



Role and impact of differently charged polypyrrole on formaldehyde sensing behavior



Pinit Ariyageadsakul^a, Viwat Vchirawongkwin^b, Chinapong Kritayakornupong^{a,*}

^a Department of Chemistry, Faculty of Science, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand

^b Department of Chemistry, Faculty of Science, Chulalongkorn University, Phayathai Road, Patumwan, Bangkok 10330, Thailand

ARTICLE INFO

Keywords:

Formaldehyde
Charged polypyrrole
Electronic and optical properties chemiresistive sensor
Optical sensor
DFT
Charged state

ABSTRACT

Structural and electronic properties of polypyrrole in neutral ($n\text{Py}$), cationic ($n\text{Py}^+$), and anionic ($n\text{Py}^-$) states exposed to formaldehyde were studied using density functional theory (DFT) and time dependent-DFT (TD-DFT) methods. The strongest adsorption energy was found for $n\text{Py}^-$ with a greater change in conductive property than other states. For optical analysis, polaron band simulated in UV-VIS-NIR spectrum of $n\text{Py}^-$ was vanished upon sensing with formaldehyde, corresponding to electron transferred from polaron state of $n\text{Py}^-$ to adsorbed molecule. In contrast, the $\pi \rightarrow$ polaron bands of $n\text{Py}^+$ complexes were all blue-shifted. With respect to human exhaled breath, interferences of carbon dioxide and humidity were studied, showing a minor contribution in terms of conductive properties. Our results revealed that negatively charged polypyrrole is a potential state of polypyrrole for formaldehyde measurement.

1. Introduction

Nowadays, human breath analysis for disease diagnosis and monitoring metabolic status has been an attractive topic for both experimental and theoretical investigations. In experiments, several techniques such as gas chromatography mass spectrometry (GCMS), ultra-performance liquid chromatography (UPLC), nuclear magnetic resonance spectroscopy (NMR), and Raman spectroscopy were utilized for monitoring volatile organic compounds (VOCs) [1–5]. However, the major drawbacks of such techniques are expensive and non-portable, stimulating the development of various measurement methods. Among VOCs, formaldehyde (CH_2O) is known as a key biomarker for breast [6], prostate, bladder [7], and lung [8] cancer diagnoses. Apart from its medical application, formaldehyde exposure also causes fatal toxicity to organisms such as dermatitis, watery eyes, pulmonary edema, asthma, and respiratory irritation [9]. Eleber et al. [6] performed breath analysis in breast cancer patients using gas chromatography (GC) equipped with frame photometric detector, expressing that level of formaldehyde in cancer patients was found in the range of 0.45–1.20 ppm, which is significantly higher than that observed from healthy persons (0.3–0.6 ppm). In addition, expired level of formaldehyde is linearly correlated to tumor size.

On the other hand, gas sensors have been an alternative and reliable technique for in situ online and remote measurement since they are compact, portable, versatile, and quick response with high sensitivity

[10–12]. Various gas sensing materials have been utilized as active layers for formaldehyde detection such as metal oxide [13–16], graphene [17–20], and conducting polymer [21–24]. Metal oxide was employed as formaldehyde sensor with high sensitivity and selectivity. However, utilization of such substrate was limited by operating at a very high temperature [13–16] due to chemical adsorption of oxygen molecules on the surface [25,26]. Sensing ability of graphene toward formaldehyde sensor was previously investigated by both experimental and theoretical studies [17–20]. The results indicated that pristine graphene possesses low sensitivity and weak binding energy to formaldehyde [17–19]. Subsequently, conducting polymer is a candidate gas sensing material for determining formaldehyde due to its high sensing ability even in room temperature [21–24].

Among conducting polymers, polypyrrole (PPy) has been extensively used in gas sensor application due to easy preparation, inexpensive, good environmental stability, and high sensitivity [27]. In addition, conductive property of polypyrrole was easily tuned via doping/dedoping chemistry. Generally, the p-type semi-conductors were widely studied in several fields of applications because of the air stables of p-type materials. The sensitivity and selectivity of PPy in reduced and p-doped forms to VOCs were investigated by experiments and theoretical calculations [12,21,28–35], indicating that PPy is a potential sensing material. In the case of formaldehyde sensing, the conductometric measurement of PPy sensor was also performed, showing that 4-ethylbenzenesulfonic acid (EBSA) doped PPy has a very

* Corresponding author.

E-mail address: chinapong.kri@kmutt.ac.th (C. Kritayakornupong).

high sensitivity by decreasing resistance about 40% after exposing to formaldehyde [21]. On the other hand, synthesis of n-doped PPy seems to be limited by experimental processes because of its low electron affinity (EA). Nevertheless, the n-type doping of PPy was studied by various theoretical investigations [36–38].

In the present work, sensing mechanisms of formaldehyde by PPy in neutral and n/p-doped states both in terms of chemiresistive and optical sensors were investigated by means of DFT and time dependent-DFT (TD-DFT) calculations. In addition, effect of interference gases in human exhaled breath i.e. carbon dioxide and humidity was also determined in order to ensure the ability of PPy applied as sensor for detecting formaldehyde in human breath. According to our calculation, formaldehyde revealed strongest interaction to negatively charged PPy in comparison with neutral and positive states. The polaron band in UV–vis-NIR of n-type PPy was clearly disappeared, while p-type PPy produced the blue-shifted peak upon formaldehyde sensing. Our results firstly demonstrated that the PPy^- is a potential material for detecting formaldehyde.

2. Computational methods

In this study, polypyrrole in neutral ($n\text{Py}$; n is number of oligomer with $n = 3, 5, 7,$ and 9), cationic ($n\text{Py}^+$), and anionic ($n\text{Py}^-$) states sensing with formaldehyde were examined using DFT calculations. The charge of $n\text{Py}$ was set to 0 with singlet state, while charges of +1 and –1 with doublet state were applied for cationic $n\text{Py}^+$ and anionic $n\text{Py}^-$ states, respectively. With respected to a very low concentration of formaldehyde in the human breath, only single molecule of formaldehyde adsorbed on oligopyrrole was investigated in this study. It is noted that structural and electronic properties such as interaction energy, HOMO, LUMO, and excitation energy of $n\text{Py}$ sensing with multiple NH_3 molecules are similar to those obtained from single molecule [34]. The N–H site of oligopyrrole was considered as binding site for C=O group of formaldehyde according to the FTIR measurement [28]. In addition, binding energies and sensitivities of oligopyrrole to H_2O and CO_2 were also investigated to elucidate selectivity of formaldehyde with breath exhaled gases.

In conductive polymer systems, various functionals based on DFT method have been used to determine structural and electronic properties [39–42]. The quality of the DFT results for conjugated polymers in comparison with experimental data is reported in the sequence; $\text{HF} < \text{BH} \& \text{H} < \text{B3LYP} \sim \text{BLYP}$, whereas choice of basis set is negligible [39]. According to previous work, band gap of polypyrrole obtained from the B3LYP exchange-correlation functional in conjunction with 6–31G(d) basis set was accurately examined by extrapolating HOMO-LUMO gap of oligopyrrole with $1/n$ with second order polynomial formula [43]. In addition, the B3LYP/6-31G(d) level of theory was also successfully applied to describe sensing mechanism, sensitivity, and selectivity of PPy to several gases [34,35]. However, due to lack of dispersion corrected parameters the B3LYP functional usually provides the underestimated binding energy. To address such issue, the asymptotical behaviour of long-range corrected (LC) functional is strongly required for determining non-covalent interaction [44–47]. The LC version of B3LYP with coulomb-attenuated method (CAM-B3LYP) was utilized, exhibiting better description of interaction energy for non-covalent interaction systems [46,47], whereas overestimated values of HOMO and LUMO energies, HOMO-LUMO gaps, and excitation energies for conductive polymer systems were pronounced [48]. To ensure the correct description of interaction energies in our systems, several test calculations were performed using CAM-B3LYP with various basis sets including 6–31G(d), 6–31 + G(d), and 6–31 + G(d,p) for single point calculations of the optimized $n\text{Py}\text{-CH}_2\text{O}$, $n\text{Py}^+\text{-CH}_2\text{O}$, and $n\text{Py}^-\text{-CH}_2\text{O}$ structures by the B3LYP/6-31G(d) method, while benchmark interaction energies were evaluated from the CCSD level of theory (see Table 1). From the CCSD results, underestimated interaction energies were observed for the case of 6–31G(d) basis as compared to the 6–31 + G(d) and 6–31 + G(d,p) results, indicating that the diffuse function plays a crucial role for evaluating the interaction energy between formaldehyde and polypyrrole. As shown in Table 1, the interaction energy with the

Table 1

Single point interaction energies (in kcal/mol) obtained from B3LYP, CAM-B3LYP, and CCSD methods in conjunction with 6–31G(d), 6–31 + G(d), and 6–31 + G(d,p) basis sets.

Complexes	$3\text{Py}\text{-CH}_2\text{O}^a$		$3\text{Py}^+\text{-CH}_2\text{O}^a$		$3\text{Py}^-\text{-CH}_2\text{O}^a$	
	ΔE	ΔE_{CP}	ΔE	ΔE_{CP}	ΔE	ΔE_{CP}
B3LYP/6-31G(d)	–6.78	–3.91	–13.10	–10.18	–32.38	–24.80
B3LYP/6–31 + G(d)	–4.50	–3.88	–10.75	–10.19	–28.22	–26.45
B3LYP/6–31 + G(d,p)	–4.56	–4.00	–10.80	–10.31	–30.09	–28.61
CAM–B3LYP/ 6–31G(d)	–8.16	–5.21	–14.79	–11.76	–38.44	–30.80
CAM–B3LYP/ 6–31 + G(d)	–5.85	–5.24	–12.36	–11.82	–34.24	–32.49
CAM–B3LYP/ 6–31 + G(d,p)	–5.91	–5.36	–12.42	–11.94	–36.13	–34.68
CCSD/6–31G(d)	–7.71	–4.26	–14.56	–11.09	–40.14	–30.03
CCSD/6–31 + G(d)	–7.24	–4.66	–13.56	–11.41	–36.37	–30.17
CCSD/6–31 + G(d,p)	–7.11	–4.74	–13.37	–11.44	–37.77	–31.37

^a All structures were optimized from the B3LYP/6-31G(d) level of theory.

additional polarization function for all hydrogen atoms calculated by the CCSD/6–31 + G(d,p) method is negligibly increased. The benchmark interaction energy (with BSSE correction) of 3Py complex obtained from CCSD/6–31 + G(d,p)//B3LYP/6-31G(d) is –7.11 (–4.74) kcal/mol, while the corresponding values of –13.37 (–11.44) and –37.77 (–31.37) kcal/mol were delivered from 3Py^+ and 3Py^- complexes, respectively. As expected, the B3LYP method results the underestimated interaction of –4.56 (–4.00), –10.80 (–10.31), and –30.09 (–28.61) kcal/mol for 3Py , 3Py^+ , and 3Py^- complexes, respectively. With the inclusion of long-range corrected functional, the CAM-B3LYP/6–31 + G(d,p) method presents the corresponding values of –5.91 (–5.36), –12.42 (–11.94), and –36.13 (–34.68) kcal/mol for $3\text{Py}\text{-CH}_2\text{O}$, $3\text{Py}^+\text{-CH}_2\text{O}$ and $3\text{Py}^-\text{-CH}_2\text{O}$, respectively, which are in good agreement with the CCSD results. According to the methodical test, the geometrical and electronic properties of $n\text{Py}$, $n\text{Py}^+$, and $n\text{Py}^-$ interacting with CH_2O , CO_2 , and H_2O were evaluated using the B3LYP/6-31G(d) method, while the long-range corrected CAM-B3LYP functional in conjunction with 6–31 + G(d,p) was chosen to determine interaction energies in this work. All optimized geometries were verified their true minima by harmonic vibrational frequency analysis (no imaginary frequencies). Basis set superposition error (BSSE) correction is a minimal requirement for weak interaction systems, thus all interaction energies (ΔE ; Eq. (1)) obtained from $n\text{Py}$, $n\text{Py}^+$, and $n\text{Py}^-$ complexes were corrected by counterpoise method (ΔE_{CP} ; Eq. (2)).

$$\Delta E = E_{\text{complex}} - E_{n\text{Py}} - E_{\text{analyte}} \quad (1)$$

$$\Delta E_{\text{CP}} = \Delta E - \Delta E_{\text{BSSE}} \quad (2)$$

Sensing ability of neutral, cationic, and anionic oligopyrrole to CH_2O , CO_2 and H_2O was described by changing in electronic properties such as HOMO, LUMO, HOMO-LUMO gaps (E_g), ionization potentials (IP), electron affinities (EA), density of states (DOS), and UV–vis spectra. IP and EA of all optimized structures were approximated with respected to Koopmans’ theorem where IP equals to negative HOMO, and EA equals to negative LUMO. It is noted that qualitative trend analysis of IP and EA are obtained from such approximation with a deviate value about 1 eV [49]. Conductivity of oligopyrrole upon interacting with analyte was represented by change of HOMO-LUMO gap, which can estimate % sensitivity (%S) as Eq. (3).

$$\%S = \left(\frac{E_{g2} - E_{g1}}{E_{g1}} \right) \times 100 \quad (3)$$

Where E_{g1} and E_{g2} correspond to the HOMO-LUMO gap of oligopyrrole before and after sensing with analytes, respectively. On the other hand, sensing ability of $n\text{Py}$, $n\text{Py}^+$, and $n\text{Py}^-$ based optical sensor was examined from the shifts in absorption bands of UV–vis and UV–vis-NIR spectra

Download English Version:

<https://daneshyari.com/en/article/5435385>

Download Persian Version:

<https://daneshyari.com/article/5435385>

[Daneshyari.com](https://daneshyari.com)