



Charge Transfer Interactions of *p*-Azoxyanisole Complexes for Electrooptical Activity

CH. RAVI SHANKAR KUMAR^{1,*}, S. DEEPTHI² and ANJALI JHA³

¹Department of Physics, Institute of Science, GITAM University, Visakhapatnam-530045, India

²Department of Physics, Lendi Institute of Engineering & Technology, Visakhapatnam-535005, India

³Department of Chemistry, Institute of Science, GITAM University, Visakhapatnam-530045, India

*Corresponding author: E-mail: rskchaval@gmail.com

Received: 6 January 2020;

Accepted: 16 March 2020;

Published online: 27 June 2020;

AJC-19919

In particular interactions due to organic-inorganic molecules results self assembled structures organize supramolecular structures for molecular, electronic and electrooptical properties. Supramolecular structures originated are complexes with organic (*p*-azoxyanisole) molecule, synthesized with metal nanoparticles (iron, copper and aluminium.) Spectroscopic studies interpret infrared spectra with wavenumbers of characteristic bands in assigned regions; wavenumbers with reduced intensity in Raman spectra attribute metal-organic framework with charge transfer. Designed frame work with dense participation of carriers interpret electron correlation and exchange interaction specifying molecular, electronic and electrooptical properties with Gaussian package using electron density method. Deterministic procedure attribute vital role of charge transfer interactions responsible in formation of complex with improvement in properties responsible for electrooptical activity.

Keywords: *p*-Azoxyanisole, Nanoparticles, FMO Contours, Polarization, Electrooptical properties.

INTRODUCTION

Supramolecular structures with metal organic framework arise due to intermolecular interactions with donor, acceptors or fusion of donors and acceptors. Modification of these molecular structures evolve due to dense participation of charge has diverted attention of researchers for design novel molecular structures for numerous applications in chemical and biological sensors, actuators and related optoelectronic devices. A recent study with charge transfer interactions relates chemical properties of metal organic complexes with liquid chromatography [1], X-ray diffraction method [2] and elemental analysis [3]. These synthesized metal organic complexes depend on oxidation, coordination number and reactivity in formation of self assembled supramolecular structures [4] that enable to understand biological evaluation [5] and optoelectronic properties [6]. Forces like short range repulsive forces, electrostatic forces, ion pairs, dipole-dipole interactions evolve due to dense charge carriers with non-covalent interactions responsible in formation of supramolecular structures in metal organic framework. Focus of present article is supramolecular structure due to self assembling in terms of charge, functionality, structure and transition

between partially filled states with the electron density method. The method culminate electron correlation and exchange interaction that provide insights of metal and organic complexes with focus on structural properties, non-linear properties [7] and molecular docking [8]. Present frame work of complexes is with metal oxide nanoparticles (aluminium oxide (ALO) [9], copper oxide (CUO) [10] and iron oxide (IO) [11]) with *p*-azoxy-anisole using ultrasonication. Accurate molecular structure of *p*-azoxyanisole (AZ) and complexes AZIO, AZCUO and AZALO with chemdraw are illustrated in Fig. 1. Bonding mechanism of these deigned structures were interpreted for bonding mech-anism with FTIR and FT Raman spectra along with shifts in wave numbers. Electron density method (B3LYP) with 6-31(d) basis set for molecular properties, frontier molecular orbital contours (FMO), polarization and first order hyperpolariza-bility responsible for electrooptical activity.

EXPERIMENTAL

Metal oxide nanoparticles and *p*-azoxyanisole were purchased from Sigma-Aldrich, used as such without further purification. Size of metal oxide nanoparticles were less than 50 nm

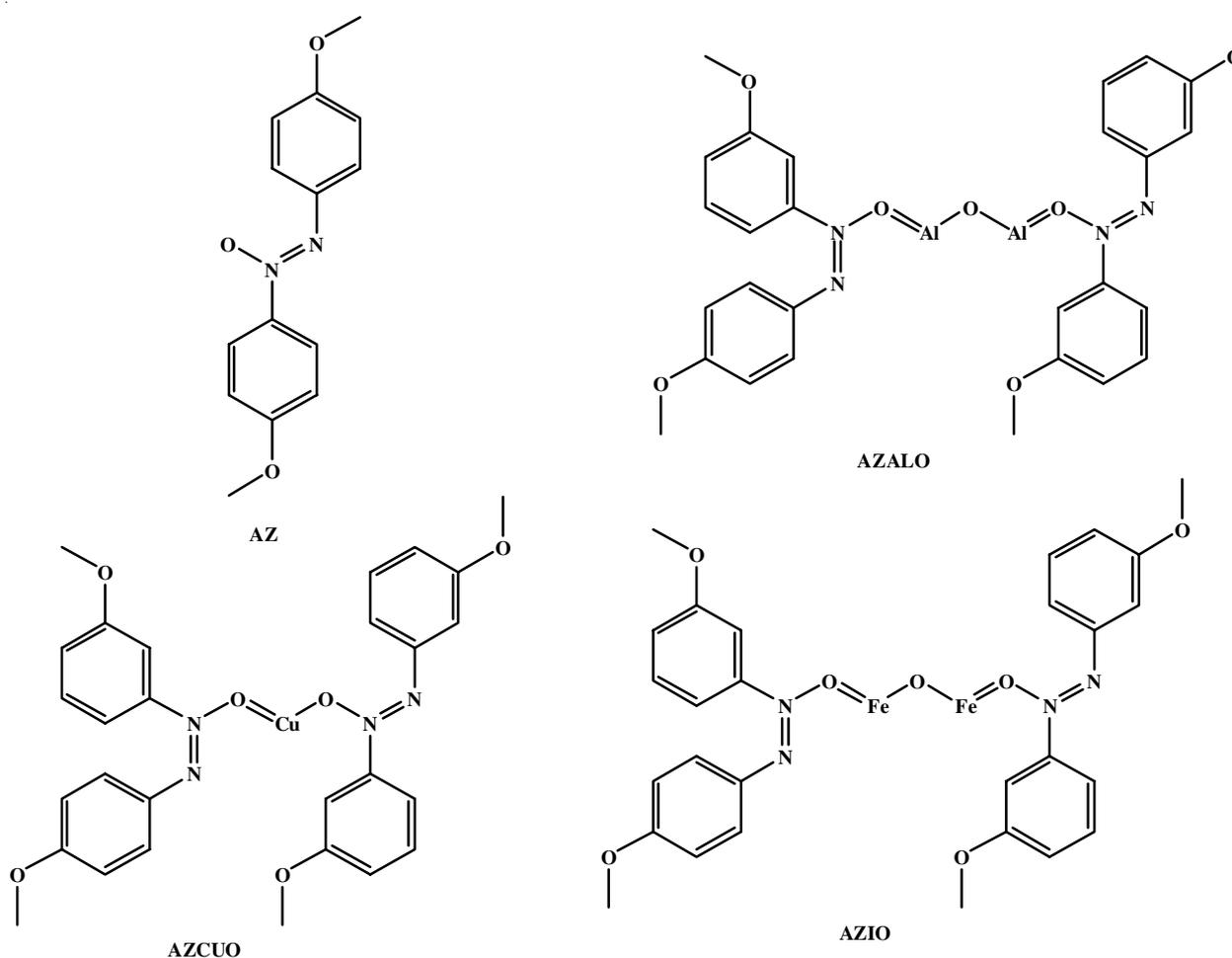


Fig. 1. Bonded molecular structure of *p*-azoxyanisole (AZ) and complexes

(IO-19 nm, ALO-47 nm and CUO-14 nm). Ultrasonication was performed with PCI analytics 250 W ultrasonic processor with a 12 mm probe operating at a fixed frequency of 50 Hz AC supply ; 220V. Sonication is a turbulence with ultrasonic frequencies for speed dissolution of the two compounds.

Synthesis of *p*-azoxyanisole nanoparticle complexes:

Powdered compounds of metal oxides were synthesized according to respective molar mass with respect to the organic compound. Synthesis of *p*-azoxyanisole with metal oxides was carried with preparing solutions for the powdered form of compounds. In the first step, 500 mg of *p*-azoxyanisole was dissolved in respective proportions of ethanol for the process of ultrasonication. In the next step, in a separate beaker iron oxide (0.075 mg), copper oxide (0.010 mg) and aluminium oxide (0.012 mg) was dissolved in ethanol solution for ultrasonication. The resultant mixtures were subjected to further ultrasonication and dried with desiccators in obtaining a yield of 96%. Spectroscopic studies were performed for bonding mechanism with infrared and Raman spectra; molecular and electronic properties were attributed with Gaussian package.

RESULTS AND DISCUSSION

IR and Raman spectral analysis: Infrared spectra was recorded with ThermoNicolet 6700 spectrometer in 4000-400

cm^{-1} wavenumbers with shifts in wavenumbers for bonding in *p*-azoxyanisole and complexes. Typical infrared spectrum of *p*-azoxyanisole in Fig. 2 and complex (AZALO) is illustrated in Fig. 3 with respective characteristic bands of fingerprint and functional groups in all complexes are listed in Table-1.

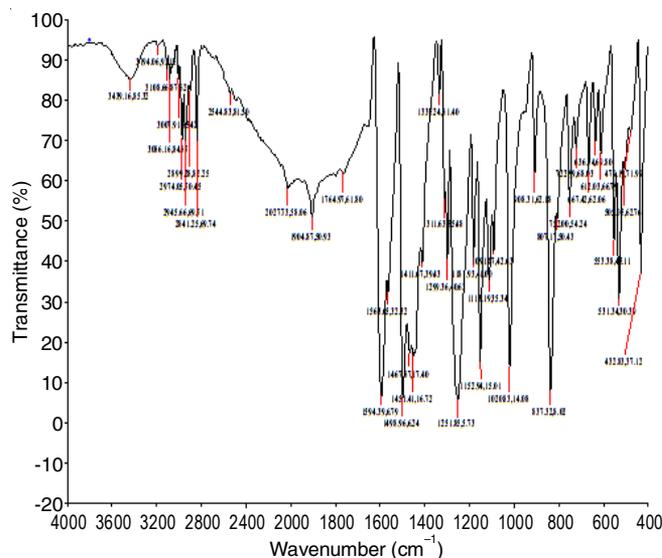


Fig. 2. Infrared spectra of *p*-azoxyanisole

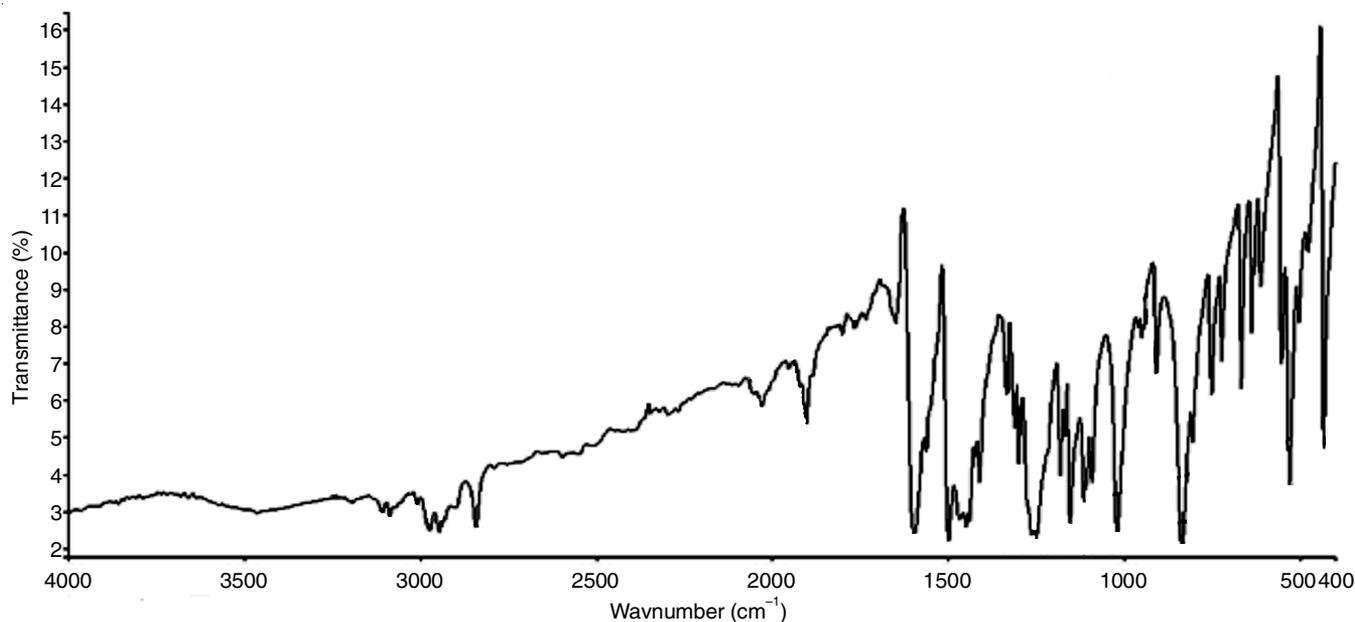


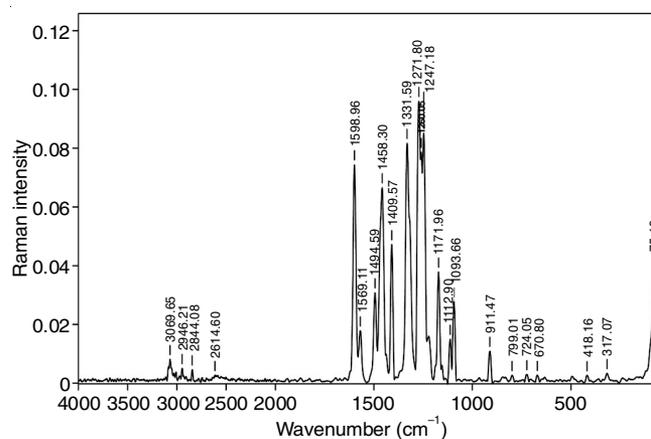
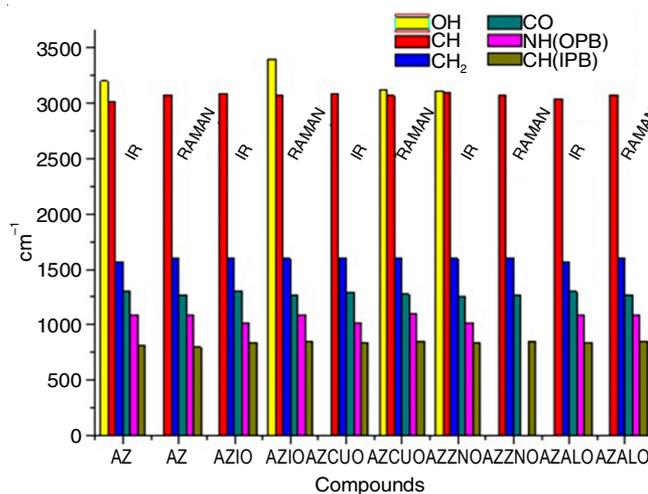
Fig. 3. Infrared spectra of complex AZALO

Compd.	C-H	CH ₂	C-O	NH _(OPB)	CH _(IPB)
AZ	3007	1563	1299	1091	807
AZIO	3084	1594	1298	1020	837
AZALO	3035	1564	1298	1092	837
AZCUO	3085	1598	1296	1019	836

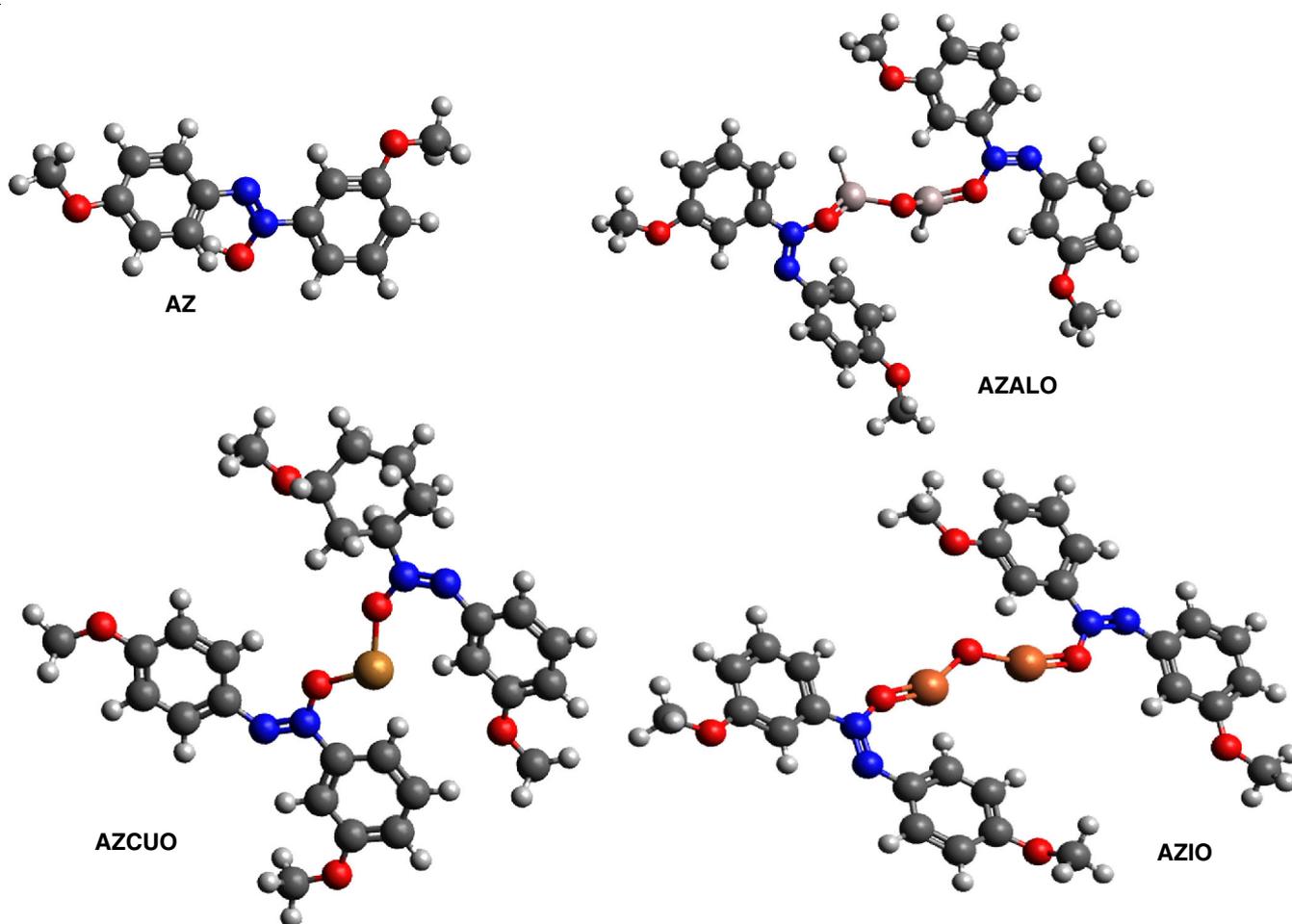
Significant peaks with wavenumbers (cm⁻¹) in *p*-azoxyanisole were 3007 (C-H), 1563 (CH₂), 1299 (C-O), 1091 (NH)_{OPB} and 807 (CH)_{IPB}. Analyzing infrared spectra revealed the hypsochromic shift (≈ 80 cm⁻¹) with complexes of oxides iron and copper and (≈ 30 cm⁻¹) with aluminium corresponding to C-H. Bathochromic shift of (≈ 70 cm⁻¹) corresponds to (NH)_{OPB} with complexes of iron and copper. All the complexes of *p*-azoxyanisole attribute a upward trend in wavenumbers in finger print region CH_(IPB). A significant feature of study is functional group C-O has not influenced complexes of *p*-azoxyanisole with unaltered shifts in complex AZALO corresponding to CH₂ and (NH)_{OPB}. These shifts in wavenumbers attribute bonding in the formation of complex with *p*-azoxyanisole.

FT-Raman spectra of the complexes revealed similar trend in wavenumbers in respective regions but with reduced intensity. Typical Raman spectra of *p*-azoxyanisole (Fig. 4) and approximate wavenumbers of infrared and Raman spectra are illustrated in Fig. 5.

Computational studies: Molecular and electronic properties were studied with electron density method B3LYP; 6-31(d) basis set of Gaussian package 03. These studies employ visualization of molecules, molecular orbital studies related to frontier molecular orbital contours and electrostatic potential (ESP) contour maps, which are responsible for electro-optical activity. Molecules are visualized in ball and stick model with representative atoms in grey (carbon), white (hydrogen), red (oxygen), blue (nitrogen) and brown (ALO, CUO and IO),

Fig. 4. Raman spectra of *p*-azoxyanisoleFig. 5. IR and Raman shifts of *p*-azoxyanisole and complexes

for molecular properties with Molecular Editor Avagadro as shown in Fig. 6. Optimized structures of complexes with

Fig. 6. Optimized structure *p*-azoxyanisole and complexes

p-azoxyanisole exhibited an increase in number of atoms, bonds, normal modes and molecular weight with designed molecular formula (Table-2).

TABLE-2
MOLECULAR PROPERTIES OF
p-AZOXYANISOLE AND ITS COMPLEXES

Compd.	Number of atoms	Number of bonds	Normal modes	Designed molecular formula
AZ	32	33	93	C ₁₄ H ₁₄ N ₂ O ₂
AZIO	45	47	135	C ₂₈ H ₂₈ N ₄ O ₇ Fe ₂
AZALO	41	44	126	C ₂₈ H ₂₈ N ₄ O ₇ Al ₂
AZCUO	41	44	126	C ₂₈ H ₂₈ N ₄ O ₆ Cu

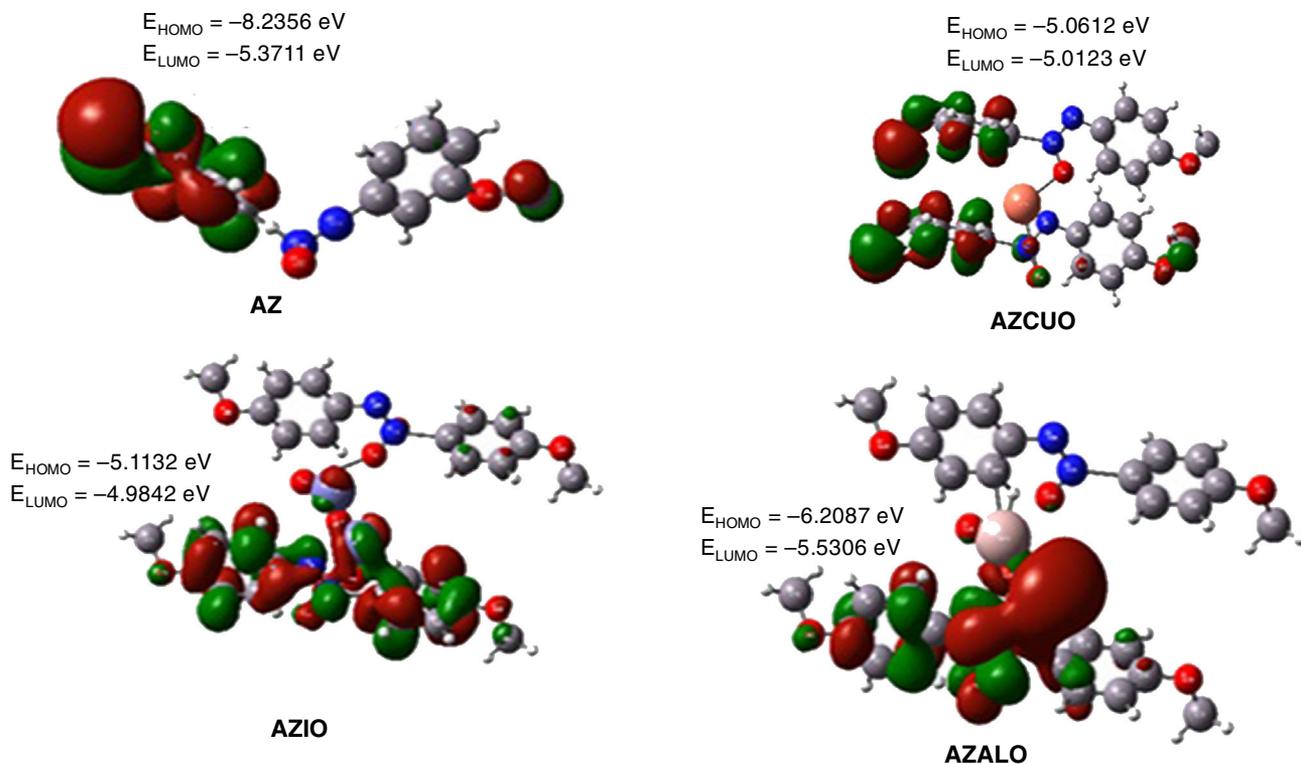
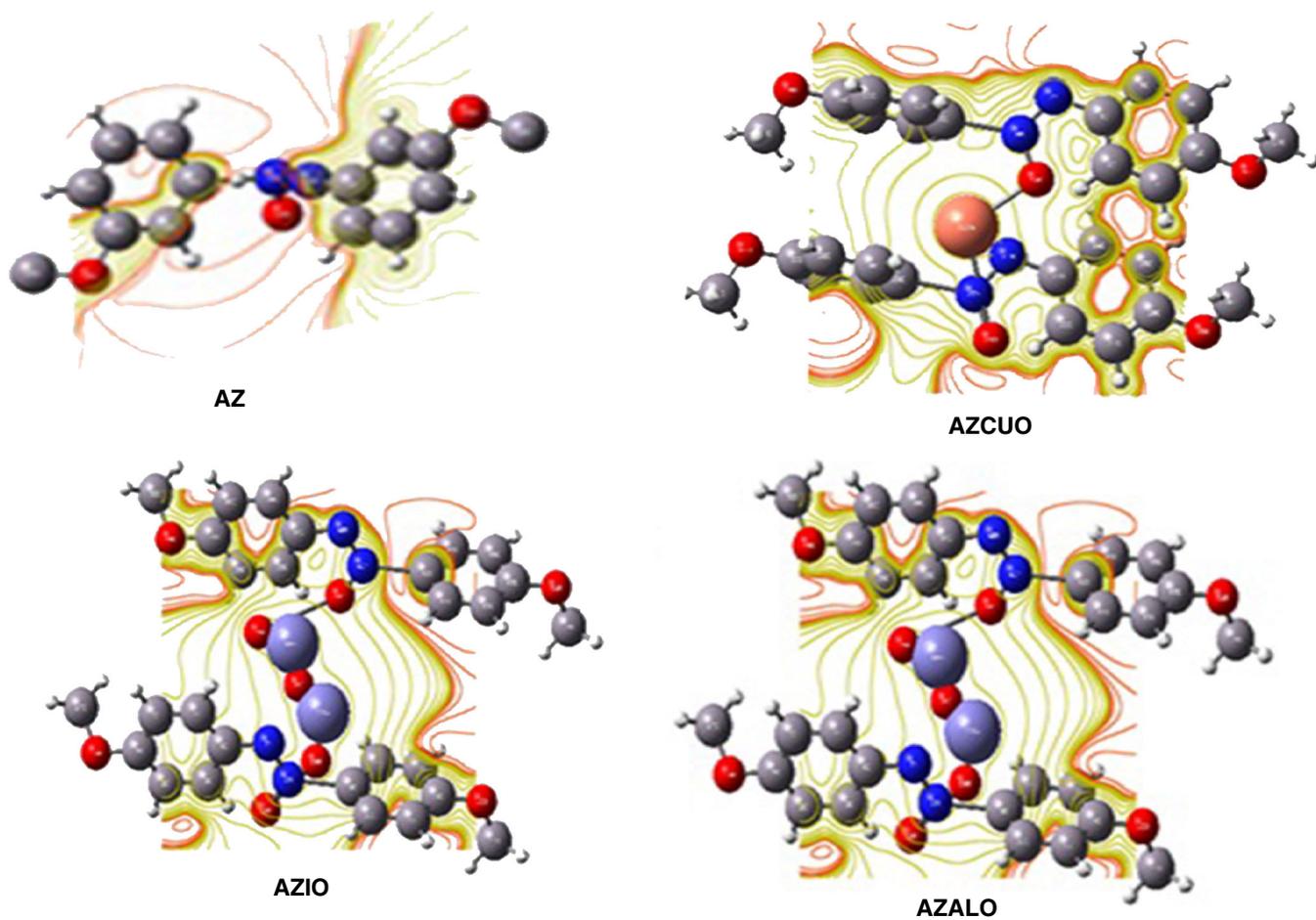
Molecular orbital studies [12] infer energies associated with charges in terms of ionization potential [13], electron affinity [13] responsible for charge transfer mechanism in formation

of complex elucidated with frontier molecular orbital contours (FMO) [14]. These contours specify regions of electropositive (green regions) and electronegative (red regions) responsible for charge distribution. Contours in red are LUMO (lowest unoccupied molecular orbital), green are HOMO (highest occupied molecular orbital) relate the electron affinity and ionization potential separated with energy gap as illustrated in Fig. 7 with electronic properties listed in Table-3.

Electronic properties responsible for electrooptical activity are the difference in energy gap (ΔE), dipole moment (ρ), chemical hardness (η), susceptibility ($\chi = -\mu$), electrophilicity index ($\omega = \mu^2/2\eta$), anisotropy of polarizability ($\Delta\alpha$), and first order hyperpolarizability (β) in respective units. Increase in high kinetic stability and dipole moment is a consequence of reduced energy gap responsible for electronic properties related electrooptical activity in terms of polarization and first order

TABLE-3
ELECTRONIC PROPERTIES OF *p*-AZOXYANISOLE AND COMPLEXES

Compound	E _{HOMO}	E _{LUMO}	ΔE (eV)	ρ (debye)	$\omega = \mu^2/2\eta$ (eV)	$\Delta\alpha$ (a.u.)	β (a.u.)
AZ	8.2356	5.3711	2.8645	2.094	16.15	122.96	77.22
AZALO	6.2087	5.5306	0.6781	3.522	50.81	543.75	176.70
AZIO	5.1132	4.9842	0.1290	3.214	202.28	311.88	616.09
AZCUO	5.0612	5.0123	0.0489	2.712	521.53	364.71	203.80

Fig. 7. Frontier molecular orbitals of *p*-azoxyanisole and complexesFig. 8. ESP contour maps of *p*-azoxyanisole and complexes

hyperpolarizability [15,16]. The performed studies reveal a intermolecular interactions with reduced energy gap and enhanced dipole moment with stabilization. The reciprocal behaviour of energy and wavelength, there is red shift resulted in high degree of aromaticity as result of electronic transition. Softness is a reciprocal of hardness infer tendency of nanoparticles in the formation of complexes AZALO, AZIO, and AZCUO with susceptibility with ultrasonication. Electronic properties [17-19] in complexes of *p*-azoxyanisole with high electrophilicity index infer electrooptical properties the polarizability and first order hyperpolarizability.

ESP contours maps itemized the electron distribution that favour low potential for high wavelength and high potential for low wavelength with gradient of colours. *p*-Azoxyanisole and its complexes revealed a greater influence of metallic oxides with large participation electron distribution (yellow lines) with high potential (Fig. 8).

Conclusion

Charge transfer interactions credit complexes of *p*-azoxyanisole with metal oxide nanoparticles. Synthesis of complexes infers greater participation of nanoparticles in exchange of charge carriers with high yield. Spectroscopic studies with shifts in wavenumbers substantiate intermolecular interactions with sharp peaks in infrared spectra. Studies with Molecular Editor symbolize enrichment in molecular properties with optimized geometry. Electronic properties assisted the formation of complexes in frontier molecular orbitals with high kinetic stability, electrophilicity index, polarization and first order hyper polarizability. Electron distribution with contour maps conveys a greater participation of electron transition with closely space contours of high potential.

ACKNOWLEDGEMENTS

The authors thank support extended by SATF, I.I.Sc., Bangalore and SAIF, IIT Chennai, India for recording the Infrared and Raman spectra, respectively. The authors thank Department of Chemistry, GITAM, India providing the necessary software for computational work.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- G.L. Mills, A.K. Hanson Jr, J.G. Quinn, W.R. Lammela and N.D. Chasteen, *Mar. Chem.*, **11**, 355 (1982); [https://doi.org/10.1016/0304-4203\(82\)90031-7](https://doi.org/10.1016/0304-4203(82)90031-7)
- A. Alkas and S.G. Telfer, *Aust. J. Chem.*, **72**, 786 (2019); <https://doi.org/10.1071/CH19213>
- Z. Adel El-Sonbati, A. Ashraf, El-Bindary and El-Sayed M. Mabrouk, *Transition Met. Chem.*, **17**, 66 (1992); <https://doi.org/10.1007/BF03325419>
- T.R. Cook, Y.-R. Zheng and P.J. Stang, *Chem. Rev.*, **113**, 734 (2013); <https://doi.org/10.1021/cr3002824>
- S.H. Sumra, M. Ibrahim, S. Ambreen, M. Imran, M. Danish and F.S. Rehmani, *Bioinorg. Chem. Appl.*, **2014**, 812924 (2014); <https://doi.org/10.1155/2014/812924>
- H. Xu, R. Chen, Q. Sun, W. Lai, Q. Su, W. Huang and X. Liu, *Chem. Soc. Rev.*, **43**, 3259 (2014); <https://doi.org/10.1039/C3CS60449G>
- P.A. Praveen, R.R. Ramesh Babu and K. Ramamurthi, *Mater. Res. Express*, **4**, 025024 (2017); <https://doi.org/10.1088/2053-1591/aa5cda>
- M.E. Zayed, F.A. El-Samahy and Gehad G. Mohamed, *Appl. Organomet. Chem.*, **33**, E5065 (2019); <https://doi.org/10.1002/aoc.5065>
- P.K. Ponnaian, R. Oommen, S.K.C. Kannaiyan, S. Jayachandran, M. Natarajan and A. Santhanam, *J. Environ. Nanotechnol.*, **4**, 23 (2015); <https://doi.org/10.13074/jent.2015.03.151145>
- Y.A. Godymchuk, G.G. Savelev and D.V. Gorbatenko, *Russ. J. Gen. Chem.*, **80**, 881 (2010); <https://doi.org/10.1134/S1070363210050026>
- E.B. Caitlin, A. Jordan, B.W. William and Z. Baohong, *PLoS One*, **7**, e34783 (2012); <https://doi.org/10.1371/journal.pone.0034783>
- D.E. Woon and T.H. Dunning (Jr.), *J. Chem. Phys.*, **103**, 4572 (1995); <https://doi.org/10.1063/1.470645>
- C.-G. Zhan, J.A. Nichols and D.A. Dixon, *J. Phys. Chem.*, **107**, 4184 (2003); <https://doi.org/10.1021/jp0225774>
- J. Conradie, *J. Phys. Conf. Ser.*, **633**, 012045 (2015); <https://doi.org/10.1088/1742-6596/633/1/012045>
- M. Arivazhagan and S. Jeyavijayan, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **79**, 376 (2011); <https://doi.org/10.1016/j.saa.2011.03.036>
- V. Krishnakumar, R. Sangeetha, R. Mathammal and D. Barathi, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **104**, 77 (2012); <https://doi.org/10.1016/j.saa.2012.10.002>
- S. Deepthi, A. Jha and Ch. Ravi Shankar Kumar, *Phys. Chem. Res.*, **7**, 27 (2019); <https://doi.org/10.22036/pcr.2018.144623.1522>
- S. Deepthi, A. Jha and C.R.S. Kumar, *Infrared Phys. Technol.*, **92**, 304 (2018); <https://doi.org/10.1016/j.infrared.2018.06.024>
- S. Deepthi, A. Jha and Ch. RaviShankar Kumar, *AIP Conf. Proc.*, **1859**, 020104 (2017); <https://doi.org/10.1063/1.4990257>