Synthesis and Quantum Chemical Studies of Metalloorganics For Electro-Optical Studies

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Abstract The dynamic nature of molecular materials are functional due to their nonlinear optical properties. Nonlinearity arising due to intermolecular interactions as self assembling phenomena between organic and metallic nanoparticles is of interest. The insight of this phenomena is attributed both by experimental and quantum chemical studies .Vibration studies performed by FTIR reveal intermolecular bonding forming metalloorganic POMZ with PAA and zinc oxide. These wave numbers were in agreement with theoretical studies performed by Gaussian 03v software package with B3LYP/6-31G basis set. Nonlinear optical properties such as energy difference, dipole moment, electronegativity, electrophylicity index and polarizability were attributed for electrical and optical properties of the material.

Keywords: FTIR , Zinc oxide, DFT

INTRODUCTION

Nonlinear optical properties are important for important for photonic technologies that require materials with effective performance. At present organics[1-3] dominated inorganics and attracted attention for nonlinear materials possessing good photochemical and thermal stability for NLO applications[4-6].Supramolecular structures formed by self assembling process are liquid crystals possess nonlinear phenomena and in particular organic liquid crystal occupied revolutionized nonlinear optical properties[7-8].Self assembling process is due their intrinsic nature, size ,texture and shape of molecules designed for functionality between the host p-azoxyanisole (PAA) and guest zinc oxide (ZO) interactions to form MOPZ. Computational studies have different starting point of view that originates to several theories in particular DFT theory[9-12] is attractive method for determining nonlinear optical properties.

METHODOLOGY

Compounds p-azoxyanisole (PAA) and zinc oxide (ZO) are obtained from SigmaAldrich and used as such without purification. Ultrasonication with 40ml of ethanol solution for MOPZ is synthesized with 500mg of PAA and 0.06gm of zinc oxide nanoparticles of size 35nm using PCi analytics 250 W ultrasonic processor with a 12mm probe operating at a fixed frequency of

50 Hz AC supply ; 220V.FTIR studies were carried with Thermo Nicolet 6700.Size confirmation of zinc oxide nanoparticles with Xray diffraction spectrometer Bruker Kappa APEXII. Computational studies with Gaussian 03v B3LYP/6-31G(d) basis set. The host-guest interaction was built by Gauss view program with optimized geometry of molecules using Avagadro.

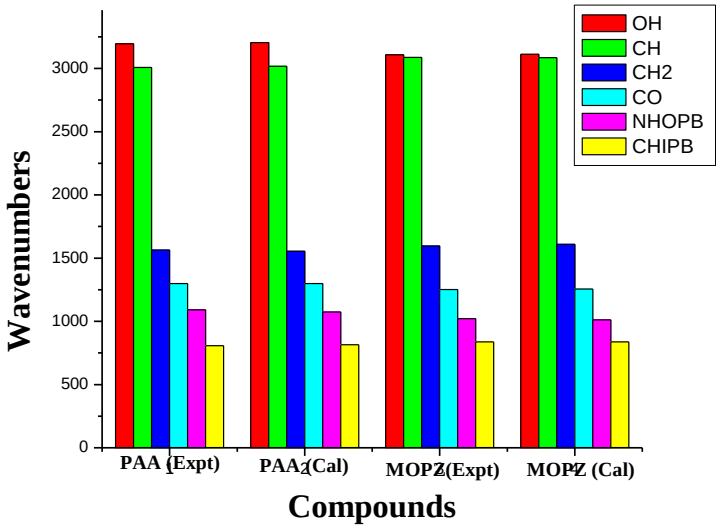
RESULTS AND DISCUSSION

Vibration studies for relating to PAA and MOPZ performed by FTIR were listed in table 1 with respective functional groups. The study reveals intermolecular bonding with hypsochromic and bathochromic shifts in forming MOPZ with reduced intensities and sharp peaks. Assignments of wave numbers with computational studies (calculated) were in agreement with experimental studies as illustrated in figure 1.

TABLE 1.Calculated and Experimental spectra of PAA and MOPZ

Name of the compound	Wavenumber assignments					
	O-H	C-H	$CH)_2$	C-O	$NH)_{OPB}$	$CH)_{IPB}$
PAA(Expt)	3194	3007	1563	1299	1091	807
PAA(Cal)	3205	3018	1554	1299	1074	815
MOPZ(Expt)	3108	3087	1596	1252	1021	837
MOPZ(Cal)	3112	3086	1609	1256	1012	838

FIGURE 1.Calculated and Experimental spectra of PAA and MOPZ



Optimized structures of PAA and MOPZ were illustrated in figure 2 and 3 with corresponding frontier molecular contours(FMO) arising due to HOMO and LUMO energies obtained by quantum chemical calculations[13] were illustrated in figure 4 and 5. Properties responsible for nonlinear optical properties include energy difference (ΔE), dipole moment (ρ), Chemical hardness (η), susceptibility (χ) and electrophilicity index (ω) are listed in table 2 along with optimized structures for PAA and MOPZ.

TABLE 2 Properties for Nonlinear Optical Phenomena.

Name of the compound	ΔE eV	ρ (Debye)	η	χ	ω	$\alpha_{tot} x10^{-24} esu$	$\Delta\alpha$
PAA	2.8645	2.094	1.4322	6.8032	16.15	94.83	122.96
MOPZ	0.1823	4.214	0.09	5.6438	176.95	202.31	273.07

FIGURE 2 Optimized structure of PAA

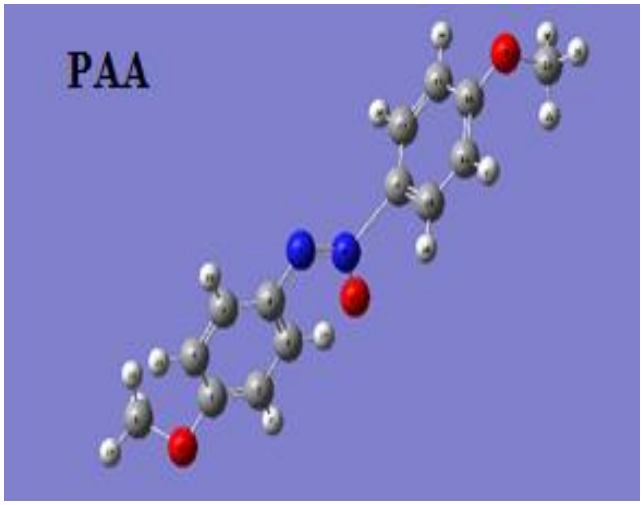


FIGURE 3 Optimized structure of MOPZ

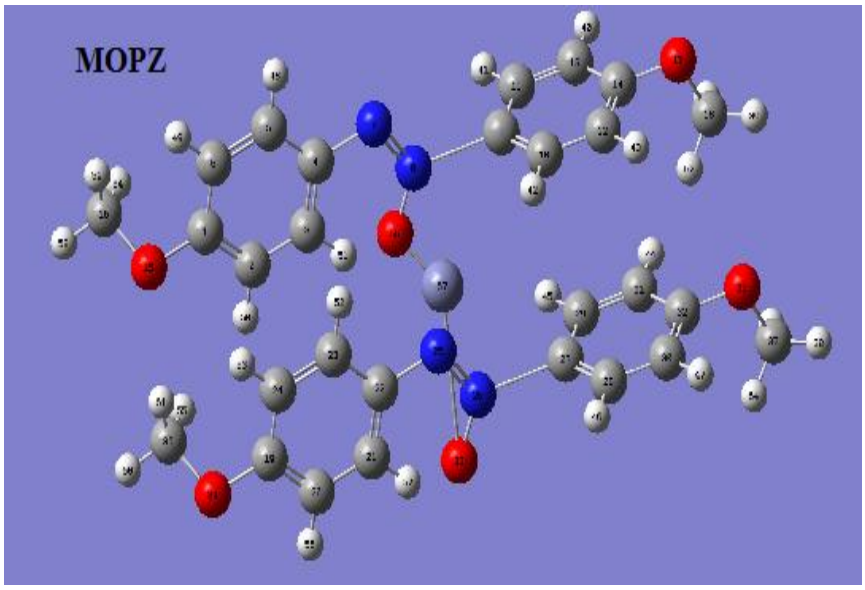


FIGURE 4 Frontier Molecular Contours of PAA

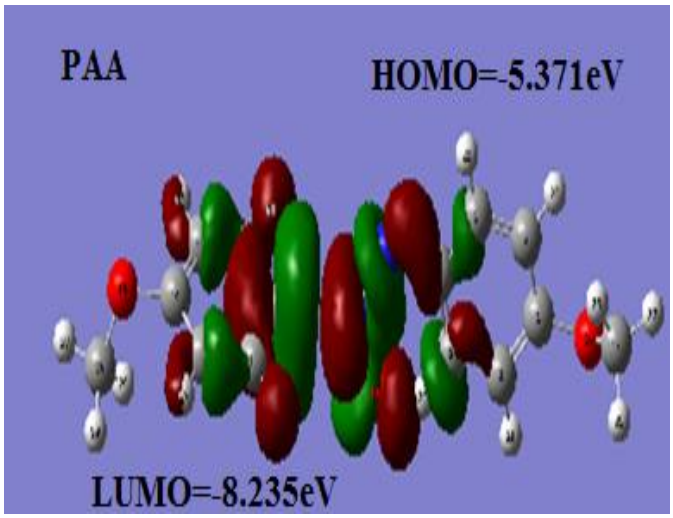
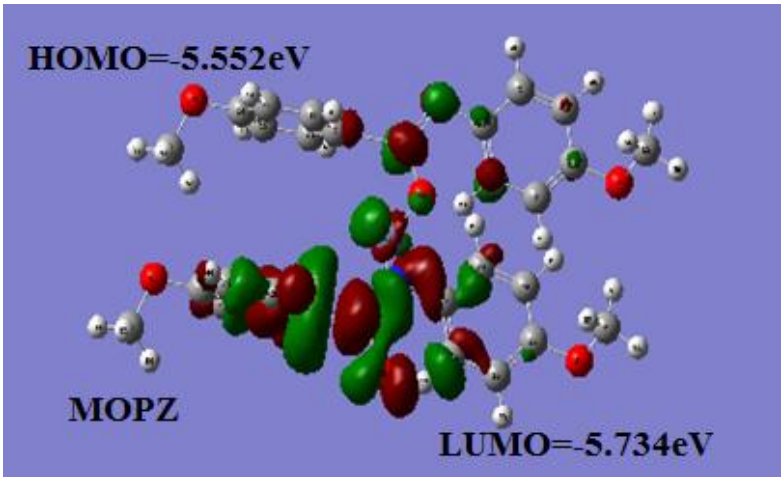


FIGURE 5 Frontier Molecular contours of MOPZ



Quantum chemical calculations performed reveal large conjugation with reduced energy gap and increased wavelength with stabilization. The reciprocal behavior of energy and wavelength ,there is red shift resulted in high degree of aromaticity as result of electronic transition. Further the softness of nonlinear materials is reciprocal of hardness gives an insight of nano particles are completed conjugated to form MOPZ with susceptibility. The electron donor acceptor interaction between host and guest with high electrophilicity index is responsibility for polarizabity lead to electro optical property on conjugation.

CONCLUSIONS

Optimization by quantum chemical calculations was studied in detail and influence of nanoparticles for electro optical studies is explained. Vibration analyses of experimental and theoretical studies were satisfactorily correlated. Properties responsible for electrooptical activity were reported and discussed. A consequence of reduced energy gap is a result of intermolecular interactions by self asembling process. Enhanced dipole moments with associated polarizability and anisotropy reflect the electroptical property of material.

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