

# A DFT study of Optoelectronic Properties and Electronic Structure of Edge functionalization of phosphorene interacting with polythiophene

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**Abstract-** The functionalization of phosphorene and its electronic interactions with the conductive polymer had been examined in this research. Edge functionalization of phosphorene is very important because it has been found to be more reactive at the edge of a phosphorene when compared to covalently bonded phosphorus in the zigzag direction. We have described the interaction of phosphorene with polythiophene, a conducting polymer to study its optoelectronic properties and the substituent effect of polythiophene on electronic properties. For the edge functionalization of phosphorene interacting with polythiophene P-X-PT. we select four different kinds of moieties, where (COOH, NH<sub>2</sub> and OH). For polythiophene polymer we were considering with number of state six. Density functional theory (DFT) approach using MPW1PW91 at the theory level 6-31(G) on Gaussian 09 package was use for optical properties. The transfer of charge between molecules, frontier molecular orbitals (FMOs), state density (DOS), transition density matrix (TDM) and binding energy is carried out for the determination of opto-electronics properties and UV / Vis spectrum.

## I. INTRODUCTION

It's predicted that in the coming years our world will need new energy sources. Since of the broad range of possibilities for incorporation into electronic and conversion devices in the next decade, two-dimensional materials have become the most important research areas for nanomaterials. Two-dimensional, few-layer black phosphorous has recently attracted attention from society and material science (Xia, Wang, & Jia, 2014). It is chemically inert, and has endless land transportation. Any semiconductor's electronic properties had been crucial for electronic applications (Lu et al., 2014). The electronic properties for phosphorene nanotubes depend entirely on the crystal orientation of the tubes (Carvalho, Rodin, & Neto, 2014; Tran & Yang, 2014). Such findings find that certain ribbon edges play a critical role in the properties of optoelectronics.

Phosphorene properties with good properties such as band gap and carrier mobility, due to high demand for reliable performance products, several more layer materials had been discovered in the direction. Among the phosphorous allotropes (Appalakondaiah, Vaitheeswaran, Lebegue, Christensen, & Svane, 2012), blue phosphorene is considered to be the most stable 2D layer material with a fixed layer structure due to its low van der Waals interlayer interaction. (R. Hultgren, N. Gingrich, & B. J. T. J. o. C. P. Warren, 1935; Thurn & Kerbs, 1966).

Phosphorene has many industrial uses, as used in flares, matchsticks, organic fertilizers and napalm bombs (Chou et al., 2001). The quest for additional layer materials is required in their main possession for a variety of high-performance devices, such as bandgap. Blue phosphorous (BP) for having a van der Waal's forces and fixed layer structure is announced as a new member of 2D layer material family because of most stable allotropes among the group (R. Hultgren, N. Gingrich, & B. Warren, 1935). Phosphorene for its unique structural characterization differentiate itself from 2D layer material. It has a packed structure by its armchair direction and a bilayer formation laterally zigzag direction. This structure can easily be seen in its local bonding configuration (Liu et al., 2014).

Black phosphorene shows different kinds of strong properties like anisotropic electronic and optical properties which are far different from other 2D structure which has been investigated so far. To examine the anisotropic electronic structure, novel photonic responses and excitonic interaction a large number of studies were performed (Cai, Zhang, & Zhang, 2014; Li & Appelbaum, 2014).

Attachment of different groups like OH, -NH<sub>2</sub>, COOH, and CN etc. with phosphorene and polythiophene composite is expected to produce a material with excellent optoelectronic properties for various advanced applications. To design the three-dimensional structure of phosphorene with edge groups like H, COOH, NH<sub>2</sub>, OH and polythiophene.

Optical properties also respond to environmental incentives, affected color shifts in reaction to changes in solvent, applied potential, temperature and binding to the other molecules (Mastragostino & Soddu, 1990). Polythiophenes have been widely studied and have been found an excess of applications (Beck & Rüetschi, 2000; Bobade, 2011; Cosnier & Bioelectronics, 1999; Parthasarathy & Martin, 1994). Polythiophene and its derivatives are of great concern in device applications (Béra Abérem et al., 2006; Ho, Najari, &

Leclerc, 2008; Le Floch et al., 2005; Le Floch, Ho, & Leclerc, 2006; Ramírez-Solís, Kirtman, Bernal-Jáquez, & Zicovich-Wilson, 2009), because of the high stability, structural modification and solution processability (Coppo, Cupertino, Yeates, & Turner, 2003; Mehmood, Al-Ahmed, Hussein, & Reviews, 2016). Polythiophene has been widely studied using theoretical and experimental methods (Kumar, Bokria, Buyukmumcu, Dey, & Sotzing, 2008; Sugiyasu, Song, & Swager, 2006).

## II. MATERIALS AND METHODS

Density functional theory is applicable in various fields of chemistry like organic, inorganic, pharmaceutical and organometallic. It also deals with the solid phase as well as gas liquid (Swart, van der Wijst, Guerra, & Bickelhaupt, 2007).

The behavior of an electron is described by the orbital in the presence of net field of all other electrons (Young, 2004). AM1 is best method for the result of activation energy in than method of MNDO. In Aluminium case AM1 method is best for the results as compared to the PM3 but AM1 method doesn't give info about the paramidalization of nitrogen.

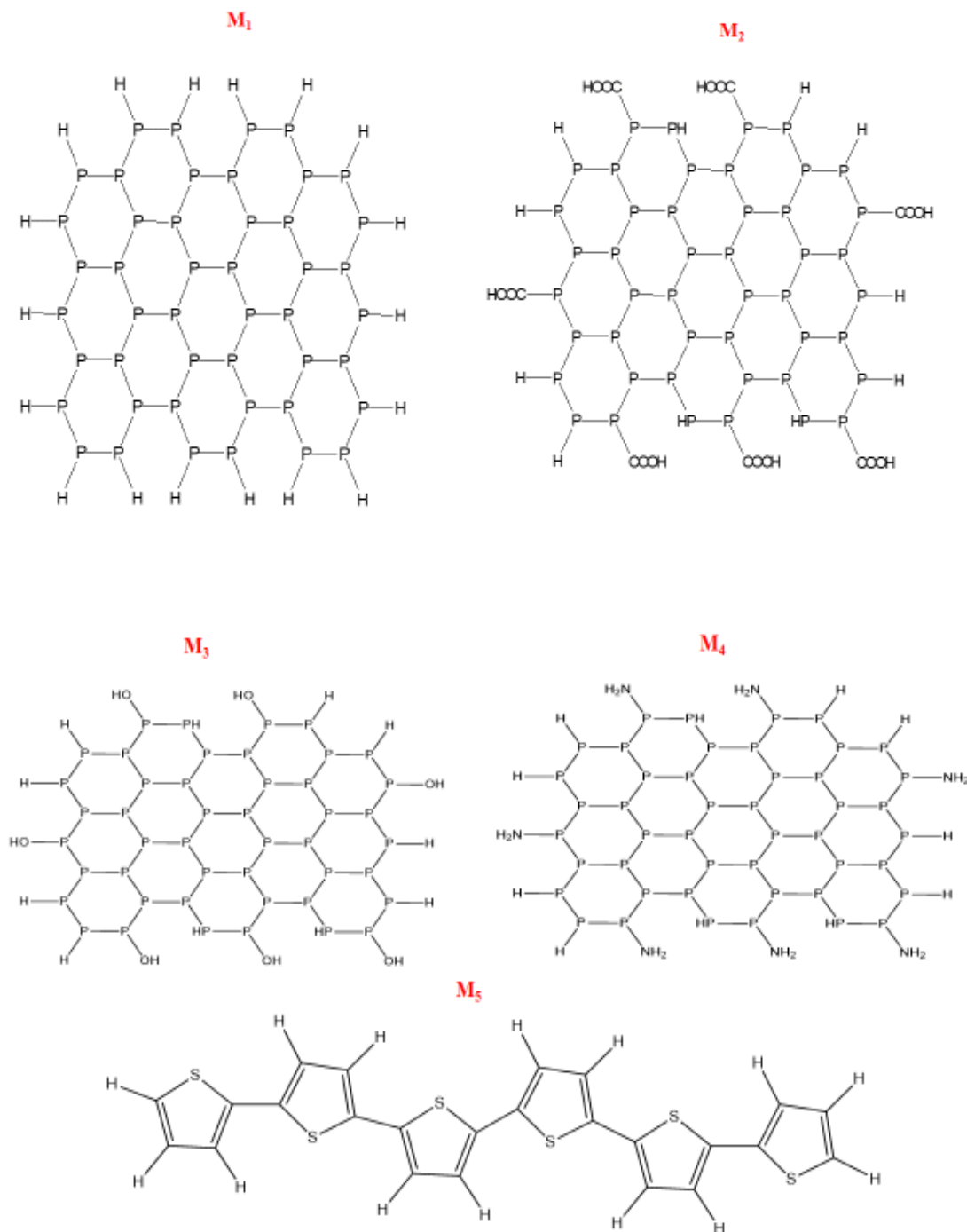
The calculations of density functional theory results may be outstanding and very poor depending on precision. It depends on functional and basic set. Production of new density functional is popular area of research now a days. Density functional theory (DFT) gives the outstanding results of organic compounds (Grimme, Antony, Ehrlich, & Krieg, 2010). HF method based on wave function. Internal density of electron is based on geometry of ground state molecules (Moore & Clarke, 1983).

Time dependent calculations provides us wave function that can be oscillate around ground and first excited state. It is more convenient way to take the values of ground state and excited state from calculations (de Wergifosse & Grimme, 2018). To calculate the geometry to the lowest possible energy, energy and energy gradients are calculated by the program (Schlegel, 1982). Calculation of atomic arrangement which increases the molecular stability is the main objective of molecular geometry optimization. Molecules are more stable at lowest energy level. There are many methods to calculate the lowest energy levels. By creating a potential surface we can observe the lowest energy level, it is a mathematical relationship geometries of different molecules (Barone, Cossi, & Tomasi, 1998).

Different tools are used in computational chemistry to observe the molecular excited states. Molecular excited states can be observed and calculated by different techniques and energy values and with the help of these calculations, wave function and other properties of molecules can be expected. For the study of spectroscopy, reaction mechanism and phenomenon of excitation these calculations are very important. To observe the ground state a wave functional same techniques and tools are used. The excited states in which geometry of ground states is apply for excitation of vertical energies (Young, 2004).

Geometry of ground state is used in vertical excitation energies therefore, it is likely the fast process to design. For excitation of electronic processes, it is more advantageous e.g. UV, spectroscopy of photo-electron. Optimized values of excited states are used in adiabatic excitation energies. When life of excited state is long, their result will closer to the experimental results (Young, 2004). Basic reaction self-consistent field is IEFPCM. PCM uses the significant of numeric which is used for calculating the effect of solvent on designed molecules (Deskevich, Nesbitt, & Werner, 2004).

In Hartree-Fock (HF) method and density functional theory (DFT) basis set is used whereas most semi-empirical (SE) methods use predefined basis set. Basic set is defined when calculations of density functional theory and ab-initio performed. Mostly, when we use basic sets of minimal values the accuracy of density functional theory (DFT) is decreases but it shows good result with Hatree-Fock (HF) basic set (Schuchardt et al., 2007). Density functional theory (DFT) for the geometry optimization, has become most efficient and reliable method. DFT is used for geometry optimization and time dependent density functional theory (TD-DFT) is used for excited state.



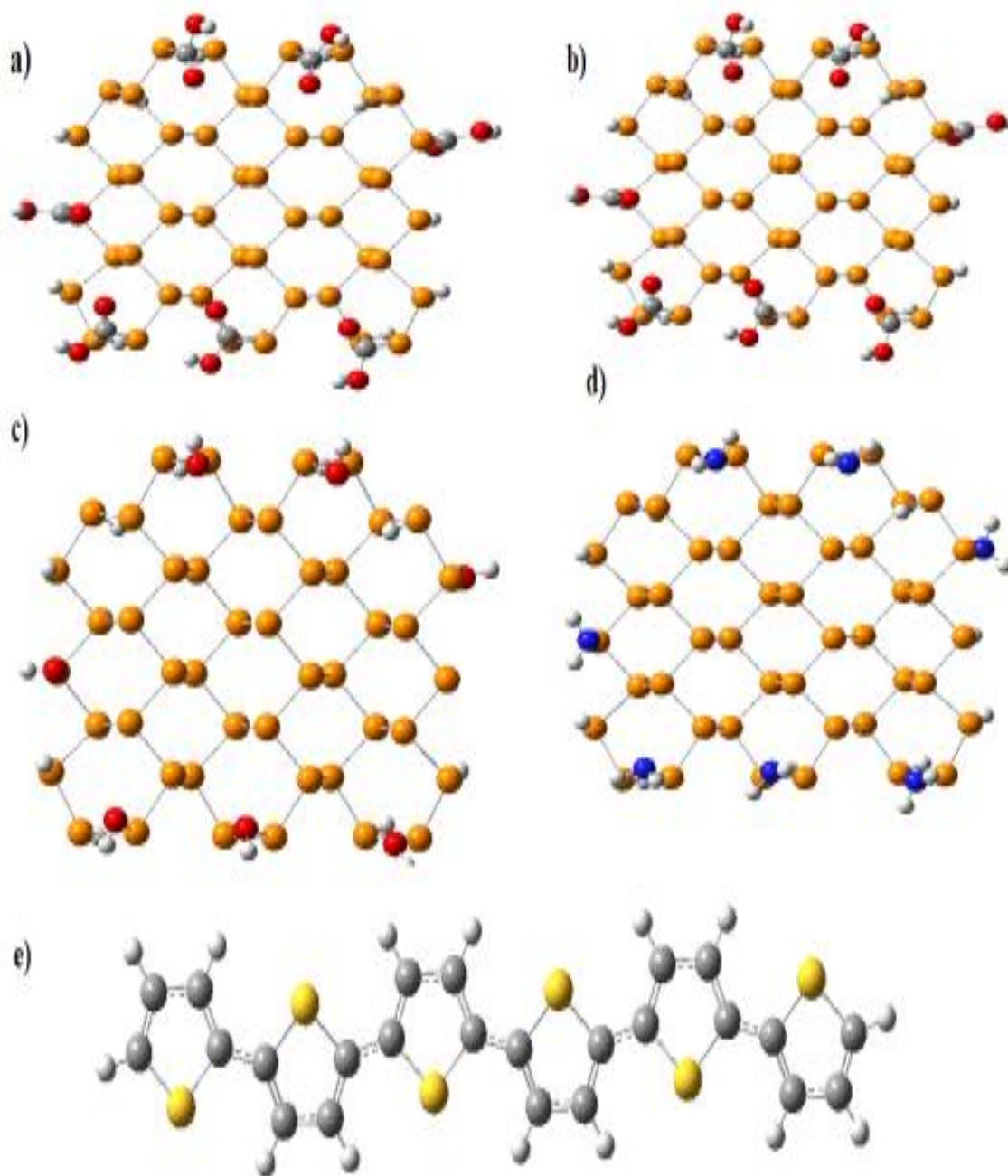
**Fig 1:** Chemical Structure of Phosphorene and designed molecules M1 to M4.

All calculations were performed on program packages from Gaussian 09. DFT method is used to optimize the configuration of phosphorene, thiophene, and phosphorene molecules with the edge group COOH, phosphorene with the edge group NH<sub>2</sub> and phosphorene with the edge OH. Firstly, all the designed molecules were calculated with DFT with different functions as B3LYP, CAM-B3LYP (Yanai *et al.*, 2004) and MPW1PW91 (Adamo & Barone, 1998) for absorption spectra of designed molecules. MPW1PW91 is the best method for theoretical calculations for these molecules and therefore it was chosen for further optimization of molecules  $M_1$ ,  $M_2$ ,  $M_3$ ,  $M_4$  and  $M_5$ . For the absorption spectra of all of these designed molecules, TD-DFT with B3LYP, CAM-B3LYP and MPW1PW91 with basis set 6-31 G (d, p) are used. We got the best absorption of these molecules with function MPW1PW91/6-31 G (d, p). So that we use MPW1PW91 and basis set 6-31 G (d, p) to perform our further calculations.

### III. RESULTS AND DISCUSSIONS

Currently, we use density functional theory with various functions such as B3LYP, CAM-B3LYP and MPW1PW91 with 6-31 G (d, p) basis set to observe the optical and electronic properties of phosphorene with different edge groups and in polythiophene composite. MPW1PW91 was selected best for UV-Visible spectrum for optoelectronic properties.

#### Optimized molecular structures

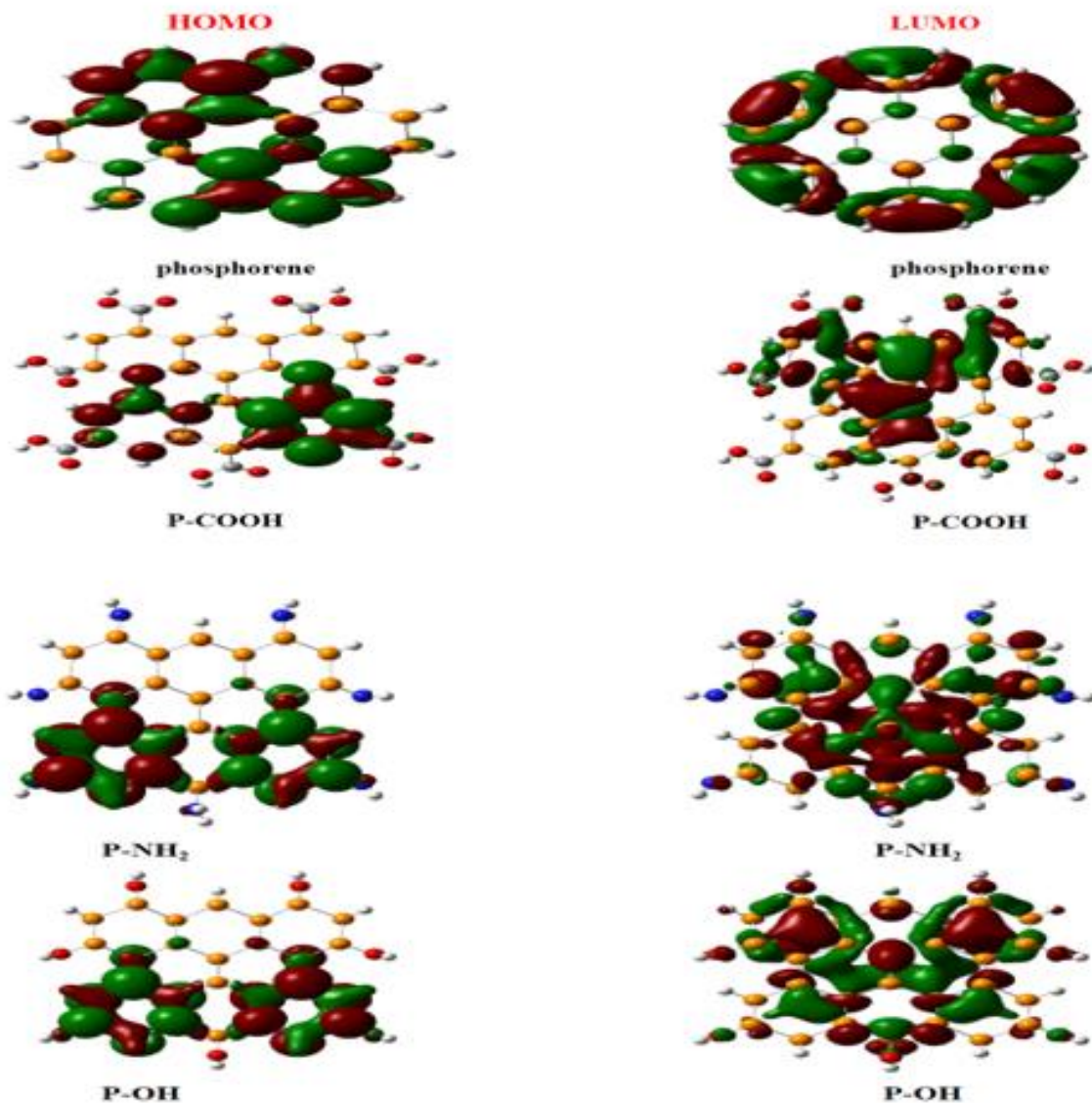


**Figure 2.** Optimized structure of phosphorene at MPW1PW91 with basis set 6-31G(d,p) attached with a) COOH b) OH c) NH<sub>2</sub> d) polythiophene

#### Frontier molecular orbitals

The optoelectronics properties are performed on the basis of the distribution pattern of P-X-Pthio's frontier molecular orbitals (X = OH, COOH and NH<sub>2</sub>). In FMOs it is possible to show the distribution of electron density around the HOMO and the LUMO. Figures

below show the distribution of FMOs around HOMO and LUMO at ground state of molecules without polymer polythiophene.



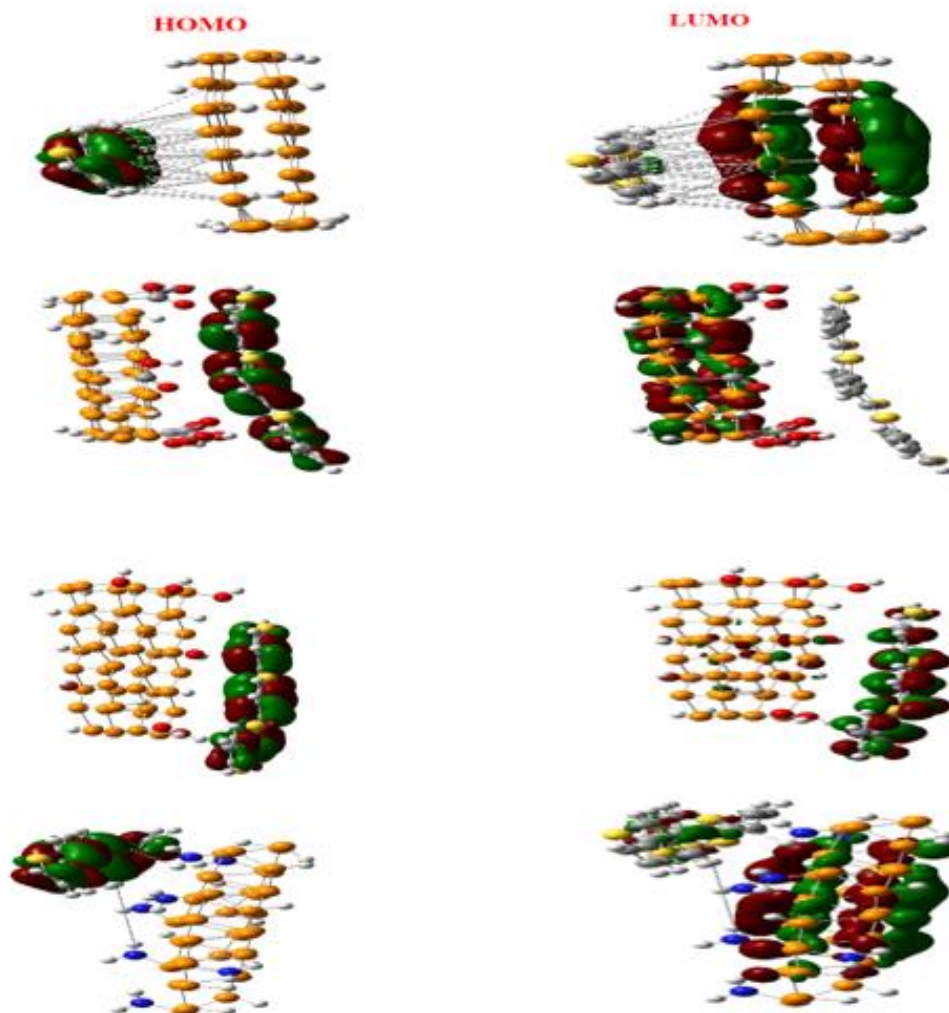
**Fig.3** Distribution of FMOs around HOMO and LUMO at ground state of molecules without polymer polythiophene

**Table .1** Energy of HOMO( $E_{HOMO}$ ), LUMO ( $E_{LUMO}$ ) and their Energy Gap ( $E_g$ ) in eV at MPW1PW91/631-G(d,p) level of theory

Molecules	$E_{HOMO}$	$E_{LUMO}$	$E_g$ (eV)
P-COOH	-0.230142	-0.07851	0.151632
P-NH <sub>2</sub>	-0.21795	-0.06145	0.1565

P-OH	-0.23151	-0.07731	0.1542
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The increasing order is P-NH<sub>2</sub> > P-COOH > P-OH, the difference in HOMO energies and in the case of LUMO energies the trend varies from P-NH<sub>2</sub> > P-OH > P-COOH. The energy difference between HOMO-LUMO varies from P-COOH > P-OH > P-NH<sub>2</sub>. The lowest energy gap is observed in P-COOH which is 0.151632 eV. The developed P-X molecules where X is COOH, NH<sub>2</sub> and OH when it comes into contact with polymer polythiophene. I have designed the plot of FMO's based on HOMO) and LUMO and their



energy gap ( $E_g$ ).

**Figure 4.** FMO at ground state of P-Pthio, P-COOH and P-OH pthio

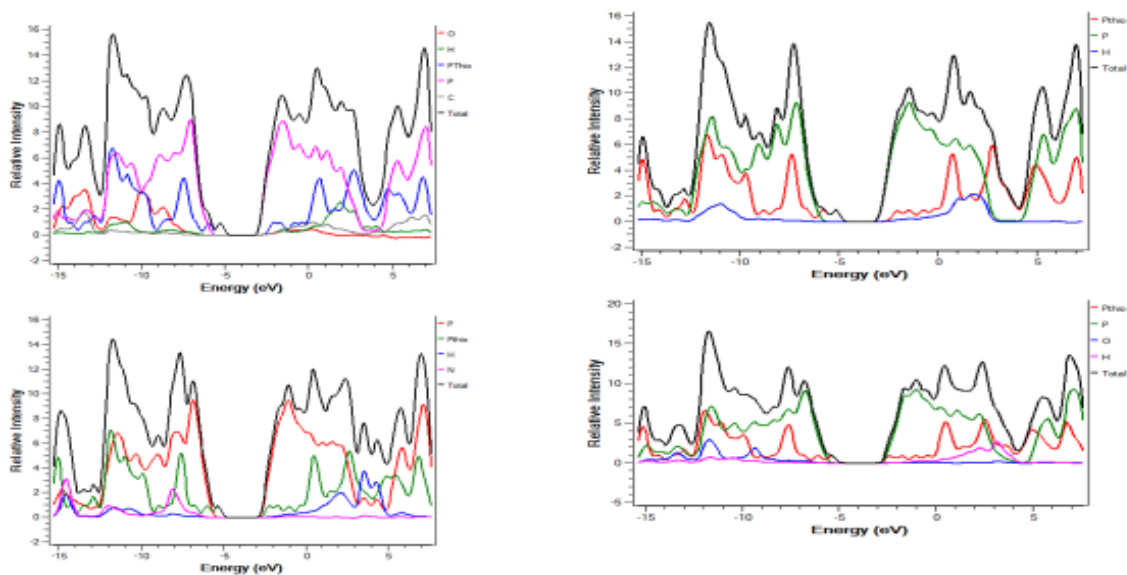
**Table .2 Energy of HOMO ( $E_{HOMO}$ ), LUMO ( $E_{LUMO}$ ) and energy difference HOMO-LUMO ( $E_g$ ) at MPW1PW91/6-31G(d,p) level of theory**

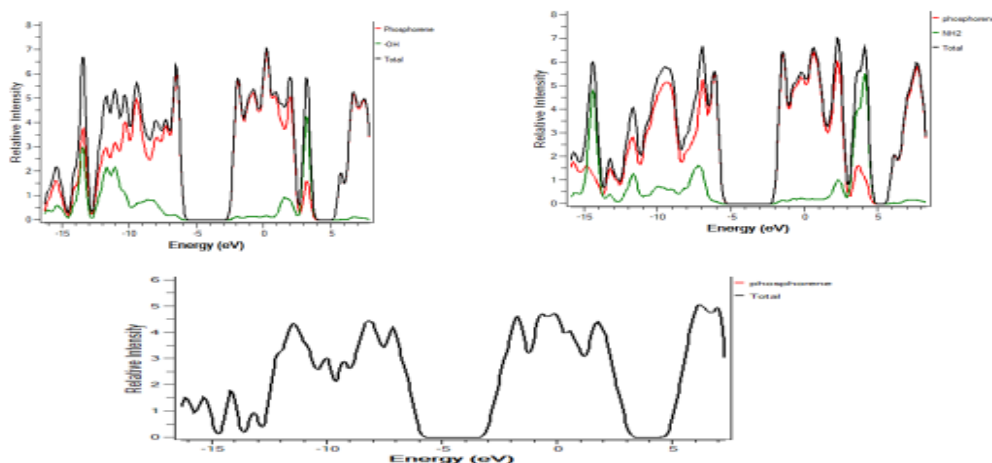
Molecule	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	$E_g$ (eV)
P-COOH-Pthio	-5.211	-2.539	2.672
P-OH-Pthio	-5.358	-2.390	2.968
P-NH <sub>2</sub> -Pthio	-5.304	-2.361	2.943

The increasing order varies from P-COOH-Pthio > P-NH<sub>2</sub>-Pthio > P-OH-Pthio. While in case of LUMO the trend will be P-NH<sub>2</sub>-PT > P-OH-PT > P-COOH-PT energy gap between HOMO and LUMO is P-OH-Pthio > P-NH<sub>2</sub>-Pthio > P-COOH-Pthio. Lowest energy gap is observed in P-COOH-PT (2.672). The lowest HOMO value is observed in P-OH-Pthio (-5.358) and lowest energy value of LUMO is observed in P-COOH-Pthio (-2.539 eV).

**Density of state (DOS) of phosphorene interaction with polythiophene**

Four types of colors in the DOS graph are red, green, black and blue. Green and blue line represents the level of HOMO energy and red line represents the level of LUMO power. The difference between HOMO and LUMO is the band gap and the disparity between red and green reveals the band gap ( $E_{gap}$ ). The density of state (DOS) of all designed molecules of HOMO and LUMO are shown in figures below:





**Figure.5 Density of state of P-COOH-Pthio, P-H-Pthio, P-NH<sub>2</sub>-Pthio, P-OH-Pthio, Phosphorene, P-COOH, P-NH<sub>2</sub>, P-OHs**

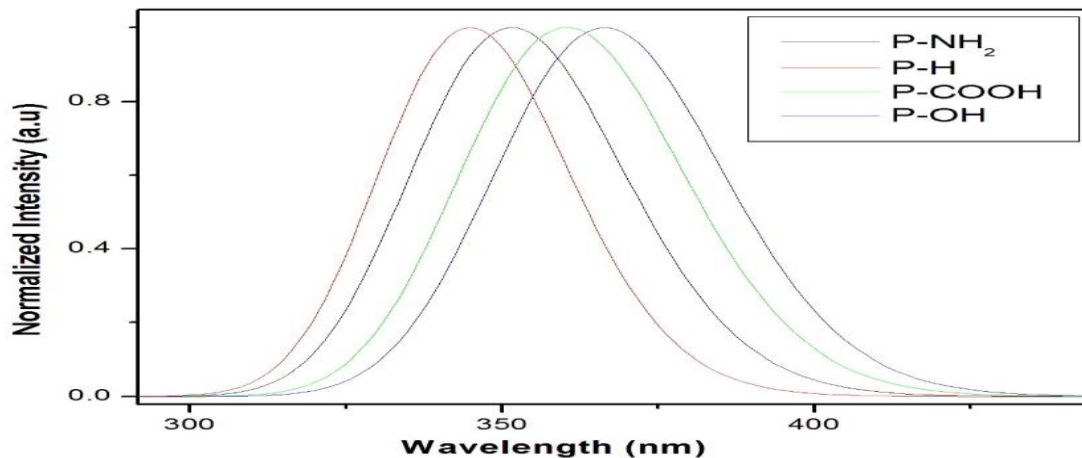
**Optical properties**

At the theory stage, MPW1PW91/6-31 G (d, p) was performed to observe the optical properties of phosphorene with different edge groups TD-DFT calculations. It showed the first 10 singlet to singlet excitation transition state, but I considered only the first excitation state because it is the most significant maximum absorption in all four structures as shown in Table 1.

**Table .3 Wavelength (nm) oscillator strength, ETC % and E<sub>ev</sub> for P-H, P-COOH, P-NH<sub>2</sub> and P-OH.**

Molecules	Wavelength (nm)	E <sub>ev</sub>	Oscillation strength (f)	Major contribution
P-H	343.80	3.51	0.03	H-1->L+0(+80%)
P-COOH	366.89	3.36	0.02	H-0->L+0(+56%)
P-NH <sub>2</sub>	344.61	3.43	0.02	H-0->L+0(+82%)
P-OH	371.20	3.41	0.01	H-0->L+1(+68%)





**Fig.5 Absorption spectra of P-H, P-COOH, P-NH<sub>2</sub> and P-OH**

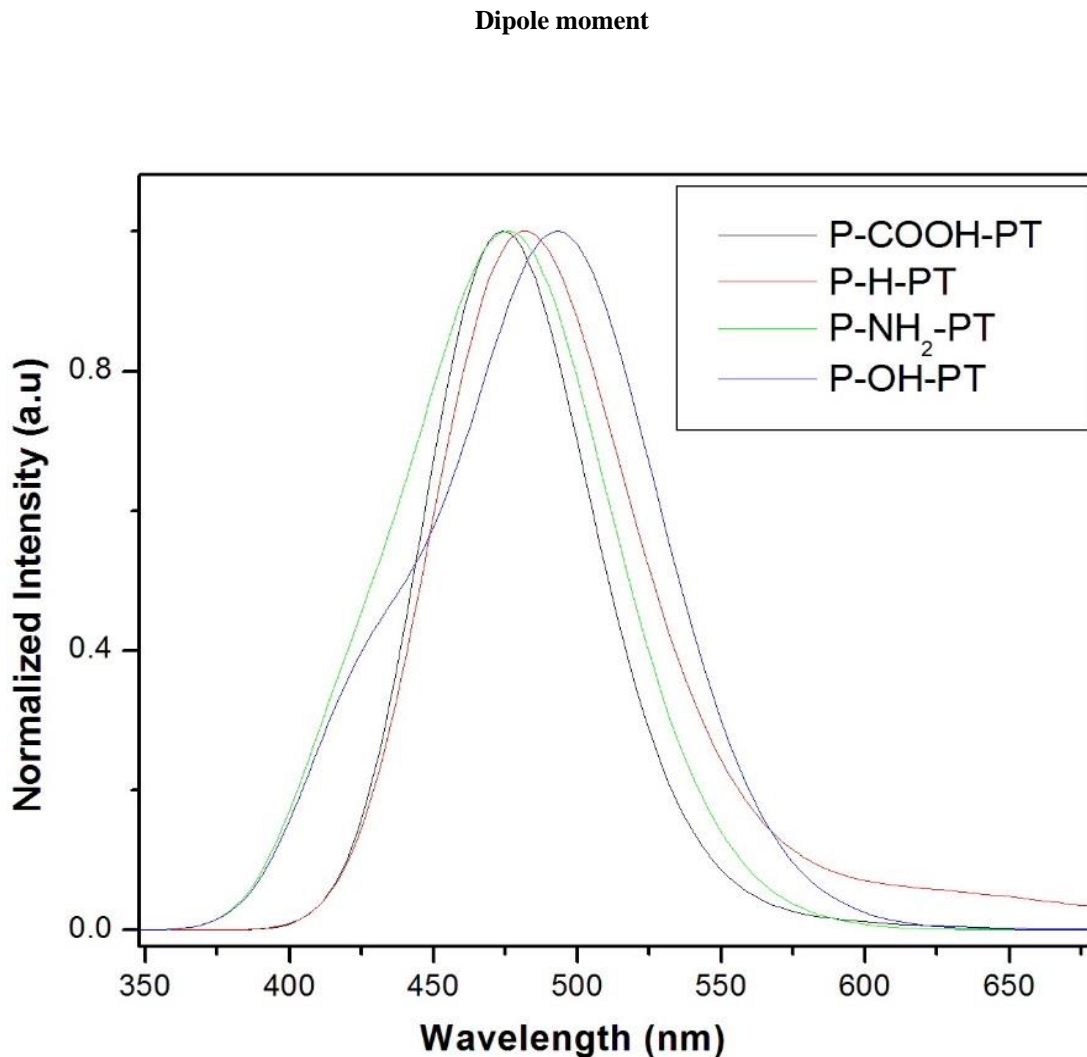
**Optical properties of phosphorene edge groups with polythiophene**

To study the optical properties of phosphorene edge functionalization with polythiophene. I performed TD-DFT calculations at MPW1PW91/6-31G(d,p) level of theory it showed first 10 singlet to singlet excitation transition but I only consider first excitation state because it is most significant with P-H-Pthio, P-COOH-Pthio, P-NH<sub>2</sub>-Pthio and P-OH-Pthio structures with maximum absorption ( $\lambda_{max}$ ), oscillator strength (f), electronic transition contribution (ETC %) as shown in table 4.

**Table. 4 Wavelength (nm) oscillator strength, ETC % and E<sub>ev</sub> for P-H-Pthio, P-COOH-Pthio, P-NH<sub>2</sub>-Pthio and P-OH-Pthio**

Molecules	Wavelength (nm)	E <sub>ev</sub>	Oscillation strength (f)	ETC %
P-H-Pthio	465	1.96	0.33	H-0->L+0(+96%)
P-COOH-Pthio	473	2.16	1.0	H-0->L+0(+98%)
P-NH <sub>2</sub> -Pthio	469	2.52	0.6	H-0->L+0(+88%)
P-OH-Pthio	495	2.49	1.0	H-0->L+0(+96%)

**Figure.6** Absorption spectra of P-H-Pthio, P-COOH-Pthio, P-NH<sub>2</sub>-Pthio and P-OH-Pthio



Dipole moment of all molecules are also calculated with MPW1PW91/6-31G (d,p) level of theory. Greater the dipole moment, greater will be the solubility. Dipole moment of all molecules is given in the table 5. Dipole moment of all molecules are calculated at ground state and as we as excited state. In ground state highest dipole moment of molecule is P-NH<sub>2</sub>-PT. Trend of dipole moment at ground state varies form P-NH<sub>2</sub>-Pthio > P-OH-Pthio > P-COOH-Pthio.

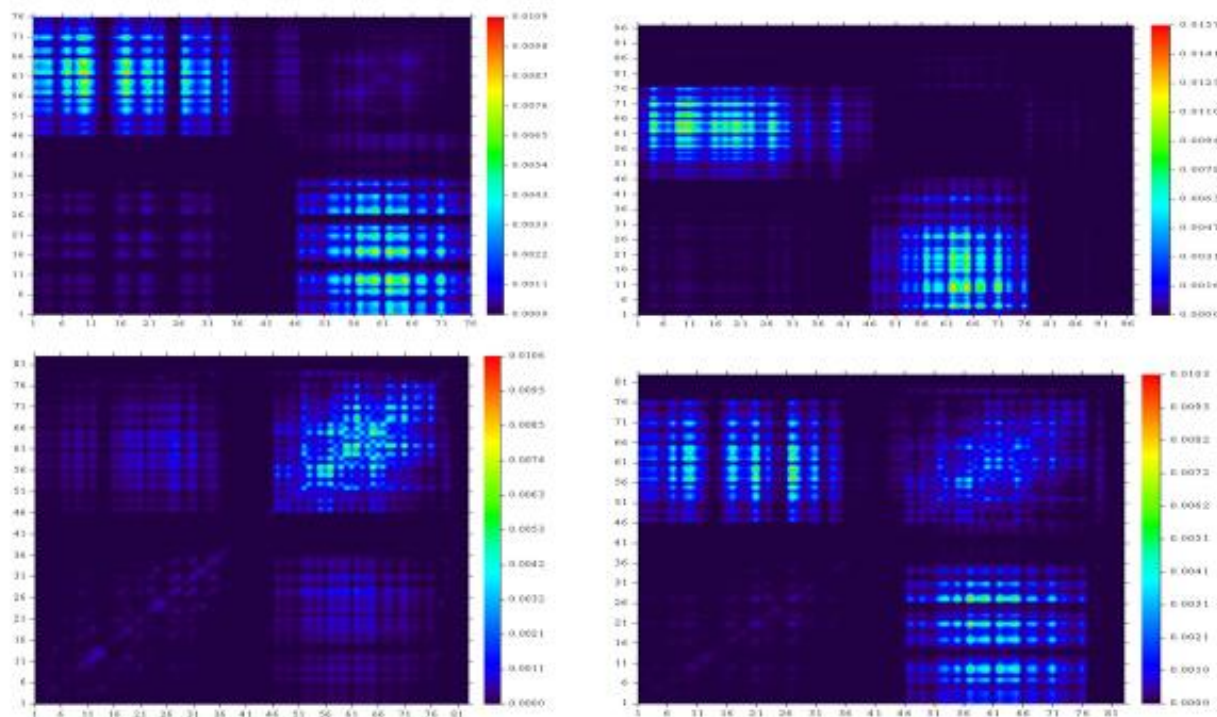
**Table 5 Dipole moments of designed molecules at ground state  $\mu_g$  and excited state  $\mu_e$**

Molecule	$\mu_g$	$\mu_e$
P-COOH-Pthio	1.8685	1.8685
P-OH-Pthio	4.8707	4.8704
P-NH <sub>2</sub> -Pthio	5.7675	5.7671

### Transition density matrix (TDM) and exciton binding energy ( $E_b$ )

For the estimation of the nature of transition, the transition density matrix of these developed molecules is computed. At the theory level of MPW1PW91/6-31 G (d, p), the TDMs for absorption and emission are calculated in vacuum with S1 state. TDM shows the interaction between donor and acceptor moieties.

Binding energy is inversely proportional to the exciton dissociation. So we can calculate binding energy by taking the difference between energy gap HOMO-LUMO ( $E_g$ ) and minimum amount of energy for first excitation  $E_{opt}$ .



**Table 6** Calculated HOMO-LUMO energy gap  $E_{H-L}$ , and  $E_{opt}$  first singlet excitation energies, exciton binding energies ( $E_b$ )

Molecules	$E_{H-L}$ (eV)	$E_{opt}$ (eV)	$E_b$ (eV)
P-COOH-Pthio	2.638	2.14	0.49
P-OH-Pthio	2.967	2.48	0.48
P-NH <sub>2</sub> -Pthio	2.936	2.50	0.43

### IV. CONCLUSION

To research the optical and electronic properties of phosphorene edge functionalization with conducting polymer polythiophene we are performing first principle DFT calculations. We select three moieties for COOH, NH<sub>2</sub> and OH edge functionalization's. Lowest band gap is seen in P-COOH-, and this molecule also shows better oscillator strength. Calculations for UV / Vis spectra were performed using TD-DFT. P-COOH- wavelength is 473 nm, and oscillator strength is 1.0. FMO was determined for the HOMO and LUMO distribution. Charge transfer is distributed precisely within the P-COOH- molecule. Calculations of the transition density matrix were performed in P-COOH- for electronic excitation between molecules and better result for TDM and binding energy which confirms the TDM result.

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