

## A DFT study on comparison of Terpyrrole, Terthiophene, and Dianiline in adsorption of nitrous oxide

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**Abstract:** The adsorption of N<sub>2</sub>O gas molecule in different orientations on three oligomers; Terpyrrole (as a simplest model of polypyrrole, denoted as TP), Terthiophene (as a simplest model of polythiophene, denoted as TT), and Dianiline (as a simplest model of polyaniline, denoted as DA) is investigated using pure density functional theory with applying basis set 6-31 G (d). The energetic, electronic properties and charge transfer have been discussed. We found that the best oligomer for adsorbing of N<sub>2</sub>O gas molecules is TP with adsorption energy of -9.8 kJmol<sup>-1</sup>. Also, the electronic character of TT is found to be not affected by the adsorption of N<sub>2</sub>O gas molecule. The results of frontier molecular orbitals reveal major hybridizing upon adsorption of N<sub>2</sub>O on TP and DA while there is no hybridizing by using TT.

**Keywords:** Density functional theory, ab-initio study, Polymeric sensor, Nitrous oxide.

### Introduction

There are different conducting polymers which have been used as sensor materials [1-4]. Among them, polypyrrole [2], polythiophene, [3], and polyaniline [4] are expansively considered as gas sensors because of their mechanical resistance and notable electrical conductivity and etc. [5-10]. As an example, in our previous work, we used density functional theory calculation to investigate the response mechanism of polypyrrole as a gas sensor towards detection of SO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O, CO, CH<sub>4</sub> and CO<sub>2</sub> [5]. We found that high capability of this sensor is achieved for detection of H<sub>2</sub>O and NH<sub>3</sub> molecules. In another work [6] we used DFT calculation to principles study of terpyrrole as a sensor for hydrogen cyanide. The application of Terthiophene as a model of polythiophene gas sensor for SO<sub>2</sub> and SO<sub>3</sub> has been investigated by our group [7]. Moreover we studied the interaction of methanol

with some aniline and pyrrole derivatives using DFT [8]. Also we have investigated on other application of Terthiophene as a model for polymeric sensor [9, 10]. The capability of these polymers to have interaction with different analytes establishes them as an ideal sensor. The recitals of conducting polymers as sensor is imperative because of some molecules in air are rather toxic and their quantity at low concentration can be unsafe for healthiness. They are very important when are compared with semiconductor transistor [11, 12] and metal semiconductors in oxide form and some other systems [13].

The nitrous oxide (N<sub>2</sub>O) emission is resulted from the burning of fossil fuels which causes to acid rainfall and so influences the ecosystems [14]. N<sub>2</sub>O gas molecule is powerfully poisonous to human beings and animals as it restrains the use of oxygen by body tissues. For the reason that it is colorless and odorless, the gas sensor with high sensitivity to its presence is very appealing. In our pervious study [15] we used Al-

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doped graphene as an active surface for adsorption of  $\text{NO}_2$  and  $\text{N}_2\text{O}$ . We found high adsorption of  $\text{N}_2\text{O}$  in the case of Al-doped graphene while there is low adsorption by using pristine graphene.

Yong et al. [16] investigated on the adsorption equilibrium of  $\text{N}_2\text{O}$  on three commercial activated carbons. Furthermore they characterized the interactions between adsorbate and adsorbent. Rusu and Yates [17] investigated on the adsorption and photochemistry of  $\text{N}_2\text{O}$  chemisorbed on  $\text{TiO}_2$  powder. They found that, adsorption on the  $\text{TiO}_2$  surface takes place through both the N and O ends of the nitrous oxide molecule while N-bonded species show a higher photoreactivity than the O-bonded species. Kim et al. [18] searched on the adsorption of  $\text{N}_2\text{O}$  on supported Pt. They obtained the oxygen monolayer coverage by  $\text{N}_2\text{O}$  adsorption/decomposition on a Pt/ $\text{SiO}_2$  catalyst. Rosario et al. [19] studied on the capacity of natural zeolites to adsorb  $\text{N}_2\text{O}$  and  $\text{NO}$  in both static and dynamic regimes. Franke et al. [20] investigated the adsorption of  $\text{N}_2\text{O}$  on Cu(100) by using scanning tunneling microscopy (STM). They found stable structure in which the molecules are considerably bent due to charge transfer.

It is proven that chemical simulation provides important information on the concept of different adsorbent-adsorbate systems [21-25]. In the present study, our aim is to study and comparison the adsorption of  $\text{N}_2\text{O}$  gas molecules on three oligomers (TP, TT, and DA) considering different configurations of  $\text{N}_2\text{O}$ . To the best of our knowledge, there are no theoretical studies of  $\text{N}_2\text{O}$  adsorption on above-mentioned polymers. The structural characteristics of adsorbed  $\text{N}_2\text{O}$  gas molecule on TP, TT, and DA is investigated and the corresponding adsorption energies are computed. In order to find the preferred adsorption site, different positions were investigated and the energy gap and HOMO-LUMO energies are reported.

## Results and discussion

We considered different potential positions of TP- $\text{N}_2\text{O}$ , TT- $\text{N}_2\text{O}$ , and DA- $\text{N}_2\text{O}$  structure with respect to allowing them to be relaxed. Geometries of isolated TP, TT, and DA and their complexes with  $\text{N}_2\text{O}$  were optimized at pure DFT/6-31G (d). As input file, we considered three sites of adsorbate as following: the terminate N-side, the middle N-side, and the O-side of  $\text{N}_2\text{O}$  closed to the heterogenic atom situated in the middle ring of TP, TT, and DA. Upon optimization of all different possible configurations for a system ( $\text{N}_2\text{O}$  on TP, or TT, or DA), only two stable configurations

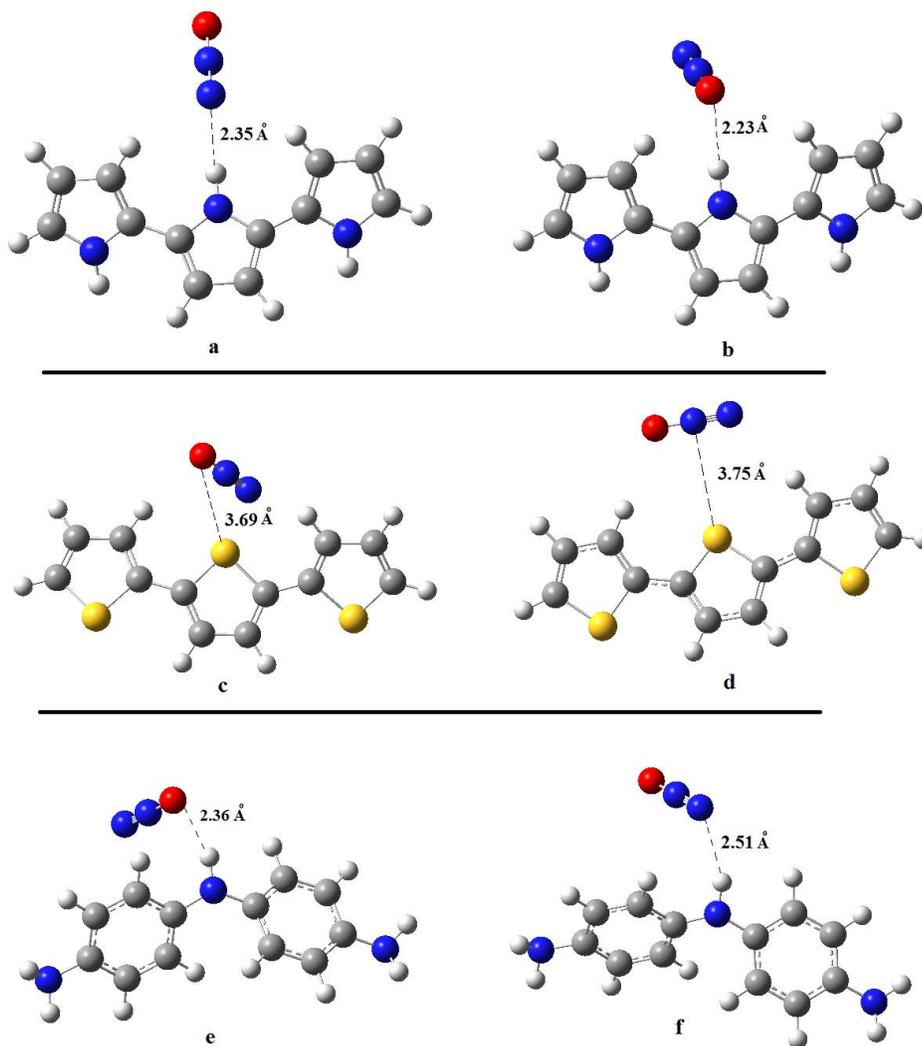
for each complex achieved. All of these relaxed structures are given in Figure 1. As shown in Figure 1, the order of distance of adsorbent-adsorbate for different systems at two configurations is TP- $\text{N}_2\text{O}$  (b) > TP- $\text{N}_2\text{O}$  (a) > DA- $\text{N}_2\text{O}$  (e) > DA- $\text{N}_2\text{O}$  (f) > TP- $\text{N}_2\text{O}$  (c) > TP- $\text{N}_2\text{O}$  (d). Based on the values of adsorption energy (see Table 1), among two possible configurations for each system, we found that in the case of TP, the position configuration (b), for TT the position configuration (d), and for DA the position configuration (e) are more energy favorable positions. Moreover we can conclude that the highest and lowest adsorption attribute to the TP and TT respectively. The values of adsorption energy as well as some important parameters for all optimized systems are listed in Table 1. The dipole moments of pristine TP, TT, and DA are found to be 2.26 Debye, 0.59 Debye, and 1.89 Debye, respectively. Comparing the dipole moments of the pristine oligomers with ones after the  $\text{N}_2\text{O}$  is adsorbed, it is clear that the values of dipole moments do not change significantly which is a confirmation for physisorption.

Our results reveal that the  $\text{N}_2\text{O}$  molecule could adsorb on TP, TT, and DA physically with the adsorption energy values of -9.80, -6.01, and 8.05  $\text{kJmol}^{-1}$  respectively. It is found that the best oligomer for adsorbing the  $\text{N}_2\text{O}$  gas molecules is TP. Higher adsorption for TP reveals the more potential of polypyrrole to be as a polymeric sensor for  $\text{N}_2\text{O}$ .

The charge transfer between the  $\text{N}_2\text{O}$  and oligomers (TP, TT, and DA) was calculated from the variation of the charge distribution on  $\text{N}_2\text{O}$  after adsorption and an isolated  $\text{N}_2\text{O}$ . This calculation has been done by using Mullikan charge analysis. Based on this method, the amount of charge transfer from  $\text{N}_2\text{O}$  to different oligomers were simulated at the pure DFT/6-31 G(d) level of theory. Figure 2 depicted the total charge distribution of isolated and complexed forms of TP, TT, and DA (for each, at the more energy favor configuration). As can be seen from Figure 3,  $\text{N}_2\text{O}$  changes the electronic structure of TP, TT, and DA via charge transfer. This charge transfer can alter the resistance and band gap of TP, TT, and DA, which are in fact measurements of sensitivity of systems. Mulliken charge of  $\text{N}_2\text{O}$  adsorbed on TP, TT, and DA are given in Table 2. Our calculations show that the adsorption of  $\text{N}_2\text{O}$  on TP, TT, and DA is due to the transferring of electrons from analyte to oligomer. Based on the Mulliken charges distribution, upon complexes formation,  $\text{N}_2\text{O}$  loses about  $0.027 e^-$ ,  $0.018 e^-$ , and  $0.015 e^-$  charge to TP, TT, and DA at proper configuration. As a result, whenever  $\text{N}_2\text{O}$  interacts with

TP, TT, and DA, a weak charge-transfer interaction takes place which proves physisorption of  $N_2O$ . These results are totally in accordance to the results of

adsorption energy. Thus, the Mulliken analysis reveals the electron-donating of  $N_2O$  during adsorption.

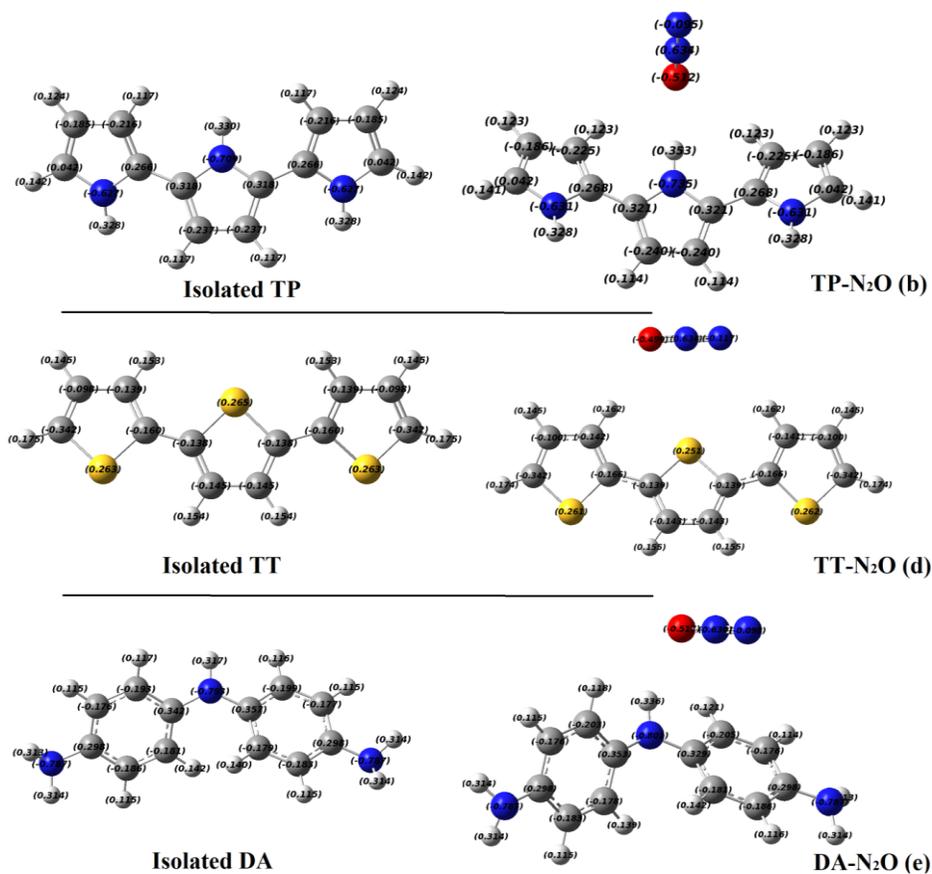


**Figure 1:** The relaxed structures of different systems: TP- $N_2O$  (position 1 (a)), TP- $N_2O$  (position 2 (b)), TP- $N_2O$  (position 1 (c)), TP- $N_2O$  (position 2 (d)), DA- $N_2O$  (position 1 (e)), DA- $N_2O$  (position 2 (f))

**Table 1:** The nearest distance of adsorbent-adsorbate (d), dipole moment ( $\mu_D$ ), calculated charge transfer by Mulliken charge analysis ( $Q_{\text{Mulliken}}$ ), the adsorption energy ( $\text{kJmol}^{-1}$ ), and counterpoise corrected energy of adsorption ( $\text{kJmol}^{-1}$ ) for all systems

System	d ( $\text{\AA}$ )	$\mu_D$ (Debey)	$Q_{\text{Mulliken}}$ (e)	$-E_{\text{ads}}$	$-E_{\text{ads}}(\text{CP})^1$
Isolated TP	-	2.26	-	-	-
TP- $N_2O$ (a)	2.35	2.08	+0.016	7.76	6.35
TP- $N_2O$ (b)	2.23	2.05	+0.027	9.80	8.72
Isolated TT	-	0.59	-	-	-
TT- $N_2O$ (c)	3.69	0.59	+0.013	4.62	4.11
TT- $N_2O$ (d)	3.75	0.94	+0.018	6.01	5.12
Isolated DA	-	1.89	-	-	-
DA- $N_2O$ (e)	2.36	1.51	+0.015	8.05	7.12
DA- $N_2O$ (f)	2.51	1.61	+0.017	6.06	5.13

<sup>1</sup> counterpoise corrected energy



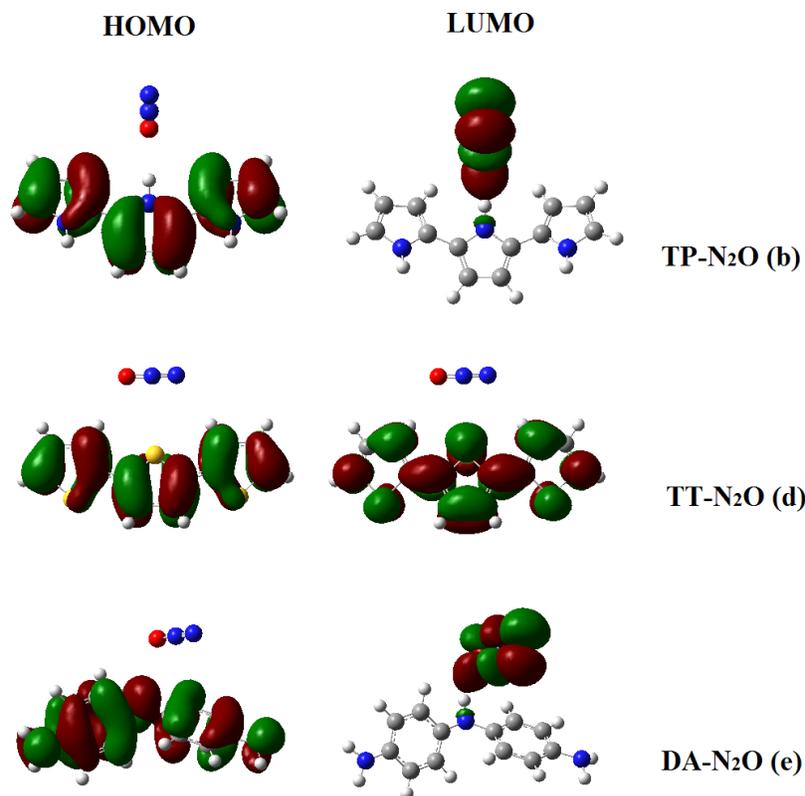
**Figure 2:** The Mulliken charge distribution for isolated (left) and complexed (right) forms of TP, TT, and DA.

The adsorption of N<sub>2</sub>O on TP, TT, and DA can be showed in terms of HOMO and LUMO energies [5-7]. Quantum mechanically, the interaction between two reactants takes place for the reason that of interaction of frontier molecular orbitals [8-10].

The HOMO and LUMO for all systems were calculated based on above-mentioned basis set and have been shown in Figure 3, and their results are listed in Table 2. The HOMO and LUMO energy orbitals for pristine TP, TT and DA are found to be (-4.42 eV, -0.07 eV), (-5.20 eV, -1.64 eV), (-4.26 eV, -0.17 eV), respectively. As can be seen from Table 2, after adsorption of N<sub>2</sub>O, these values are changed to (-4.33 eV, -0.91 eV), (-5.19 eV, -1.61 eV), (-4.26 eV, -0.64 eV) for TP-N<sub>2</sub>O, TT-N<sub>2</sub>O, and DA-N<sub>2</sub>O respectively. Comparing the HOMO-LUMO energies of the pristine TP, TT, and DA with ones after the adsorption of N<sub>2</sub>O gas molecules, it is clear that major hybridizing happens upon adsorption of N<sub>2</sub>O on TP and DA. The data show that when the N<sub>2</sub>O is adsorbed on TT, the HOMO and LUMO remain unchanged and are situated on TT but in the case of TP and DA, the LUMO shifts on adsorbate while the HOMO remains

on oligomer which proves orbital hybridization upon adsorption on TP and DA. These HOMO-LUMO distributions correspond to decrease in the  $E_{\text{gap}}$  ( $E_{\text{HOMO}} - E_{\text{LUMO}}$ ) of resulted complexes (TP-N<sub>2</sub>O and DA-N<sub>2</sub>O) than their isolated forms (TP and DA) which means more conductivity of adsorbed systems. These results confirms the possibility of TP and DA as an adsorbent/sensor for N<sub>2</sub>O, while TT seems to be unsuitable for this purpose since there is no orbital hybridizing upon adsorption of N<sub>2</sub>O on TT.

To more understand of the electronic properties of TP, TT, and DA upon adsorption of N<sub>2</sub>O, the density of states (DOSs) were calculated for the isolated oligomers as well as their complex with N<sub>2</sub>O. Figure 4 plots the DOSs for the above-mentioned systems near the Fermi level ( $E_{\text{F}}$ ). By focusing on the data of DOSs (see Figure 4), one can find that adsorption of N<sub>2</sub>O gas molecules on TT does not affect the band gaps of TT. However the adsorption of N<sub>2</sub>O reduces the values of band gaps for TP and DA. The band gaps of the pristine TP, TT and DA are calculated and are listed in Table 2.



**Figure 3:** The molecular orbitals of HOMO and LUMO for complexed structure of TP, TT, and DA.

**Table 2:** The HOMO energies ( $E_{\text{HOMO}}$ ), LUMO energies ( $E_{\text{LUMO}}$ ), energy of Fermi level ( $E_{\text{FL}}$ ), HOMO/LUMO energy gap ( $E_g$ ) of complexed and non-complexed forms of TP, TT, and DA.

System	$E_{\text{HOMO}}$ (eV)	$E_{\text{FL}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_g$ (eV)
N <sub>2</sub> O	-9.31	-4.91	-0.52	8.79
TP	-4.42	-2.24	-0.07	4.35
TP-N <sub>2</sub> O (b)	-4.33	-2.62	-0.91	3.42
TT	-5.20	-3.42	-1.64	3.56
TT-N <sub>2</sub> O (d)	-5.19	-3.40	-1.61	3.58
DA	-4.26	-2.05	-0.17	4.43
DA-N <sub>2</sub> O (e)	-4.26	-2.45	-0.64	3.62

## Conclusion

The gas sensing behavior of TP, TT, and DA, by considering different adsorption sites are reported. The adsorption of N<sub>2</sub>O gas molecule on above-mentioned oligomers are studied using pure DFT/6-31 G(d). Two different adsorption sites are applied on each case. It is found that the adsorption of N<sub>2</sub>O gas molecules on TT does not affect the electronic character of the TT, however the adsorption of N<sub>2</sub>O on TP and DA reduces the band gap of both TP and DA. As a result we introduce the polypyrrole as the most sensitive sensor than polythiophene and polyaniline toward N<sub>2</sub>O detection.

## Computational Methods

All calculations were performed with the density functional theory (DFT) as implemented within G09W package [26] by applying basis set 6 - 31 G (d). All pristine TP, TP, and DA as well as their complex with N<sub>2</sub>O were fully optimized. The adsorption energies of N<sub>2</sub>O molecule ( $E_{\text{ads}}$ ) were calculated from Eq. 1:

$$E_{\text{ads}} = E_{\text{Complex}} - (E_{\text{Oligomer}} + E_{\text{N}_2\text{O}}) \quad (\text{eq.1})$$

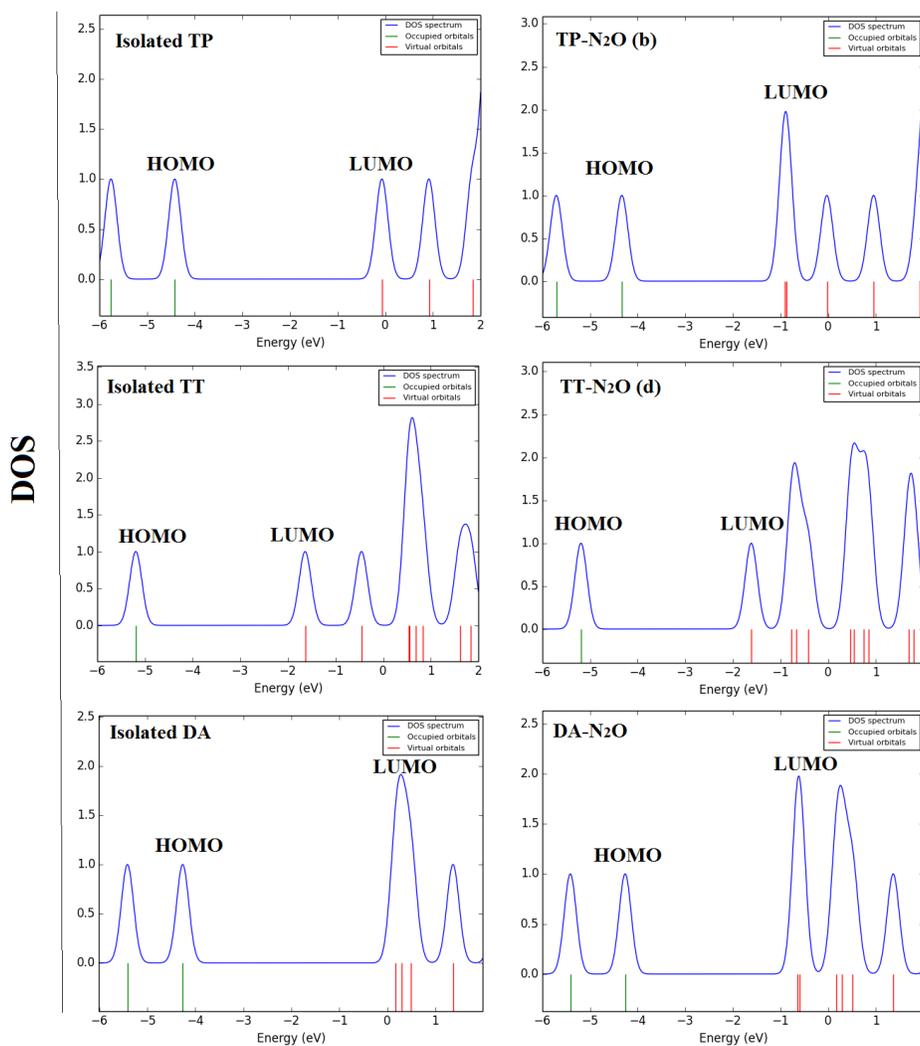
where  $E_{\text{Complex}}$  and  $E_{\text{Oligomer}}$  are the total energies of complexed and non-complexed forms of TP or DA or TT respectively.  $E_{\text{N}_2\text{O}}$  is the total energy of N<sub>2</sub>O gas molecule. We calculated the counterpoise corrected energy from the following eq.

$$E_{\text{CP}} = E_{\text{ads}} - E_{\text{BSSE}} \quad (\text{eq.2})$$

which  $E_{CP}$  is counterpoise corrected adsorption energy of related complexes and  $E_{BSSE}$  is basis set superposition errors energy.

Calculations of charge analysis, density of states (DOS), the energy of lowest unoccupied molecular orbital (LUMO), the energy of highest occupied

molecular orbital (HOMO), and the HOMO-LUMO energy gap ( $E_g$ ) have been done using above-mentioned basis set.



**Figure 4:** The DOSs of isolated TP, TT, and DA (left) along with their complex with  $N_2O$  (right).

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