of Molecular Graphics and Modelling 106 (2021) 107929*

Models	ΔE (kcal/mole)							
	Au_6-SUP				Au_6-SeUP			
	CAM-B3LYP		wB97XD		CAM-B3LYP		wB97XD	
	6-31+G*	TZVP	6-31+G*	TZVP	6-31+G*	TZVP	6-31+G*	TZVP
S/Se-a	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
S/Se-b	5.91	6.04	8.64	8.91	5.59	6.34	9.78	9.54
S/Se-c	4.00	4.44	8.53	9.35	6.84	6.51	9.29	9.36
S/Se-d	2.21	2.69	0.16	0.48	4.72	4.41	1.59	1.73
M2a	8.24	8.72	9.24	9.45	8.26	8.71	9.29	9.48
M2b	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

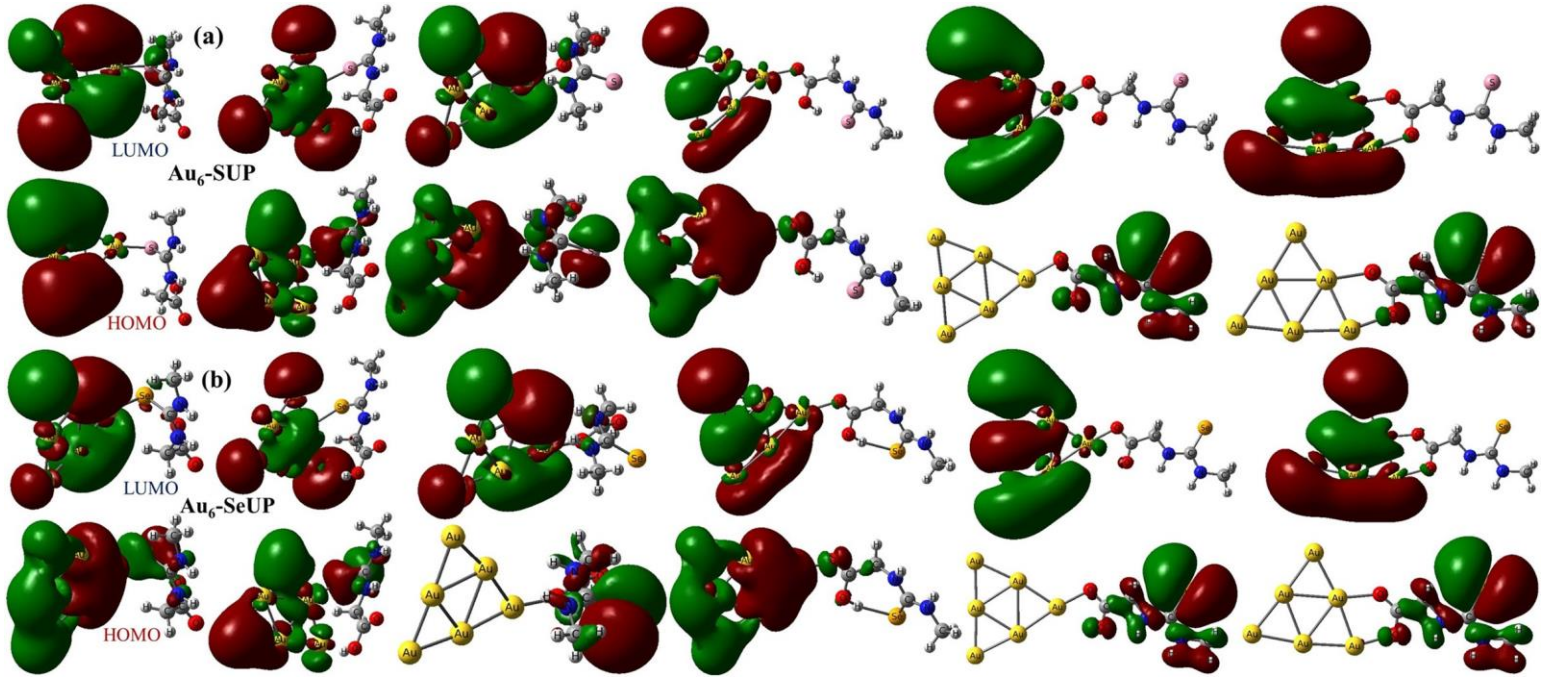
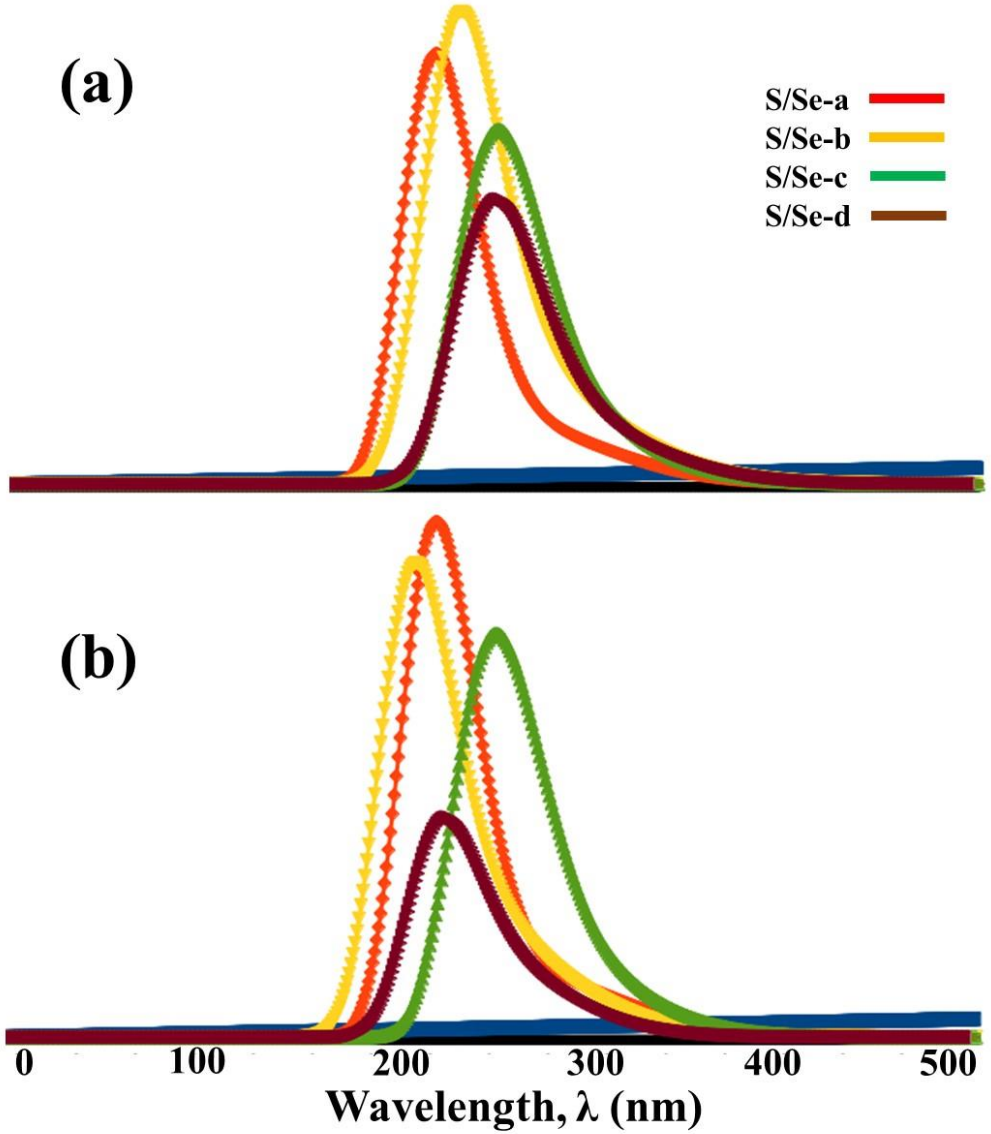


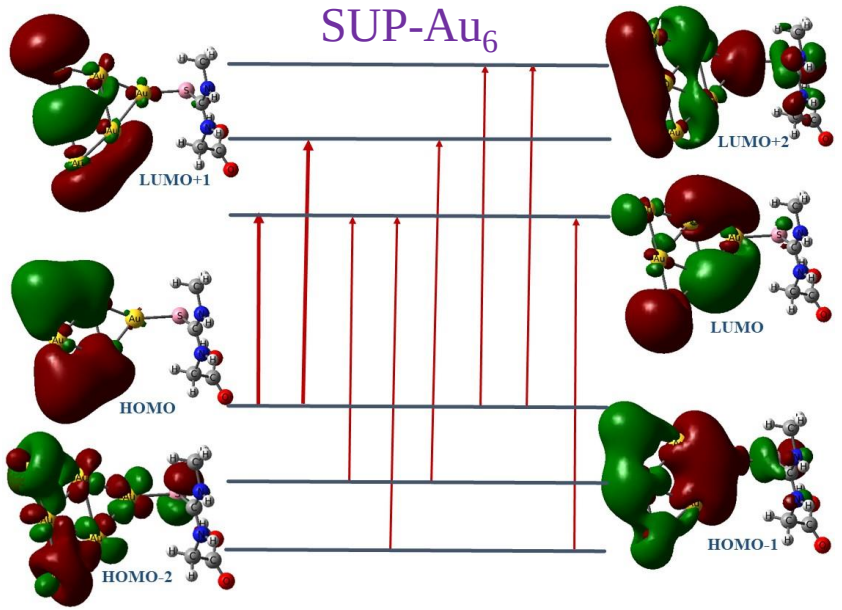
Figure. Computed molecular orbital plots (a) Au_6-SUP and (b) Au_6-SeUP of various binding modes with the counter value of 0.02 $Å^{-3}$.

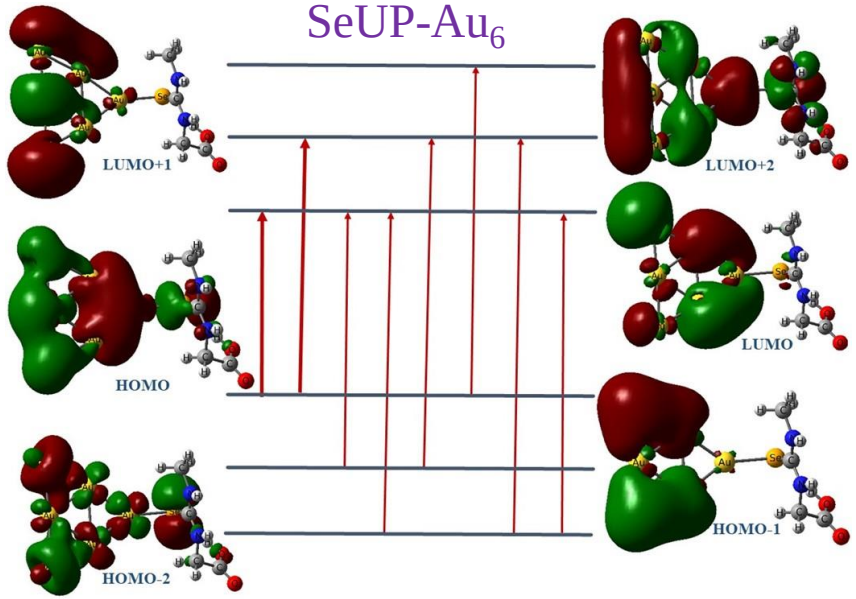
Charge Distribution

Models	Natural charge population in e									
	Au_6-SUP					Au_6-SeUP				
	Au_6	Ureido end	Carboxylate end	Peptide fragment	Interface atoms	Au_6	Ureido end	Carboxylate end	Peptide fragment	Interface atoms
S/Se-a (Au-S/Se)	-0.046	-0.037	0.013	0.046	-0.002 -0.277	-0.207	0.004	0.013	0.208	-0.037 -0.209
S/Se-b (Au-S/Se)	-0.235	0.005	0.054	0.235	-0.228 -0.189	-0.288	0.049	0.053	0.288	-0.268 -0.119
S/Se-c (Au-O)	-0.077	-0.118	-0.002	0.077	0.105 -0.709 -0.651	-0.076	-0.120	-0.002	0.076	0.104 -0.708 -0.651
S/Se-d (Au-HN: Au-HN)	-0.068	-0.164	0.019	0.068	-0.146 -0.216 0.142 -0.240	-0.071	-0.163	0.022	0.071	-0.156 -0.212 0.146 -0.238
M2a (Au-O)	0.723	-0.113	-0.218	-0.723	0.083 0.282 -0.352 -0.271	0.724	-0.114	-0.219	-0.724	0.083 0.284 -0.352 -0.271
M2b (Au-O) (Au-O)	0.734	-0.108	-0.245	-0.734	0.149 -0.361 0.294 -0.304	0.734	-0.109	-0.245	-0.734	0.148 -0.362 0.294 -0.303

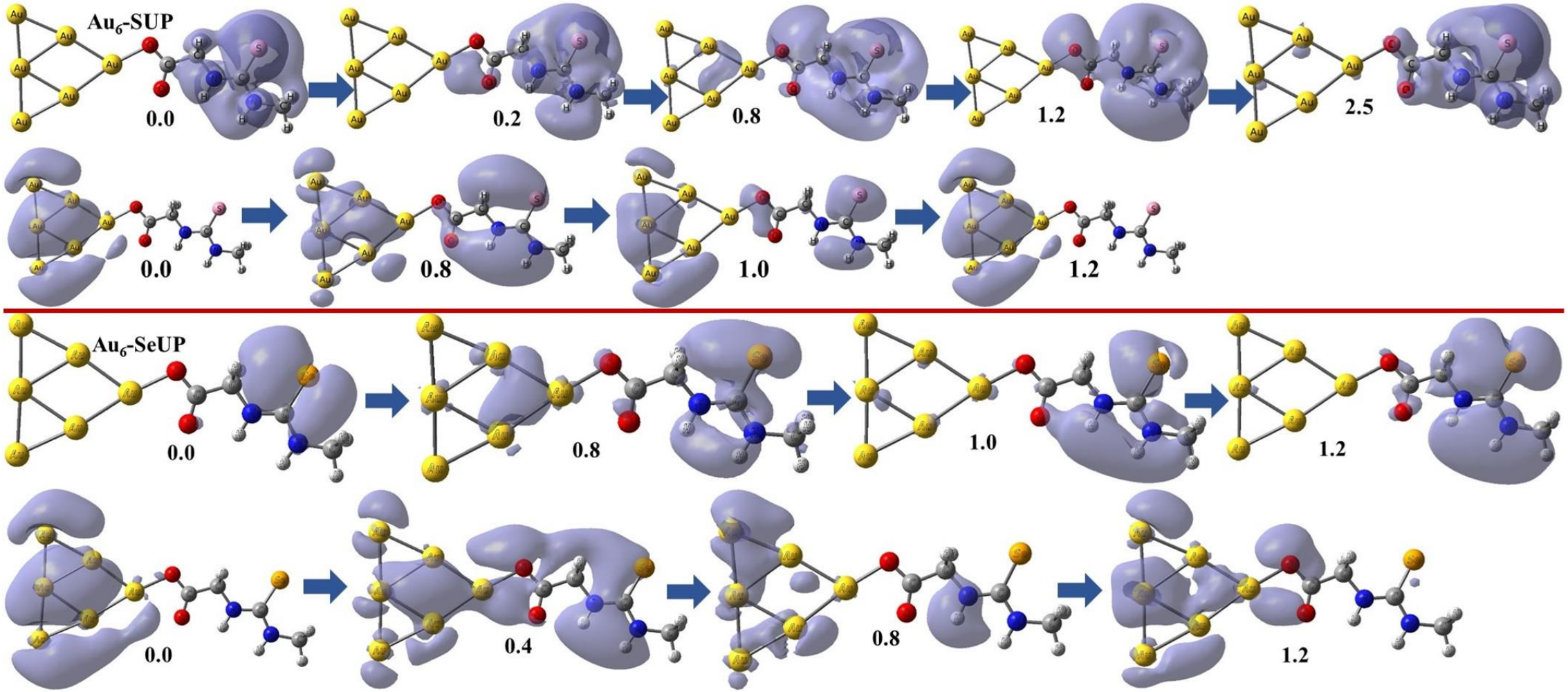
Optical Properties







Charge Transfer Dynamics



Densities are plotted with an isocontour value of 0.002 $Å^{-3}$

F. Remacle, R.D. Levine, Proc. Natl. Acad. Sci. U. S. A. 103 (2006) 6793–6798.

THANK YOU

Acknowledgment

We thank the Department of Science and Technology-Core Research Grant, India (DST-CRG) for funding.