

High sensitivity of polypyrrole sensor for uric acid over urea, acetamide and sulfonamide: A density functional theory study

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ABSTRACT

Polypyrrole is experimentally reported as an excellent sensor for biological molecules including urea and uric acid. DFT calculations at M05-2X/6-31++G(d,p) are performed to gain theoretical insight into the sensing mechanism of polypyrrole for urea, uric acid, acetamide and sulfonamide. Geometry optimization and electronic property calculations have been performed on a series of oligopyrrole (1, 3, 5, 7 and 9) complexes, and the properties are extrapolated to infinite polymer through 2nd degree polynomial fit. Energy decomposition analyses (SAPTO) have been performed to demonstrate the contribution of electrostatic, induction, exchange and dispersion. The trend of SAPTO interaction energies is very much comparable to that of binding energies. The noncovalent components of SAPTO regularly increase with oligomer chain length; however, these components become almost constant after trimer for urea, acetamide, and sulfonamide. The increase in interaction and SAPTO energies illustrate an increase in sensitivity of polypyrrole. Charge transfer and electronic properties also illustrate the high sensitivity of polypyrrole for uric acid. Energy difference between HOMO and LUMO orbitals of polypyrrole decreases upon doping with analytes. The decrease in the HOMO-LUMO gap shows an increase in the conductivity of polypyrrole. Our results indicate that polypyrrole has the highest sensing ability for uric acid, consistent with the experimental observations.

1. Introduction

Research in conducting polymers expanded rapidly soon after Pohl and coworkers synthesized first semiconducting polymer, in 1960s [1]. The conducting polymers are also referred as conjugated polymers because of alternate single and double bonds in their backbone [1,2]. Conjugated polymers are conducting due to the delocalization of electrons [3]. Conjugated polymers find applications in photochemical cells [4], photovoltaic cells [5], batteries [6], electromechanical devices [7], light emitting diodes (LEDs) [8], optical molecular switches [9] and sensors [10–12]. During last fifteen years, conducting polymers have emerged as excellent sensors [13], due to their versatile properties such as high environmental stability [14], electrical conductivity [15], high sensitivity [16], short response time [16], good mechanical properties [16] and low cost. The change in the chemical, optical and electronic properties of conjugated polymers occur as a result of complexation with analytes [17]. Generally, these polymers are used as electrochemical sensors because complexation with analytes results in marked change in electrical conductivity of the polymer. Sensor properties of conjugative polymers are very important to detect toxic volatile compounds such as liquefied petroleum gas (LPG), liquefied natural gas

(LNG), compressed natural gas (CNG), carbon monoxide (CO), sulphur dioxide (SO₂), nitrogen dioxide (NO₂), sulphur trioxide (SO₃), methane, ethane, propane and cigarette smoke *etc* [18]. Moreover, conducting polymers also express virtuous response toward ionic analytes such as NO₃⁻ [19] and halide ions (F⁻, Cl⁻, Br⁻) [20]. Conjugated polymer based sensors are superior to other conventional sensors due to remarkable electrical conductivity [21]. Polythiophene (PTh), polypyrrole (PPy) and polyaniline (PANI) are the most extensively used as sensor because of their most striking electrical, physical and chemical properties [22]. Literature reveals that polypyrrole [23] based sensors [24] are extensively studied experimentally or theoretically, compared to polythiophene and polyaniline.

A number of reports reveal that polypyrrole has been used as a sensor for ammonia. Ratcliffe et al., [25] used ultra-thin layer of polypyrrole for the detection of ammonia and hydrazine and showed that the polypyrrole is more sensitive to low concentration of hydrazine. Magaraphan et al., [26] applied nanocomposites of polypyrrole with organo-clay as gas sensor for volatile organic compounds, i.e., CH₄ and C₂H₄. Hosseini et al., [27] used blended polypyrrole film for the detection of toxic gases including hydrogen halides, hydrogen cyanide, and halogens. Radhakrishnan et al., [28] studied conducting polymers

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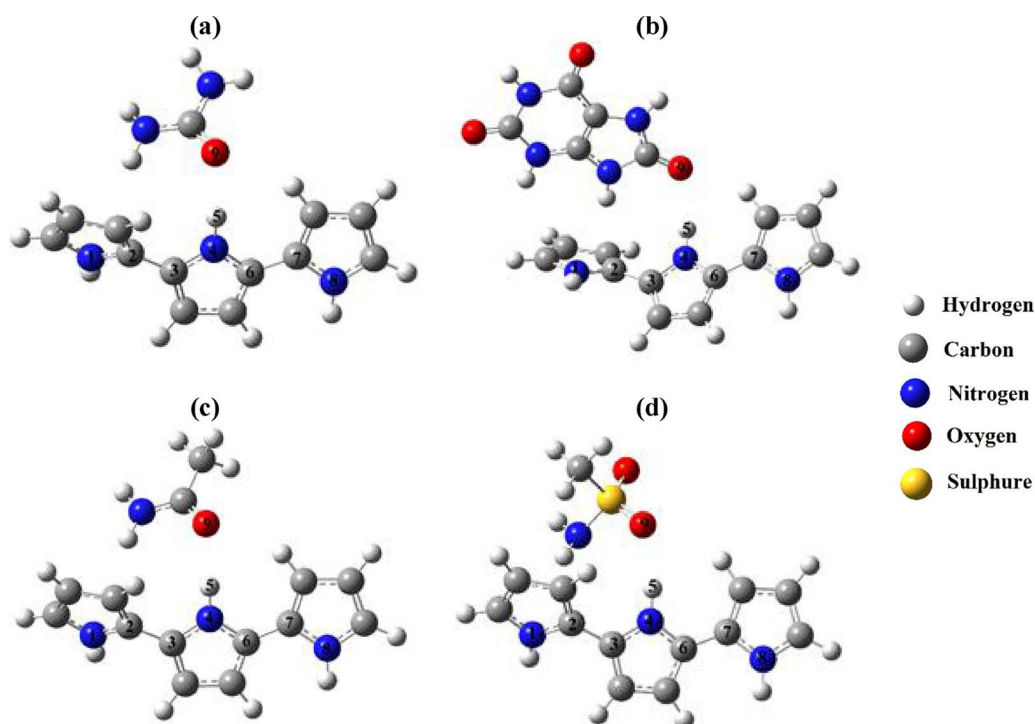


Fig. 1. Optimized geometry of a) 3Py-U, b) 3Py-UA, c) 3Py-AM and d) 3Py-SA complexes.

including polypyrrole as a sensor for NO_2 , CH_3OH and NH_3 . Their results revealed that polypyrrole is highly sensitive towards NO_2 , compared to methanol and ammonia. Similarly, Slater et al., [29] studied polypyrrole for the detection of different gases and vapors by measuring mass change and resistance change. This study asserted, the sensing abilities of polypyrrole is due to the combined response of physical and electric effects.

Numerous theoretical studies were also reported on sensing properties of polypyrrole. First theoretical study on the doping of polypyrrole was reported by Bredas et al. [30] at HF/STO-3G. Ullah et al. [18] theoretically studied the sensing properties of polypyrrole oligomer for ammonia at B3LYP/6-31G(d) level of theory. Rad and co-workers comparatively analyzed sensing of oligopyrrole (3Py) for SO_2 , NH_3 , H_2O , CO , CO_2 and CH_4 [31], at B3LYP/6-31 + G(d) level of theory. Our group has recently reported the response behavior of polypyrrole toward nitrate ion (NO_3^-) in both gaseous and aqueous phase [19]. Various other theoretical studies are also found in the literature [11,31–35] which reveals that polypyrrole is an excellent sensor, due to its excellent redox properties [36].

All of the above theoretical and experimental studies were limited to small gaseous neutral molecules except the recent report on nitrate ion. We become interested in gaining insight on how complex molecules of biological significance interact with polymer. These biologically important molecules have multiple sites for hydrogen bonding therefore, theoretical insight into their sensing mechanism is quite important. In this regard, literature reveal that, polypyrrole based sensors are reported for the detection of urea and uric acid. Cete et al. synthesized polypyrrole film for the detection of uric acid [37]. Mariana et al. prepared polypyrrole based electrochemical sensors for the detection of urea [38]. Despite significant advancement in the experimental sensor of urea and uric acid, no theoretical study exists on the sensing mechanism of conducting polymers towards urea and uric acid. Structurally relevant biologically active compounds such as acetamide (AM) and sulphonamide (SA) along with urea (U) and uric acid (UA) are taken for the sake of comparative study. The main objective of this study is an accurate comparison of the sensing abilities of polypyrrole with acetamide, sulphonamide, urea and uric acid. Symmetry adapted perturbation theory (SAPT0) is also applied for accurate determination

of (exchange, electrostatic, induction and dispersion) components of non-covalent interaction energy. SAPT0 calculations deliver useful information regarding the nature of interaction. Joana C and coworkers used symmetry adapted perturbation theory for accurate determination of noncovalent interaction energies for S22 test set [39]. Moreover, the change (either increase or decrease) in the conductivity of polypyrrole with the increase in the chain length are also analyzed.

2. Computational details

All calculations are performed with Gaussian 09 [40] and results are visualized via GaussView 05 [41]. Geometry optimization and interaction energy calculations are performed at M05-2X/6-31 + +G(d,p) level of theory. M05-2X is a hybrid *meta*-exchange-correlation function, well suited for the non-covalent interactions [42]. Non-covalent interactions play vital role in stabilizing macromolecules [39] hence, their accurate determination is very essential. To accurately determine the components of non-covalent interactions, SAPT0 calculations are performed using Psi4 [43]. Charge transfer (Chelpg) analysis are performed at M05-2X/6-31 + +G (d, p). Electronic properties such as energies of HOMO and LUMO, HOMO-LUMO gaps are calculated at B3LYP/6-31G(d) because of the established accuracy of B3LYP method [2]. UV-vis calculations are performed at time dependent (TD-DFT) B3LYP with 6-31G(d) basis set.

3. Results and discussion

3.1. Optimized geometries

Geometry of nPy-analyte complexes are optimized at M05-2X/6-31 + +G(d,p). Change in the optimized geometries of complexes deliver important information about the response behavior of nPy towards analytes (vide supra). An oligopyrrole has more than one pyrrole units, and all of these pyrrole rings have tendency to make hydrogen bonding with analytes. It is necessary to consider all different orientations at different interaction sites in order to find the position with most favorable interaction with analytes (high exothermicity). All such possible geometries of complexes were optimized at low level (for quick

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