RESEARCH PAPER

Effect of oxygen heteroatom on sensor-cyanide anions binding

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Abstract: The study aims to analyze the effect of heteroatom replacement on benzimidazole derivative chemosensor compounds on the ability to form hydrogen bonds with anions. In this case, the N heteroatom in the benzimidazole derivative sensor compound (S1) is replaced with the O heteroatom to become a benzoxazole derivative sensor compound (S3). Calculating the energy of the molecules involved in the electron level gives the following results: replacing heteroatoms with more electronegative atoms increases the HOMO energy of the sensor molecules, making the sensor more reactive to anions and strengthening the binding of the sensor with cyanide anions.

Keywords: oxygen, heteroatom, anions binding, sensor

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INTRODUCTION

Research on the design and development of an artificial molecular sensor for the recognition and sensing of anion is currently attracting much interest because anion plays numerous fundamental roles in chemical and biological processes [1]. Using chemosensor compounds provides various advantages because they have high sensitivity and are easy to use [2].

The cyanide anion is one of the most rapidly acting and powerful poisons [3]. It is an extremely toxic anion and can directly lead to the death of human beings in several minutes. The cyanide anion can be recognized either by H-bonding or by the deprotonation of proton in the receptor in an organic solvent [4].

In the previous study, we designed a chemosensor compound derived from benzimidazole (**S1**) [5] and benzoxazole (S3) [6], which are active as a receptor to detect a cyanide anion. The **S₁** is a simpler sensor with an imidazole ring containing nitrogen heteroatom, which could detect cyanide anions with the value of k_{bind} is 2.5 ($\pm$0.26) x 10^6 M^{-1}. Meanwhile, the **S3** is a simple sensor with an oxazole ring containing an oxygen heteroatom, making a complex host-guest interaction with cyanide anion through hydrogen bonding. Its detected cyanide anions with a value of k_{bind} are 2.6 × 10^7 M^{-1}.
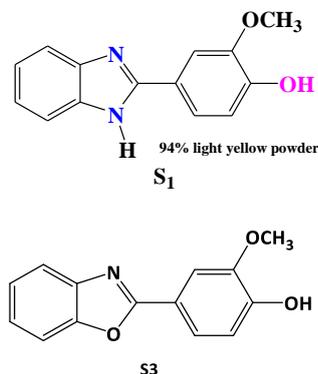
Figure 1. The molecular structure of compounds S1 and S3 with different heteroatoms.

The replacement of heteroatoms resulted in a change in the binding strength between the S1 and S3 sensors (Figure 1.). The substitution also affects the interaction of the sensor and the cyanide anion. A lot of theoretical studies using calculations and computational chemistry have been done to study the interaction of sensor compounds and anions. One of the benefits of computational chemistry is that it can visualize the structure of compound sensors and their interactions with anions [7]. One method widely used in calculating the theoretical sensor-anion interaction is the density function theory (density functional theory, DFT). The DFT method is often

used to predict sensor interactions with anions because it can provide good calculation results, including interactions such as hydrogen bonds or van der Waals [8]. In this study, we will discuss the theoretical strength of how the sensor interacts with cyanide anions based on the state of the molecule in its orbital due to the replacement of heteroatoms

MATERIALS AND METHODS

Fluorescent spectra were measured using a Spectro Fluorophotometer Shimadzu RF-6000. Optimization of the structure of S1 and S3 was carried out using the DFT method at the theoretical level at B3LYP/6-31G(d). All

geometric calculations were performed using Gaussian 09 [9]. The effect of the solvent was measured using a continuum solvation model approach. The dielectric constant in the solution follows the Gaussian 09 default.

RESULTS AND DISCUSSION

Figure 2 shows that before the addition of the cyanide anion, max shifted to the right from λ 291 nm (E_{ex} 4.3882 eV/S1) to λ 320 nm (E_{ex} 3.5485 eV/S3) due to heteroatom substitution (N in S1 was replaced by O in S3).
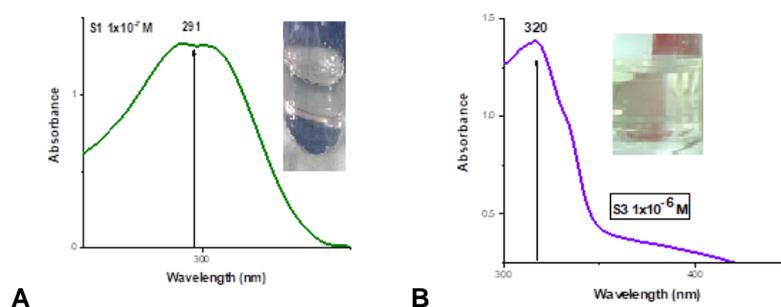
Figure 2. Absorbance Wavelength shifted from 291 nm (S1)/A to 320 nm (S3)/B

After the addition of cyanide ion, S1 did not respond in the UV region, so the absorbance wavelength did not change, while S3 sensors responded by increasing the color strength to brown at λ_{max} 375 nm (E_{ex} 3.2668 eV). Fluorescence measurements showed S1 sensor emitted at λ 358 nm. The addition of cyanide ions causes the emission to shift to 440, experiencing a redshift with a stroke shift of 52. Meanwhile, the S3 sensor, which undergoes emission at 360 nm in the presence of cyanide ion emission, undergoes a redshift to 425 nm so that there is a stroke shift of 65.

After the addition of cyanide ion, S1 did not respond in the UV region, so the absorbance wavelength did not change, while S3 sensors responded by increasing the color strength to brown at λ_{max} 375 nm (E_{ex} 3.2668 eV). Fluorescence measurements showed S1 sensor emitted at λ 358 nm. The addition of cyanide ions causes the emission to shift to 440, experiencing a redshift with a stroke shift of 52 (Figure 3 and 4). Meanwhile, the S3 sensor, which undergoes emission at 360 nm in the presence of cyanide ion emission, undergoes a redshift to 425 nm so that there is a stroke shift of 65.
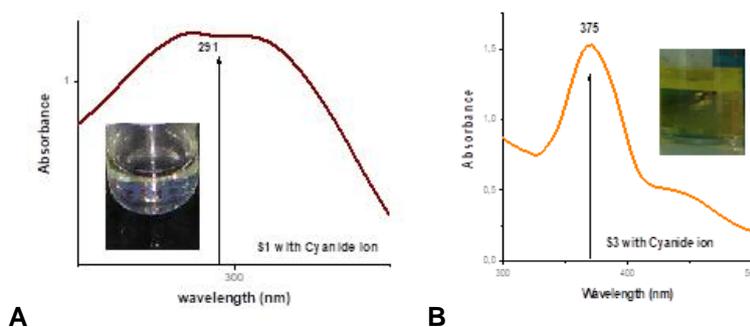
Figure 3. After the cyanide ion was added, Absorbance Wavelength shifted from 291 nm (S1) to 375 nm (S3)
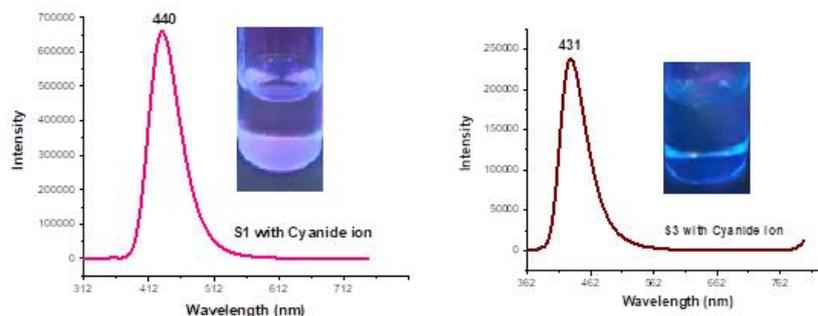
Figure 4. λ_{max} of S1 and S3 after cyanide ions added

The shift in absorbance and emission due to the addition of cyanide anions indicates that S3 interaction with CN⁻ ions has formed hydrogen bonds [10], and the replacement of heteroatoms resulted in wider absorption (redshift occurs). It happens because the replacement of heteroatoms can affect the HOMO energy, which determines the reactivity of a molecule in the bond formation process. The higher the HOMO energy of a molecule, the smaller the ionization potential, so electrons are easily released and can form bonds.

We performed density functional analysis using the Gaussian 09 with B3LYP/6-31G(d) to investigate the nature of the sensing mechanism between S1/S3 and cyanide anions. For the S1 sensor, in free receptors and their receptor cyanide complexes, the lowest unoccupied molecular orbital (LUMO) is 1.433 eV, and the highest occupied molecular orbital (HOMO) (5.8562 eV); meanwhile, the S3 sensor, LUMO is 2.4915 eV, and HOMO is 5.8028 eV. The bandgap of the optimized structure in the gas phase for the S1 sensor is 4.42 eV and 3.31 eV for the S3 sensor. The presence of anion induction at the receptor in the solution phase reduces the bandgap from 4.42 eV to 3.46 eV for the S1 sensor and from 3.31 eV to 2.85 eV for the S3 sensor. It gives a redshift band in the observed UV-VIS spectrum. The redshift shape change indicates that the anion is bound to the receptor [11].

The energy level states of the two sensor molecules show that after the replacement of the heteroatom from the N atom (in the S1 sensor) to the O atom (in the S3 sensor), the HOMO energy of the sensor increases by 0.0534 eV, this causes the ionization potential in S3 to be smaller, so electrons are more easily released. It is easier to form hydrogen bonds with cyanide anions. It is because the electronegativity of the O atom is greater than that of the N atom. After all, a larger electronegativity value indicates that the molecule is more difficult to reach equilibrium, so the molecule becomes more reactive [12]. The replacement of the heteroatoms also results in a lower bandgap on the S3 sensor than S1 because the lower the HOMO-LUMO energy difference possessed by a molecule, the easier it will be for an electron to be excited [13-15].

CONCLUSION

The replacement of the N heteroatom (on the S1 sensor) with a more electronegative O atom (in the S3 sensor) increases the LUMO energy of the sensor molecule, thereby increasing the reactivity of the sensor in forming hydrogen bonds with cyanide anions.

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