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Quantum Molecular Descriptors of 6-Thioguanine Adsorbed PPy-PNVK Conducting Polymer: A DFT Analysis

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6-Thioguanine (6-TG) is an important drug to cure cancer with fierce adverse effects on human being, necessitating its frequent monitoring. Present work reports the computational analysis of a copolymer (PPy-PNVK), synthesized using polypyrrole (PPy) and poly(9-vinyl carbazole) (PNVK) host polymers. The sensing ability of these polymers for 6-TG, has been performed through the DFT formulated *ab initio* approach employing the generalized gradient approximations (GGA), considering the revised-Perdew, Burke and Ernzerh (rPBE) pattern of parameters. The suitability of these polymers for 6-TG sensing application, has been assessed by analyzing the variations in the HOMO-LUMO gaps, density of state (DOS), Mulliken population, molecular energy spectrum (MES), adsorption energy (E_{ads}), bond variation, chemical reactivity of the surface, the recovery time (τ) and the electron density plots. The estimated negative adsorption energy confirms the physisorption and stability of 6-TG on PPy, PNVK and their copolymer counterpart. Considering the recovery time, range of detection, reusability and quantum molecular descriptors as an important sensing parameters, it has been observed that the computationally synthesized copolymer is relatively better in comparison to its host polymers.

Keywords: 6-Thioguanine, polypyrrole, Poly(9-vinyl carbazole), Copolymer, Molecular energy spectrum, Recovery time.

INTRODUCTION

It is a well-known fact that significant resources are invested in cancer diagnosis, prevention and treatment. Cancer reports the highest morbidity and mortality in human diseases [1,2] with indicators for escalation of estimated mortalities by 2030. Once diagnosed through the cancer biomarker detection technique, diverse therapies with various anticancer drugs are considered [3]. The discovery and development of anticancer drugs are major work fields for pharmaceutical companies. 6-Thioguanine (6-TG) is a close structural analogue of guanine, providing some advantage for drug development in the anticancer field [4]. Reports confirm that in the aqueous medium, 6-TG is exist as thione N_9H, thione N_7H and thiol N_9H forms, with a high proportion of thione N_9H [5,6] in comparison to other isomers. This compound also termed as thiopurine antimetabolite, is the first purine analogue fit to benefit for the treatment of neoplastic disease, reportedly efficacious in the cure of acute leukemia, breast cancer and seditious bowel problems [7,8]. As a cytotoxic agent, 6-TG has a crucially important narrow therapeutic index and reported to be associated with myelosuppression and liver damage [8-10]. Hence, the monitoring and detection of 6-TG is essential for its use in cancer therapy. Therefore, several analytical methods like chromatographic [11], electrochemical [12], phosphorimetry [13], localized surface plasmon resonance [14], fluorimetry [15] and spectroscopic [15] methods have been reported so far. However, all the above cited methods require expensive high end instrumentation, separation procedure and complex sample progression; thus, these can be treated as limitations and demerits.

A variety of materials like Pt/MWCNTs [12,16], ionic liquids [17] and caffeic acid functionalized Fe_3O_4 nanoparticles [18] have been reportedly employed to detect 6-TG at the trace level. The competence of electrochemical and biosensors depends on the material properties of the electrodes interface

[19]. To enhance the sensing performance of the interface, nanomaterials [20], semiconductor materials, metals and metal oxides, polymers and inorganic mediators have been used as modifiers to decorate the sensor interface [21]. Conductivity, external interface and robustness are key factors for a rating of the sensor performance [22].

Conducting polymers (CPs) are useful resource for the varieties of sensor materials, owing to their unique physicochemical characteristics, adjustable architecture, adaptability, versatility of working temperature window and sensitive of electrochemical response with slight modifications in their surface [23,24]. Nanoparticle composite with the conducting polymers generally does not compromise its processability [25]. Conducting polymers such as polypyrroles, polyanilines and polythiophenes have attracted considerable attention of the scientific community, due to their excellent electrical conductivity, film-forming property, outstanding transparency in the visible region and excellent shelf life [26].

Several electrochemical sensors [12,27,28] may further prove promising for the detection and quantification of 6-thioguanine and other analytes. Additionally, the electrochemical sensors [29-31] provide the possibility of simultaneous measurements of various analytes in a short period of time which is the most expected feature for cancer-related biosensor detection. The computational analysis of such interactions and suitability of any new material for the detection of 6-TG is a cost effective solution, prior to actually performing the lab experiment or even validating the lab findings. The present study paves the way for designing copolymer structures as biosensors, which can investigate the presence of 6-TG, an anticancer drug with high sensitivity and selectivity. Thus, the computationally modeling can illustrate the correct prospects for exploiting and modifying material properties without experimental and trial research. Herein, a new copolymer and its suitability for detecting 6-TG presence in the human being is reported. In comparison to its host polymers, the energetics, electrical characteristics and recovery time have all been used to investigate the presence of 6-thioguanine (6-TG).

COMPUTATIONAL METHODS

For sensing of 6-thioguanine (6-TG), the suitability of polypyrrole (PPy), poly(9-vinyl carbazole) (PNVK) and their copolymer has been adjudged using Atomistix Tool kit (ATK) package [32], a density tunctional theory (DFT) [33] based *ab initio* tool. The ATK-VNL kit enhances the precision of TranSIESTA, as it employs the basis sets as developed in SIESTA. Generalized gradient approximation has been applied as exchange-correlation functional with revised-Perdew-Burke-Ernzerhof (rPBE) geometry optimization of the anticipated assembly of molecules to calculate the electronic properties [34]. Double zeta double polarization basis cliques are considered to represent various electronic states. A mesh cutoff of 75 Rydberg has been found sufficient for the improved electron flora on a regular real-space grid. Different possible configurations have been attempted and optimized to confine the structure of PPy, PNVK and their copolymer in the incidence of 6-TG. During the optimization of geometries, the maximum stress tolerance has been set to 0.05 eV/Å^3 with a maximum force of 0.05 eV/Å, respectively.

Polypyrrole (PPy) containing 8 carbon atoms, 8 hydrogen atoms and 2 nitrogen atoms and poly(9-vinyl carbazole) (PNVK) containing 28 carbon atoms, 20 hydrogen atoms and 2 nitrogen atoms have been considered as host materials for the polymeric drug sensor and to further design a new conducting copolymer containing 36 carbon atoms, 26 hydrogen atoms and 4 nitrogen atoms to understand its sensing ability for 6-thioguanine (6-TG).

RESULTS AND DISCUSSION

Structural energetics: The optimized geometries of polypyrrole (PPy), poly(9-vinyl carbazole) (PNVK) and their copolymer in the presence/absence of 6-TG are shown in Fig. 1, which have been studied for their structural stability, discussed in terms of their total energy. The computed total energy of PPy, PNVK and their copolymer is -1931.555 eV, -5274.045 eV and -7173.462 eV in the absence of 6-TG and it decreases to -4516.529 eV, -7859.055 eV and -9758.475 eV in the presence of 6-TG. The computed energy of PPy and PNVK in the presence/absence of 6-TG confirms that PNVK has better stability compared to PPy. However, their modeled and optimized copolymer has shown even better stability than its host polymers.

To better understand the chemical interactions of 6-TG with PPy, PNVK and their copolymer, their optimized geometries have been analyzed in terms of interaction type and the structural parameters, such as bond length and bond angle. In all three cases, the interaction is physisorption in nature. The variation in the structural parameters during the interaction between adsorbate and adsorbent has been analyzed. As the nitrogen atom is electronegative and *p*-block element, its valence shell is partially filled ($1s^2$, $2s^2$, $2p^3$) and one loan pair is present. Nitrogen atom is a highly electronegative element in the optimized system and follows the trend as hydrogen (H) < carbon (C) < sulfur (S) < nitrogen (N) over Pauling scale are 2.20, 2.55, 2.58 and 3.04, respectively, responsible for the variations in the structural parameters.

Interestingly, the 6-TG orientation affects the structural parameters of PPy, PNVK and their copolymer on adsorption. The bond length of PPy (C_{10}-C_6, C_{10}-C_2 and C_2-C_3), PNVK (H_{37}-C_9, C_{15}-H_{40}) and their copolymer (C_2-C_3, C_4-C_5 and N_{10}-H_{49}) in the presence of 6-TG is minutely changed by 0.01 Å. While the bond angle is highly varied in the case of PNVK ($\angle H_{37}$-C_9-C_8) and the value is 2.16º. On the other hand, the structural parameter of 6-TG is also affected due to the interaction between adsorbate and adsorbent. The bond length of 6-TG is slightly varied with PPy (C_4-S_{14}, C_3-N_9) and copolymer (C_3-N_9) by 0.02 Å in both cases. However, the bond angle is highly altered with PNVK and the value is 2.83º, which corresponds to $\angle S_{14}$-C_4-N_5.

To further understand the nature of the interaction between adsorbate and adsorbent, 6-TG is exposed to a random site of PPy, PNVK and their copolymer surface and the system is optimized. The adsorption energy (E_{ads}) of 6-TG adsorbed PPy, PNVK and their copolymer system have been calculated using eqn. 1 and reported in Table-1.

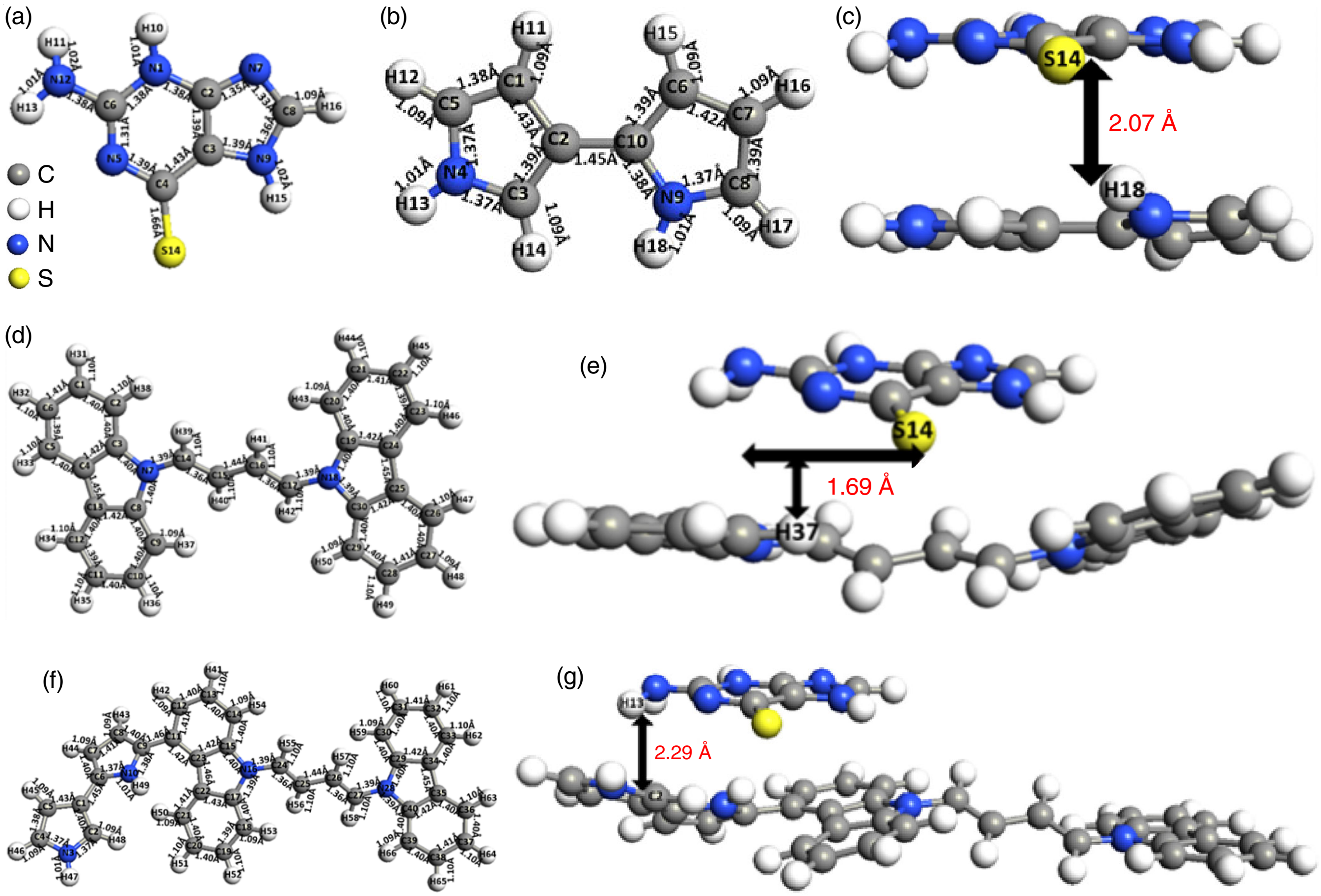

Fig. 1. Optimized geometries of (b,c) PPy, (d,e) PNVK and their (f,g) copolymer in the presence/absence of (a) 6-TG

TABLE-1
ADSORPTION ENERGY OF 6-TG ADSORBED PPy, PNVK AND THEIR COPOLYMER SYSTEM

System	Adsorption energy (eV)	Type of interaction
PPy + 6-TG	-0.578	Physisorption
PNVK + 6-TG	-0.615	Physisorption
Copolymer + 6-TG	-0.618	Physisorption

$$E_{ads} = E_{T\,(y\,+\,6\text{-}TG)} - E_{T\,(y)} - E_{T\,(6\text{-}TG)} \qquad (1)$$

where, $E_{T(y\,+\,6\text{-}TG)}$ is the overall energy of the system, $E_{T(y)}$ is the total energy of PPy, PNVK and their copolymer and $E_{T\,(6\text{-}TG)}$ is the total energy of 6-TG. In eqn. 1, y corresponds to PPy, PNVK and copolymer, respectively. According to previous reports [1-3], it is concluded that the negative values of E_{ads} indicate the physisorption and exothermic reaction between adsorbate and adsorbent, indicating the adsorption system as stable. The computed E_{ads} using PBE type parameterization is slightly higher than the conventionally observed energies reported for physical adsorption. However, while considering the revised PBE type pattern, the E_{ads} is in close agreement with that observed elsewhere [35], confirms the physisorption between 6-TG and PPy, PNVK and their copolymer, as no chemical bond is formed between them. This can also be visualized and verified through the optimized structural geometries and electron density plots, as shown in Fig. 1c,e,g and Fig. 2c,e,g, respectively. The E_{ads} for the case of copolymer being the minimum, followed by PNVK and PPy host polymers for its interaction with 6-TG.

The range of detection has also been computed for these three interactions, as shown in Fig. 1c,e,g and found that the copolymer has a relatively larger distance and hence, a better sensing ability in comparison to its host polymers. The optimized distance in the PPy and 6-TG system is 2.07 Å, followed by the PNVK at 1.69 Å and copolymer at 2.29 Å (Table-2).

TABLE-2
DISTANCE (RANGE OF DETECTION) AND HOMO LUMO GAP PROFILES BETWEEN PPy, PNVK AND THEIR COPOLYMER WITH 6-TG

System	Optimized distance (Å)	HOMO-LUMO gap (eV)
PPy + 6-TG	2.07	2.04
PNVK + 6-TG	1.69	2.15
Copolymer + 6-TG	2.29	2.02

Recovery time (τ) is an additional significant indicator for a good sensor, associated with its physical adsorption energy (E_{ads}) [36].

$$\tau = \nu^{-1}\exp\left(-\frac{E_{ads}}{K_b T}\right) \qquad (2)$$

where K_b is the Boltzmann constant and ν is the attempt frequency of the sensor at the operational temperature T. Adsorption energy exhibiting the PPy > PNVK > copolymer trend, the

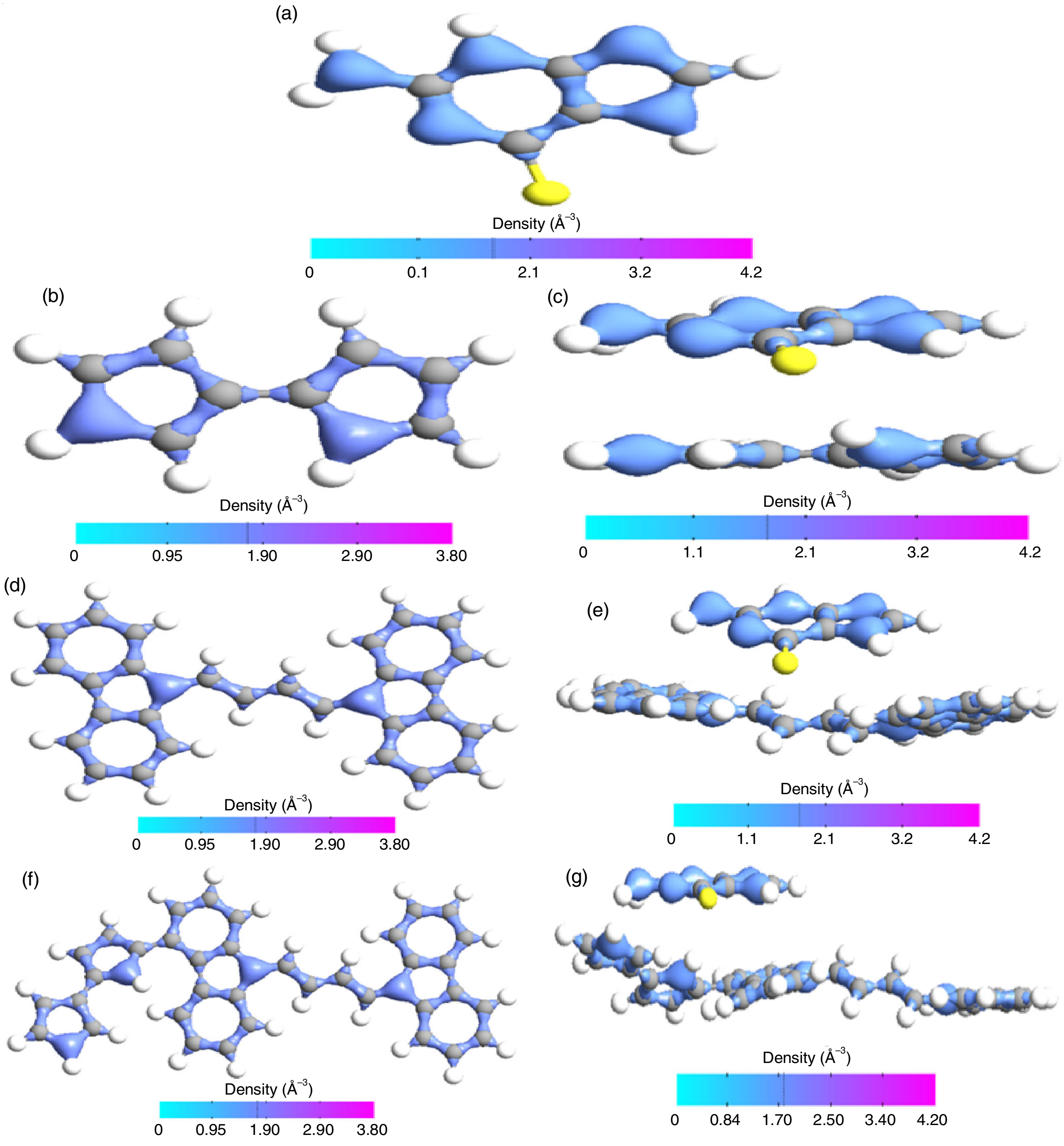

Fig. 2. Electron density plots (isovalue = 1.75094) of (b,c) PPy, (d,e) PNVK and their (f,g) copolymer in the presence/absence of (a) 6-TG

recovery time having an inversely proportional relationship with E_{ads} have been computed using eqn. 2. Results furnish that PPy < PNVK < copolymer trend for recovery time and approve a quick recovery time of copolymer for 6-TG sensing, in comparison to its PPy and PNVK host polymers (Table-1). The sensitivity of 6-TG at different orientations on the PPy, PNVK and their copolymer has also been analyzed.

Charge transfer analysis: To understand the chemistry of interaction between adsorbate and adsorbent, the charge transfer has also been computed through the Mulliken population analysis, using eqn. 3 and further analyzed through electron density plot.

$$\Delta\rho = \rho_{(y + 6\text{-TG})} - \rho_{(6\text{-TG})} \qquad (3)$$

where $\rho_{(y + 6\text{-TG})}$ is the charge on 6-TG of adsorbed system and $\rho_{(6\text{-TG})}$ is the charge on 6-TG in pure form. In eqn. 3, y corresponds to PPy, PNVK and their copolymer, respectively. The negative values of charge transfer confirm that 6-TG transfer the charge to the targeted copolymer as well as host polymers considered for the sensing of the 6-TG drug. The PPy shows the higher value of charge transfer (-0.087e) in comparison to PNVK (-0.058e) and copolymer (-0.026e) respectively.

The movement of localized electrons is fixed between two nuclei and participate in complete overlapping and the spin of these electrons in the opposite direction, which means localized electrons are not participating in the charge transfer process. However, the π-electrons and loan pair are highly delocalized in nature and hence represented by conjugation. The delocalized electrons are not fixed between two nuclei and participate in sidewise overlapping. So these electrons move from one atom to another atom and participate in the charge transfer process. In present case, the charge transfer from 6-TG to PPy, PNVK and their copolymer due to the presence of delocalized electrons.

The computed charge transfer results from interactions between 6-TG and host polymers and their copolymer and the same has been shown through the electron density plots of the adsorbed systems (Fig. 2a-g). It has been observed that the proposed copolymer as well as PPy, PNVK host polymers, acquire charge from the 6-TG, as confirmed by dark sky blue colour over the PPy, PNVK and their copolymer. Overall, there is no evidence of chemisorption between the adsorbate and adsorbent and the value of charge transfer further supports the physisorption type interaction.

Electronic properties: Furthermore, the variation in electronic property of host polymers and their copolymer on the adsorption of 6-TG is analyzed, in terms of the HOMO-LUMO gap, MES plots and DOS profiles; as depicted in Fig. 3a-c. The electrical conductivity of semiconductor materials is directly proportional to ~ $\exp(-E_g/K_BT)$ [37], where, E_g is the bandgap, K_B is the Boltzmann constant and T is the absolute temperature. The conductivity of materials is control by the bandgap. The HOMO–LUMO gap, similar to the bandgap for materials, is indicated in the DOS profiles (Fig. 3a-c) for all adsorbed systems. The computed HOMO-LUMO gap of PPy, PNVK and their copolymer is 3.76 eV, 2.52 eV and 2.16 eV in the absence of 6-TG and it decreases to 2.04 eV, 2.15 eV and 2.02 eV in the presence of 6-TG (left panel of Fig. 3a-c). The copolymerization improves the performance of modified carbon conducting materials on various drugs, as reported elsewhere [38].

Furthermore, the DOS profiles of PPy, PNVK and their copolymer in the presence of 6-TG indicate that the HOMO-LUMO gap gets reduced by 45.74%, 14.68% and 6.48%, respectively. It is worth noting that the variation in DOS profiles of the adsorbed systems is in line with their MES profiles. From the DOS profiles, we can observe that the peaks of HOMO and LUMO are shifted towards the Fermi level in all adsorbed systems and resulting in variations of the HOMO–LUMO gap (shown in right panel of Fig. 3a-c). In case of PPy in the presence of 6-TG, few extra peaks appear and the height of few peaks varies in the valence/conduction band. Similarly, in case of PNVK, few extra peaks appear in the valence/conduction band; however, there is a minute change in the height of the peaks. Whereas, in case of copolymer in the presence of 6-TG, one extra peak in valence band and the height of few peaks varies in valence/conduction band were observed.

Moreover, the variation of HOMO-LUMO gap as a function of detection range for all the adsorbed systems is shown in Fig. 4. Here, the HOMO-LUMO gap decreases as the separation between the adsorbent and adsorbate decreases; thus, indicating an enhanced conductance in all the adsorbed systems. These findings further confirmed the sensing of 6-TG with PPy, PNVK and their copolymer. The best range of detection has been observed in case of the newly synthesized copolymer *i.e.* PPy-PNVK.

Quantum molecular descriptors: In order to further understand the reactivity of PPy, PNVK and their copolymer with 6-TG; chemical potential ($\mu = (E_{HOMO} + E_{LUMO})/2$), softness ($S = 1/\eta$), global hardness ($\eta = (E_{LUMO}-E_{HOMO})/2$) and global electrophilicity index ($\omega = \mu^2/2\eta$) have been calculated using Koopman theorem [39]. Here, the value of μ specifies the escaping proclivity of electrons from a molecular system in its equilibrium state, which is associated with high chemical reactivity. The calculated μ for the copolymer and complexes indicate that post adsorption of 6-TG, the value of μ in case of copolymer increases from -0.19 to -0.13 eV in comparison to PPy and PNVK host polymers (Table-3).

The value of S is minimum for 6-TG adsorbed copolymer, which indicates that the copolymer is comparatively less soft than its host polymers. The softness of adsorbed system is also verified through the hardness due to the inverse relationship between them. The η is indicative of resistance towards electron cloud change of the chemical system. Hence, the hardness and HOMO-LUMO gap of the molecule are associated with stability and reactivity; the high value of hardness and lower value of HOMO-LUMO Gap indicates that the molecule is more stable and highly reactive. From Table-3, the value of η for copolymer increases on adsorption of 6-TG. On the other hand, the value of ω also increases upon adsorption of 6-TG, which indicates that the adsorption of 6-TG on copolymer increases the electrophilic character of the system and thus is

TABLE-3
CALCULATED ENERGIES OF FRONTIER MOLECULAR ORBITALS (E_{HOMO}, E_{LUMO}), CHEMICAL POTENTIAL (μ), SOFTNESS (S), GLOBAL HARDNESS (η) AND GLOBAL ELECTROPHILICITY INDEX (ω) OF SYSTEMS

System	E_{HOMO} (eV)	E_{LUMO} (eV)	μ (eV)	S (eV)	η (eV)	ω (eV)
6-TG	-1.08	1.08	0	-0.925	-1.08	0
PPy	-1.88	1.88	0	-0.531	-1.88	0
PNVK	-1.63	0.89	-0.37	-0.793	-1.26	-0.054
Copolymer	-1.27	0.89	-0.19	-0.925	-1.08	-0.016
PPy + 6-TG	-1.02	1.02	0	-0.980	-1.02	0
PNVK + 6-TG	-1.26	0.89	-0.185	-0.930	-1.075	-0.015
Copolymer + 6-TG	-1.14	0.88	-0.13	-0.990	-1.01	-0.008

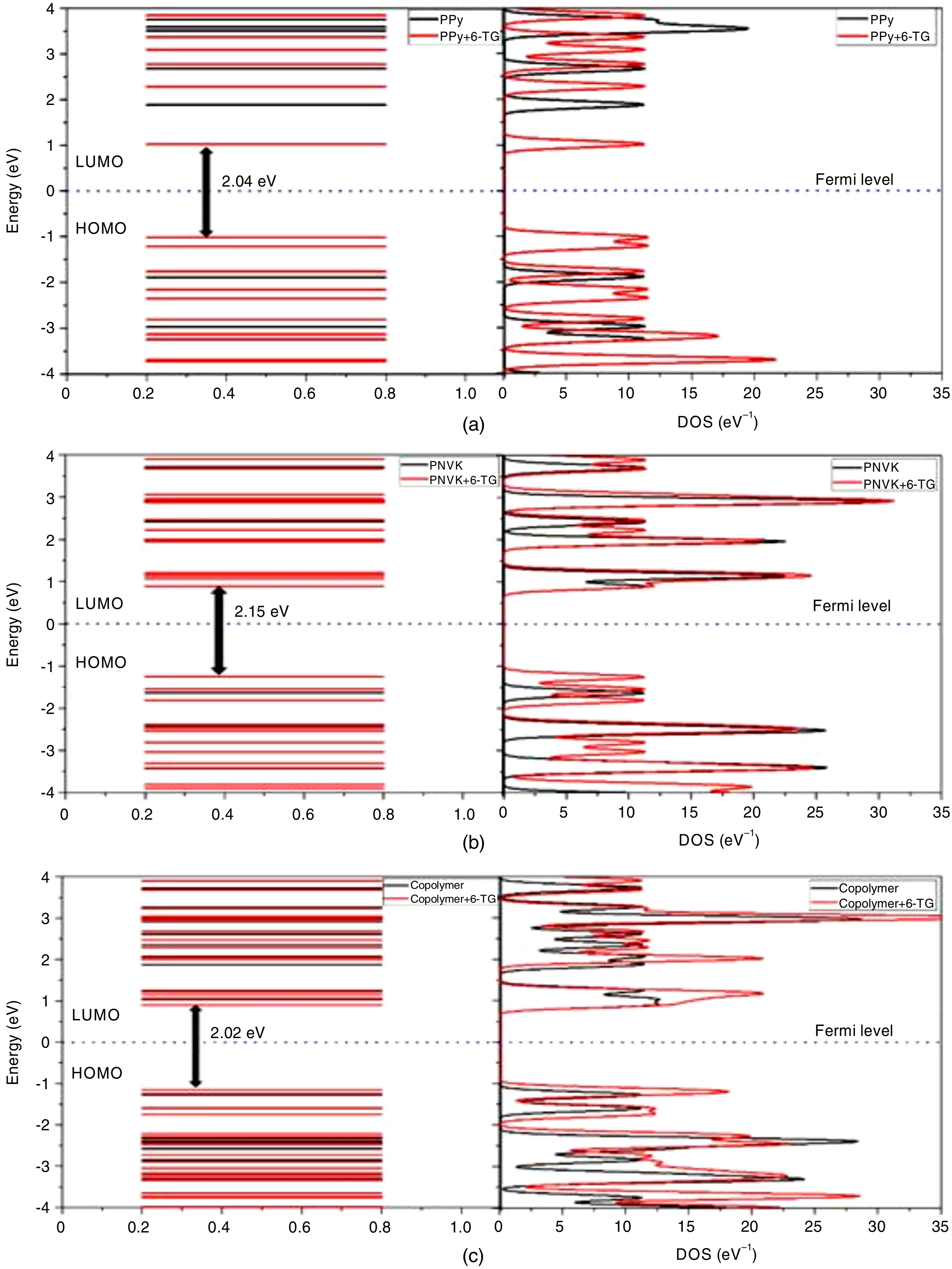

Fig. 3. HOMO-LUMO and DOS profiles of (a) PPy, (b) PNVK and their (c) copolymer in the presence/absence of 6-TG

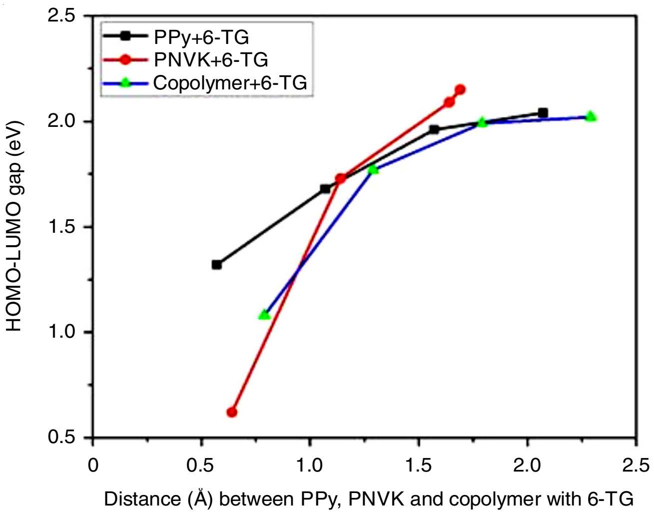

Fig. 4. HOMO-LUMO gap as a function of the distance between PPy, PNVK and copolymer with 6-TG

more potent towards attracting nucleophiles [40,41]. It has been observed that the 6-TG adsorbed copolymer is relatively better in terms of sensing and increases the chemical reactivity in comparison to PPy and PNVK host polymers.

Conclusion

In present study, the computational synthesis of a new conducting copolymer (PPy-PNVK) from its polypyrrole (PPy) and poly(9-vinyl carbazole) (PNVK) host polymers has been reported for its suitability as a polymeric drug sensor for 6-thioguanine (6-TG), a cancer drug. The MES profile, DOS profile, HOMO-LUMO gap, adsorption energy, recovery time, Mulliken population and electron density plot have been analyzed as the polymeric drug sensor. The significant variations in the electronic properties of copolymer and host polymers confirmed the presence of 6-TG. The computation of quantum molecular descriptors also confirms the sensing through variations in its chemical potential, softness, hardness and electrophilicity on adsorption of 6-TG. The observations also confirm that the newly computationally synthesized copolymer is relatively better sensing material for 6-TG sensing than its host polymers. Specifically, the proposed copolymer has relatively better stability, reactivity, better range of detection, having fast recovery time and reusable sensing material due to physical adsorption, in comparison to PPy and PNVK host polymers.

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CONFLICT OF INTEREST

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

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