

Influence of Br on the nanostructure properties of PMMA Polymer and p-Quaterphynel laser Dye: DFT study

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ABSTRACT

The main characteristic of our research focuses on the effects of adding Br to PMMA and structure tetra methely-p-Quaterphynel Dye, the optimized structure of PMMA and structure of tetra methely-p-Quaterphynel Dye in pure case and after doping has been modeled using Gaussian 09 with density functional theory (DFT) calculation and basis set B3LYB. Our work focuses on modify of the electronic properties of PMMA and tetra methely-p-Quaterphynel Dye, energy gap has been deacres after added Br to PMMA and tetra methely-p-Quaterphynel Dye, as well as uv-vis peak position and intensity. IR spectrum showes appears of new bond at reang of 500-750 in the case of PMMA refer to C-Br. **Acknowledgement** The authors acknowledge Asst.Prof. Hussein Neama AL-Khegani from Department of Laser Physics, College of Science for woman, University of Babylon, Hilla, Iraq for helpful advices in this work.

Keywords: Tetra methely-p-Quaterphynel Dye; PMMA-Br; DFT; Electric properties; IR & Raman

1. Introduction

Substitutions effect on molecules have always been a subject of study because it is our goal to modify molecules based on our needs. A way in which to study this phenomenon is to analyze the effects of substituents on the spectra of molecules. Solvent [1], substituent [2] and synthesis effects [3], as well as combinations of these effects [4], have been shown .

Recently, the polymeric materials have extensive uses because of their amazing combination of properties, durability, light weight and simplicity of processing. However, these materials face some problems like their weak thermal stability and also poor mechanical stability. Therefore, a large number of additives especially metal nanoparticles were added to polymeric matrix to overcome these problems and designed polymer matrix nanocomposite[5]. Polymer nanocomposites can be defined as materials in which nanoscopic inorganic particles, in at least one dimension, are dispersed in an organic polymer matrix to improve its performance properties. Polymer nanocomposites represent a new alternative to conventional filled polymers. Because of their size, the filler dispersion that nanocomposites exhibit markedly improves their properties when compared to pure polymers [6–12] or their traditional composites. Polymers are a viable option for creating flexible lasers with adjustable thresholds, wavelengths, and polarization [13,14]. Tunable RLs have recently been demonstrated by stretching or bending nanowire/nanoparticle implanted in polymers. By stretching silver nanowires implanted in

polydimethylsiloxane (PDMS), Zhai and co-authors achieved a wavelength-tunable RL (from 558 to 565 nm) [15]. In this paper, we report a new design of Br-PMMA and Br-p-Quaterphynel laser Dye. It contains Br grafting and studying its effects on the electronic and optical properties and its effect on the Oscillator strength, as it is considered the important sign in increasing the possibility of spontaneous emissions, which increases the efficiency of the medium in the random laser work.

2. Arithmetic Methodology

It is possible through computational chemistry to find (predict or speculate, for new and unknown compounds) Molecular Energy and Stereo structure of Transition States, Bond Energy, interaction energy, molecular orbitals, dipole moments, atomic charges, Vibration frequencies, RAMAN, IR spectroscopy, NMR properties, polarization, thermochemical properties and reaction method (reaction mechanism) [16-17]. As well as Various spectrophotometers such as RAMAN, UV, NMR, IR and special . can be predicted and calculated for new and unknown component.

Avogadro software was used to generate the molecular structures, and calculations were performed using GAUSSIAN 06. Density functional theory (DFT) was implemented for the frequency and energy optimization. Time-dependent DFT (TD-DFT), were employed for the theoretical study of excited states. For all the study was employed the same level of theory, the 6-311 G(d,p) basis set and-Lee-Yang-Parr (B3LYP) functional were employed. Plot and origin software programs used to evaluation and analysis the final result.

Cohesive energy "is defined by" required "energy to break" "condensing "material" into discrete "atoms". Which is mathematically defined as [18]

$$E_{coh} = \frac{E_{tot}}{n} - E_{free} - E_0 \quad (1)$$

where E_{tot} is the total energy, E_{free} is the free atoms energy, "an atom number", and E_0 vibrational "energy of lower state ". "The HOMO (highest energy were electrons filled it) "And LUMO (lowest energy that is empty) "are major in determining the properties" such as "molecular interaction" and the ability of molecule" to absorb the photon".

depending on "Koopmans" theory, the "band gap" equation:

$$E_g = E_{LUMO} - E_{HOMO} \quad (2)$$

"Ionization potential (IE) defined as "the energy amount that's required to takeout an electron from "separated atom or molecule and "show as the difference of energy between positive charged energy (E_+) and the neutral (E_n)" as the equation = $E_+ - E_n$ ". as well as, the "HOMO energy used to calculate" I_E in the form of Koopmans theory "which is mathematical form "as:

$$IE = -E_{HOMO} \quad (3)$$

"Electron Affinity (EA)" of a molecule or atoms the energy change" due to "adding electron to the neutral atom forming a negative ion and shows as the difference energy between neutral energy (E_n) and the negative charged energy (E_-) due to the relationship: $EA = E_n - E_-$. In addition, the LUMO energy was used to computing "EA" depending on "Koopmans" theory like:

$$EA = -E_{LUMO} \quad (4)$$

"Hardness (H) is a measure of molecule resistance" to the distortion or changing and defined as the form:

$$H = \frac{1}{2} \left(\frac{d\mu}{dN} \right) v(r \rightarrow) \quad (5)$$

"In terms of IE and EA", the hardness is the energy gap divided by 2 between two frontier orbitals as

follow:

$$H = \frac{IE - EA}{2} \quad (6)$$

"Hard molecule has huge or big energy gap . chemical hardness theoretically were Submitted by the DFT as the second derivative of electronic energy with respect to the number of electrons N , for a constant external potential $V(r)$ "shown in the Eq. (7):

$$H = \frac{1}{2} \left(\frac{d\mu}{d^2E^2} \right) v(r \rightarrow) = \frac{1}{2} \left(\frac{dN}{d\mu} \right) v(r \rightarrow) \quad (7)$$

"Electrophilicity" index (ω) is a measure of energy "cut down or (energy lowering) as a result of maxima electron stream in "between donor and acceptor, the electrophilicity index" gives by [18]:

$$\omega = \frac{\mu^2}{2H} \quad (8)$$

3. Results and Discussion

Molecular structure

Figure1 present the molecular structure of optimized PMMA, structure after adding 3Br and 6Br to PMMA respectively.

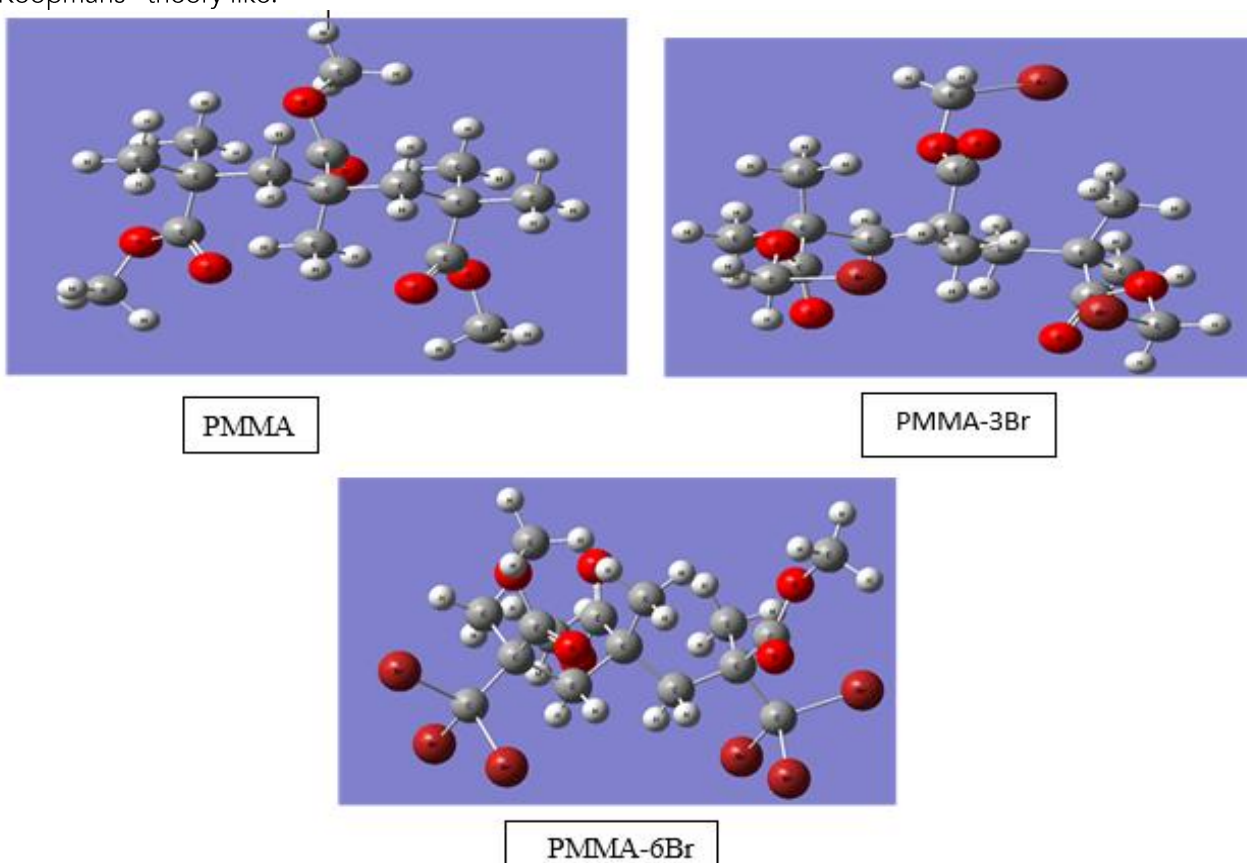


Figure1. Schematic molecular structure of PMMA and its composites

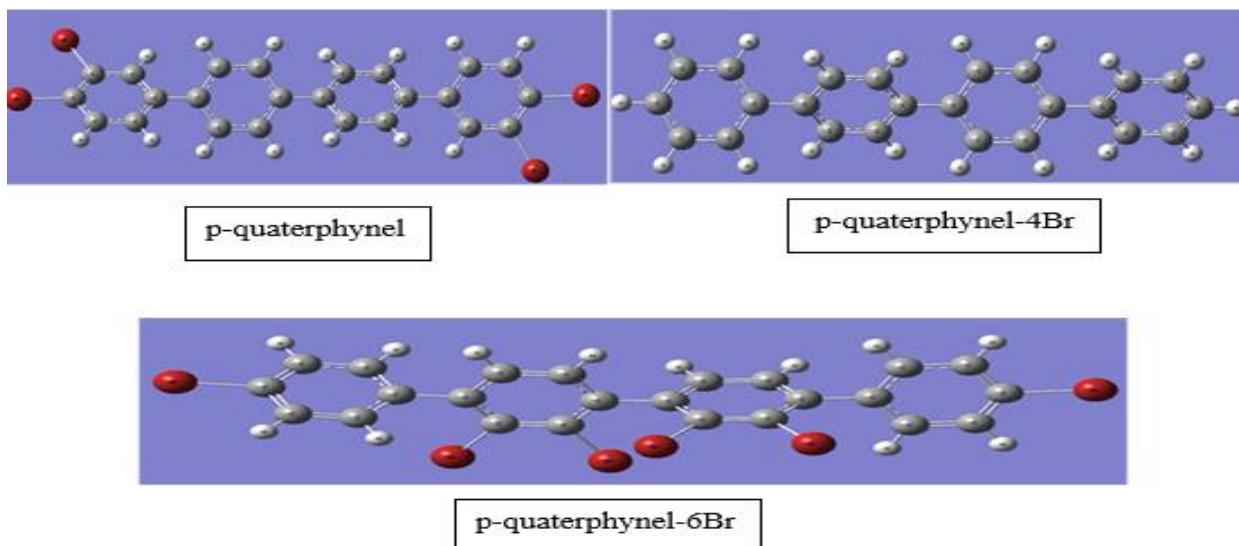


Figure2. Schematic molecular structure of p-quaterphynel Dye and of p-quaterphynel-Br.

Figure2 molecular structure of optimized p-Quaterphynel Dye and optimized structure after adding 4Br and 6Br respectively. While Figure3molecular structure of optimized p-

Quaterphynel Dye –PMMA and optimized structure after adding 3Br respectively

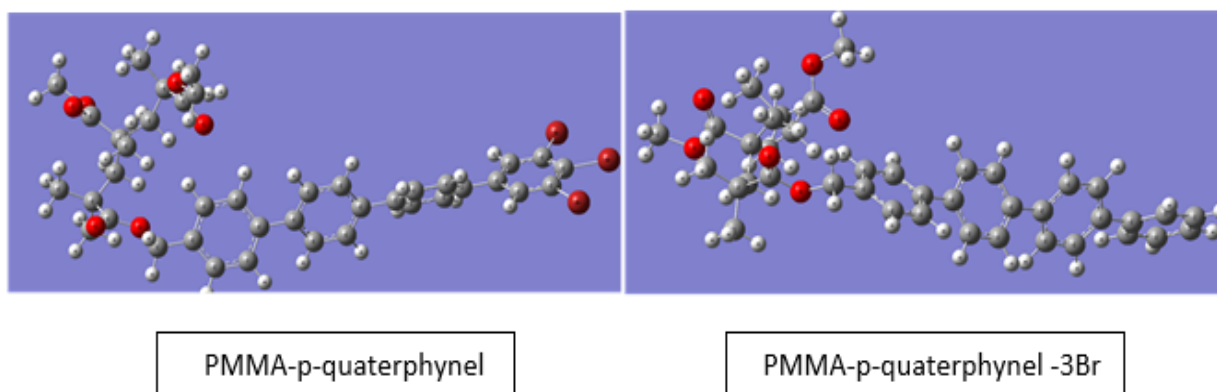


Figure3. Schematic Molecular structure of PMMA-p-quaterphynel Dye and PMMA-p-quaterphynel-3Br.

Table1. shows the electronic properties of pure PMMA and p-quaterphynel Dye and after doping which shows that energy gap had been decrees in the case of PMMA and p-quaterphenyl Dye after adding Br which eventually effect on all electronic properties , also Figure 9 showed the effect of Br on the total energy of PMMA and p-quaterphenyl Dye, were the Et decreased after adding Br in both case.

Table 1. The Electronic Properties PMMA and of p-quaterphenyl without and with the presence of Br

Molecular	HOMO (eV)	LUMO (eV)	Eg (eV)	IE	EA	chi poten(X)	HAR	Sof
PMMA	-7.4422	-0.4063	7.0359	7.4422	0.4063	-3.9242	3.5180	0.1421
PMMA+3Br	-7.2047	-0.8890	6.3157	7.2047	0.8890	-4.0468	3.1578	0.1583
PMMA+6Br	-7.0275	-1.9437	5.0838	7.0275	1.9437	-4.4856	2.5419	0.1967
p-Quaterphynel	-5.6897	-1.2397	4.4500	5.6897	1.2397	-3.4647	2.2250	0.2247
Quaterphynel+4Br	-6.2876	-1.8792	4.4085	6.2876	1.8792	-4.0834	2.2042	0.2268
Quaterphynel+6Br	-8.9753	2.3581	11.3334	8.9753	-2.3581	-3.3086	5.6667	0.0882

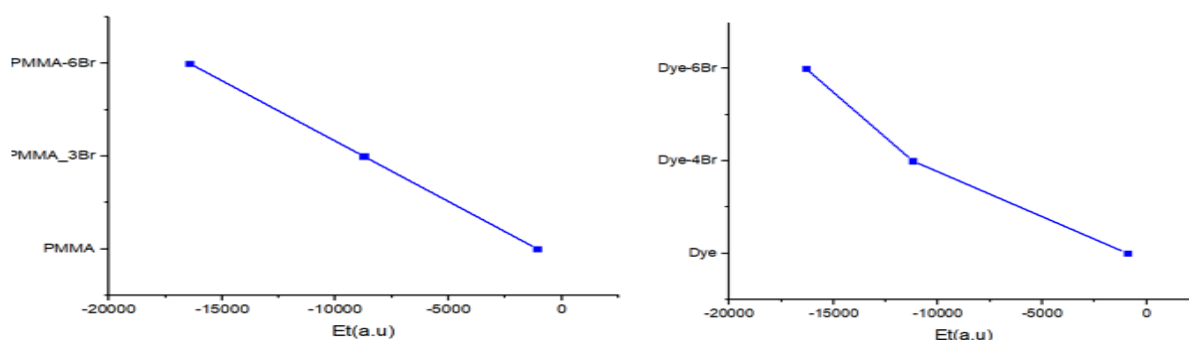


Figure 4. Effects of adding Br to PMMA and p-quaterphenyl dye.

Figure 5. shows HOMO and LUMO Orbital distribution which an indicator to the electronic density of structure , in our structure the electron density higher in the case of HOMO rather than LUMO ,which means its HOMO transition dominated

as it shown in figure below but its noticeable that after adding Br atoms electronic density of structure are equal in HOMO AND LUMO as appear in Figure11 and 12.

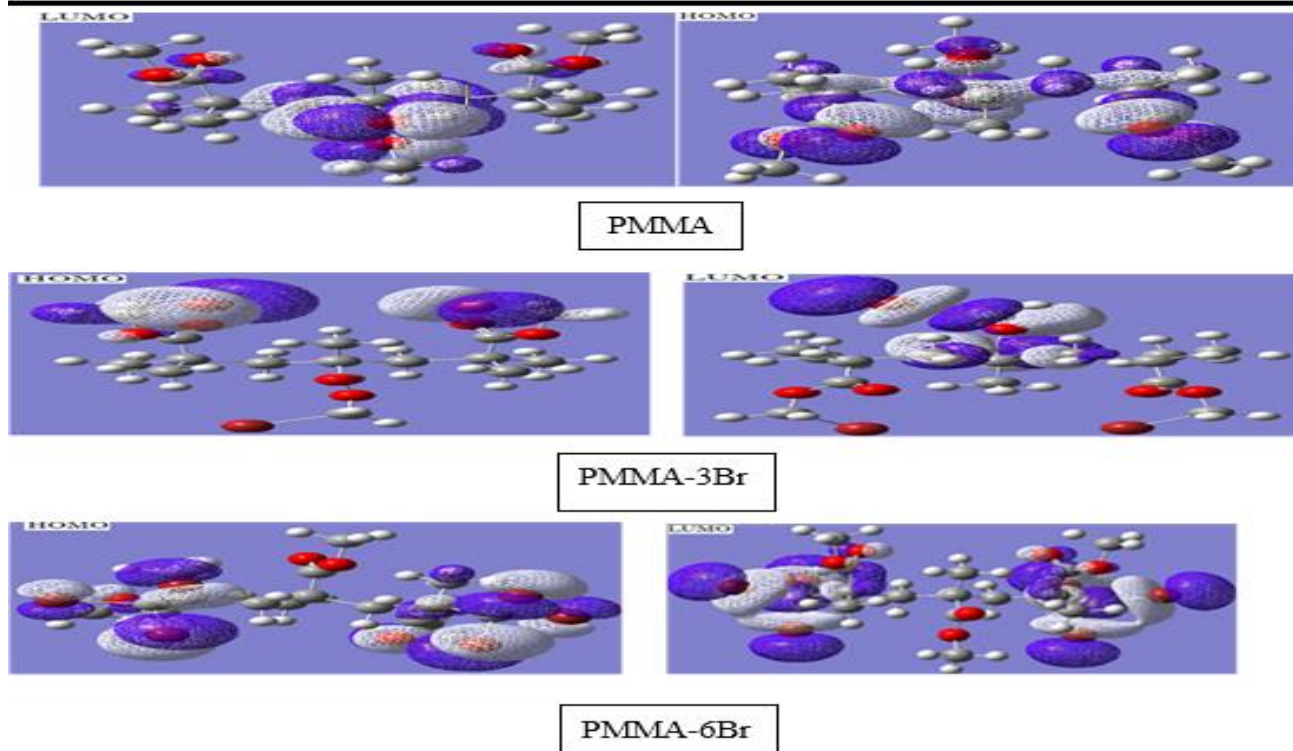


Figure5. Schematic HOMO LUMO of PMMA and PMMA-Br

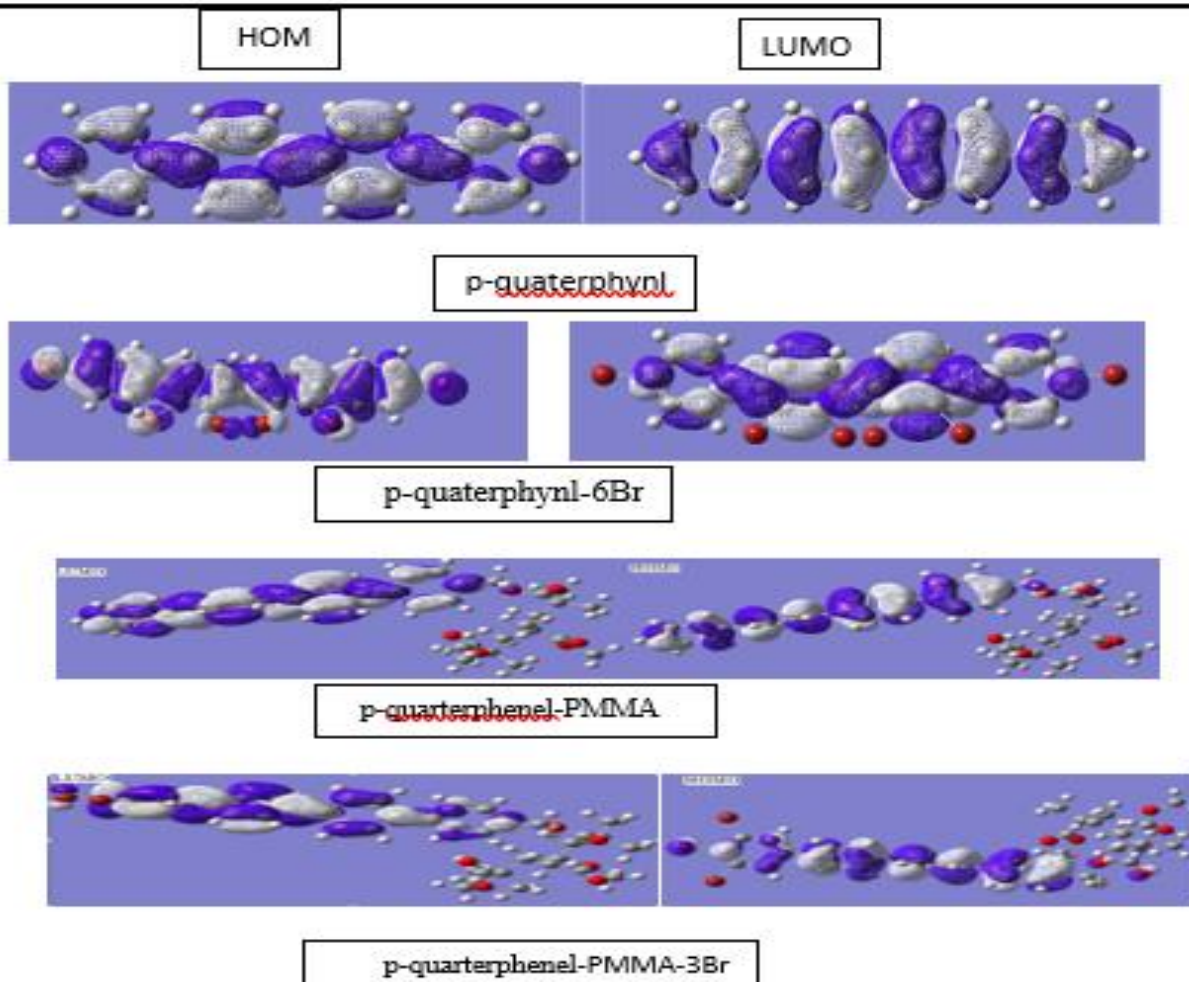


Figure 6. HOMO LUMO distribution of p-quarterphenyl, p-quarterphenyl-PMMA and p-

Figure 6. shows HOMO and LUMO Orbital distribution of p-quaterphenyl before and after adding Br which an indicator to the electronic density of structure, where in HOMO Orbital 3C participated while in LUMO Orbital 2C effects, and the effects of Br aperies obviously at HOMO orbits. As well as Figure 6 shows the HOMO LUMO distribution of the molecular structure of PMMA with p-quaterphenyl -3Br, indicate the electronic charge distribution more dominated around the Dye, which means its overcome the charge distribution of PMMA, in HOMO orbital 3C participated while in LUMO 2C.

IR and Raman spectrum

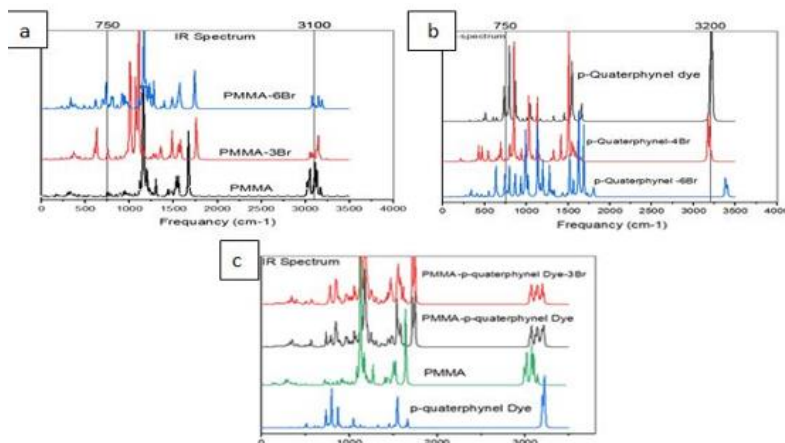


Figure7. IR spectrum of (a)PMMA -Br,(b) p-quaterphenyl-Br and (c) p-quaterphenyl-PMMA-Br

Figure 7b. show IR spectrum of p-quarterphen before and after Br addition, in p-quarterphenecase two region appears which are 3200 cm⁻¹ which is indicatre to C-H bond ,C-C (1000-1800) cm⁻¹ and (1500-1800) cm⁻¹ for C=C and after adding Br a new bond apper Br-C at (500-750) cm⁻¹. Obviously we can notice after added 6Br to p-quarterphenel dye the region of C-H (3200) cm⁻¹ has been shifted to longer wavelength which is indicator to decaesd in bond length; befor added Br C-H (1.085 Å) as mention in table 3 while after added 6Br C-H (1.07Å).

UV-Visble spectrum

UV-vis. Spectrum of PMMA befor and after adding

Figure 7. show IR spectrum of PMMA before adding Br and after added it, in PMMA case two region appears which are 3100c m-1 which it indicator to C-H bond and (1720-1750) cm⁻¹ due to the presence of C=O and (1000-1260)cm⁻¹ refer to C-O(ester bond), band from 950-650cm⁻¹ is due to the bending of C-H ,and after adding Br anew bond appear Br-C at (500-750) cm⁻¹. [19] from Figure 18 the peak position (1000-1260) cm⁻¹ has blue shift after add 3Br this is due to the increase of bond length of C=O which increase from 1.37Å° to 1.4Å°while after doping with 6Br the bond length returned to 1.37Å°.

Br , shows peak intensity after add 6Br has been decreased while after adding 3Br the peak intensity has been increas and with red shift in peak position as presented in Figure 8a. While Figure8b. shows the UV-Vis. of p-quarterphenel before and after adding Br, its show that after added 4Br the pesk intensity has been increas with kind of red shift in peak position ,while after added 6Br its suffer from noticnoticeable blue shift and the peak intensity decreas. Figure8c. Uv-Vis of p-quarterphenel-PMMA ,p-quarterphenel-PMMA-3Br., shown red shift in peak position after added Br .

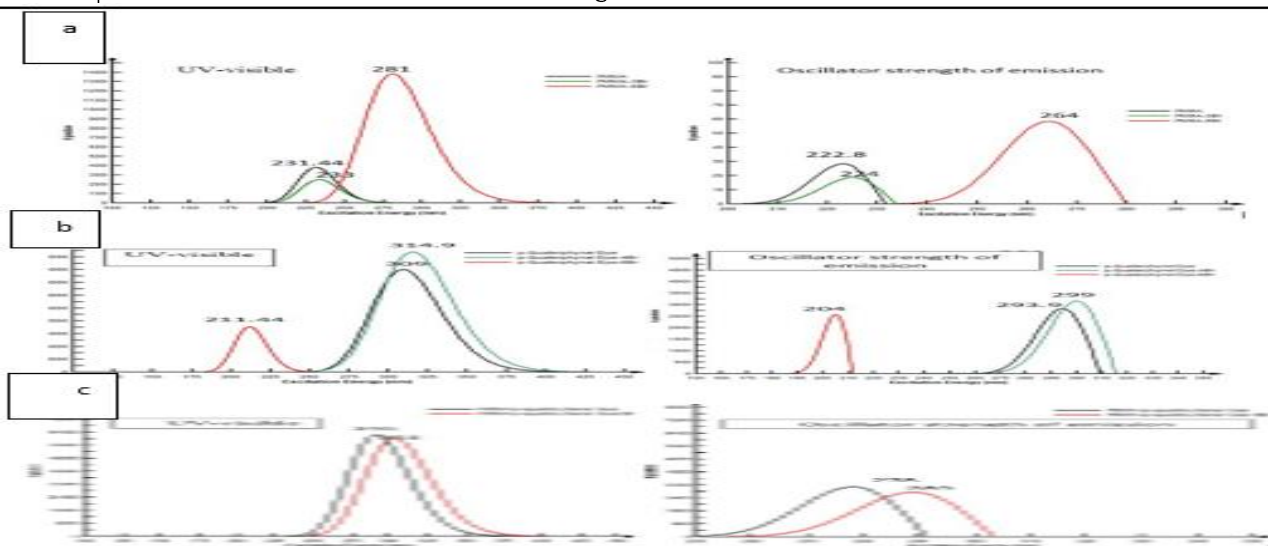


Figure7. Uv-vis spectrum of (a)PMMA -Br ,(b) p-quaterphenyl-Br and (c) p-quaterphenyl-PMMA-Br

Density of state (DOS)

The density of states (DOS) is a measure of the number of electronic states in a band per unit energy. The DFT calculated DOS spectra for the isolated molecule versus energy are shown in Figure. (23 and 24), along with the value of the gap in DOS, which is the distance between the first onset of electron density from left to right between the HOMO and LUMO peaks, which is approximately (5.31, 5.29 and 4.067) eV for PMMA, PMMA-2Br and PMMA-4Br molecules respectively and (5.11, 5.11, 3.928 and 5.84) eV for p-quarter phenel, p-quarter phenel -2Br and p-quarter phenel -4Br and p-quarter phenel -6Br molecules respectively also (4.25 and 4.085) eV for p-quarter phenel -PMMA and - p-quarter phenel PMMA-3Br molecules respectively. As shown, the degeneracy of occupied molecular orbitals is more than that of virtual molecular orbitals in all compounds, indicating that the HOMO was localized and the LUMO was delocalized, and an indicator that the DOS was distributed more in the conduction band than in the valence band.



Figure 7. DOS of (a) PMMA -Br, (b) p-quarterphenyl-Br and (c) p-quarterphenyl-PMMA-Br

4. Conclusion

Using computational model of basis set DFT, B3LYP/6-311g(d,P) stage, the electronic properties of PMMA and p-quarterphenyl before and after adding Br have been calculated.

We have noted that adding of Br to PMMA or to p-quarterphenyl enhanced their stability by decreasing the E_t , as well as the E_g has been decreasing. PMMA and p-quarterphenyl before adding Br its HOMO transition dominated, while after adding Br its HOMO LUMO transition dominated, PMMA -p-quarterphenyl -3Br composite, show the electronic charge distribution more dominated around the Dye. We have noted that PMMA-Br composite cause a blue shift in C=O bond as well as appear of new peak due to C-Br bond. While p-quarterphenyl-Br cause red shift in C-H. red shift and enhanced in Uv-vis peak of PMMA-6Br and p-quarterphenyl-4Br.

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