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# Copper(II) ion-sensing mechanism of oligo-phenylene vinylene derivatives: syntheses and theoretical calculations

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# ABSTRACT

Oligo-phenylene vinylene (oligo-PV) with two picolinamide side-groups and six methoxy end-groups was synthesized in order to be a fluorescent sensing molecule. Various metal ion solutions  $(1.5 \times 10^{-4} \text{ M})$  were added to the  $1.5 \times 10^{-6}$  M acetonitrile solution of the fluorescent molecule. The fluorescent emission spectra showed that, at about the same concentration  $(1.5 \times 10^{-4} \text{ M})$ , only Cu(II) ion can quench the fluorescent emission of the picolinamide-PV solution. Possible metal ion-sensing mechanisms could be either the binding at picolinamide side-groups or methoxy end-groups, or interchain-stacking driven by the metal ions. Hence, oligo-PVs with six methoxy end-groups but without substituted side-groups, and another oligo-PV with six methoxy end-groups and two ethoxy side-groups were synthesized for comparison. These molecules turned out to be inactive to any metal ion solutions. Moreover, quantum calculation was used to confirm the result. Binding energy and conformation were calculated and simulated. It could be concluded that nitrogen and oxygen atoms of the picolinamide group and one oxygen atom from the methoxy group are involved in the metal ion-binding process.

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# 1. Introduction

The detection of metal ions has been developed through many processes. Although there were reports on many practical methods for detecting heavy metal ions,<sup>1–4</sup> researchers are still looking for more precise, sensitive and selective protocols. One of the popular methods is a fluorescence technique due to its great sensitivity. The general molecular composition of fluorescent sensing molecules includes reporting fluorophores and metal ion-binding units. When appropriate metal ions bind to the fluorescent molecules, the fluorescent emission of the system is changed. The fluorescent sensing processes can be categorized into turn-on and turn-off. The term 'turn-on' is used when the fluorescent emission intensity of the system is enhanced by the metal ions;<sup>5–8</sup> and 'turn-off' when the fluorescent emission intensity is quenched by the metal ions.<sup>9</sup> In some cases, more than one type of fluorophore can be presented in the systems. This strategy employs fluorescence resonance energy transfer (FRET) between fluorophores as a sensing mechanism. A typical event is the disturbance of the FRET process by certain analytes resulting in changes of the fluorescent emission. The changes due to the FRET process could be either the emission intensity or the shift of emission wavelength. Another example of fluorescent sensing is the formation of excimer in the excited state, which results in excimer fluorescent emission.<sup>10,11</sup> In this case, the presence of metal ions resulted in a decrease of excimer fluorescent emission and an increase of monomer fluorescent emission.

Typical light-emitting materials are conjugated polymers, for examples, poly(phenylene ethynylenes) (PPEs), poly(*para*-phenylene vinylenes) (PPVs) and poly(thiophene). PPEs have been extensively used in many applications, such as sensing molecules. The structures have been modified by attaching water-soluble unit, so they can be utilized as biosensors. There have been reports on preparing PPE derivatives as sensor arrays for detecting biological substances, such as cancerous cells and proteins.<sup>12,13</sup> PPE was also designed as a cruciform shape in order to meet varieties of applications. Cross-shaped PPEs have been reported to be fabricated as a metal-sensing system<sup>14</sup> and metal sensor arrays.<sup>15–17</sup>

Phenylene vinylene (PV) is another common conjugated organic molecule well known as a light-emitting unit. The synthesis of PV is quite straightforward so there have been many reported methods for modifying the structures as desired.<sup>18</sup> PVs have been used in many applications, such as organic light-emitting diode (OLED),<sup>19–21</sup> organic field-effect transistor (OFET)<sup>22</sup> and fluorescent imaging.<sup>23</sup> In this article, oligo-*para*-phenylene vinylene derivatives with six methoxy end-groups were synthesized for use as fluorescent sensing molecules. Picolinamide units were laterally attached to the PV core unit of the first derivative in order to be metal-binding sites. Oligo-PV with two ethoxy side-groups and





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another oligo-PV without functional group were synthesized for comparison. It was hypothesized that these two molecules cannot interact with metal ions since they did not contain metal-binding site.

Quantum chemical calculations were performed using Gaussian03<sup>24</sup> program in order to gain insight into the structural electronic properties of the sensing molecule.<sup>25</sup> The 3D free and metalbound molecules were analysed and reported.

# 2. Results and discussion

# 2.1. Synthesis and experiments

A fluorescent metal ion-sensing molecule was designed by using oligo-phenylene vinylene as a fluorescent-reporting unit. Six methoxy groups were attached as end groups to help improve the solubility. Two picolinamide units were incorporated to both sides of the PV unit as metal-binding sites (Fig. 1). A typical reaction for generating the main phenylene vinylene unit was Heck cross-coupling reaction with palladium diacetate as a catalyst. The picolinamide-functionalized phenylene vinylene (I) was soluble in common organic solvents, such as acetonitrile and methanol. Absorption and fluorescent emission spectra of the molecule in acetonitrile were shown in Fig. 2. The molecule emitted light in the blue region,  $\lambda_{em(max)}$ =440 nm. The quantum efficiency ( $\phi$ ) was measured to be 0.18 in methanol with quinine bisulfate in 0.1 M sulfuric acid as a reference.



Fig. 1. Picolinamide-functionalized phenylene vinylene (I).



Fig. 2. Absorption and emission spectra of picolinamide-PV (I) in acetonitrile.

The metal ion-sensing experiments were performed in acetonitrile to ensure the solubility of the picolinamide-PV and metal ions.  $1.5 \times 10^{-6}$  M solution of the picolinamide-PV was mixed with various metal ion solutions ( $1.5 \times 10^{-4}$  M), one at a time, at a volume ratio of 1:1. In this experiment 1 mL of the picolinamide-PV solution and 1 mL of the metal ion solution were mixed together, so the final concentration of the picolinamide-PV was  $7.5 \times 10^{-7}$  M and the concentration of the metal ion was  $7.5 \times 10^{-5}$  M. The fluorescent emission intensities (Fig. 3) with fluorescent emission spectra (in set—Fig. 3) showed that only Ni(II) and Cu(II) ions can obviously



Fig. 3. Responses of picolinamide-PV (I) towards metal ions.

quench the fluorescent emission intensity of the picolinamide-PV. It could be roughly explained that either the excited state interaction between the metal ions and the picolinamide units or other sites on the main phenylene vinylene chain caused the fluorescent quenching.

A straightforward strategy to determine if the side-chain picolinamide units involved in the metal-binding process was to synthesize another oligo-phenylene vinylene (II) for comparison. This molecule had the same core unit and methoxy end-groups as in the picolinamide-PV but contained no side-unit (Fig. 4). Compound II also emitted light in blue region ( $\lambda_{em(max)}$ =447 nm) with a quantum efficiency ( $\phi$ ) of 0.6 in acetonitrile. The absorption and emission spectra of the molecule in acetonitrile were shown in Fig. 5.



Fig. 4. Oligo-phenylene vinylene II.



Fig. 5. Absorption and emission spectra of oligo-PV II in acetonitrile.

A  $1.5 \times 10^{-6}$  M solution of oligo-PV II was also combined with the same group of metal ion solutions ( $1.5 \times 10^{-4}$  M) used in the experiment of picolinamide-PV to test the metal-sensing property, at the same volume ratio of 1:1. In each sample, solution of oligo-PV II (1 mL) was combined with metal ion solution (1 mL) and the fluorescent emission spectrum was measured. It was shown in

Fig. 6 that the fluorescent emission of oligo-PV **II** cannot be obviously quenched by any metal ions used in this experiment. The emission intensity scarcely dropped from the initial point, which could possibly rise from a weak interaction between the metal ion and the electron cloud on the main phenylene vinylene chain, or the lone pair electrons of the methoxy groups.



Fig. 6. Responses of II towards metal ions.

Moreover, another oligo-PV containing two ethoxy side-groups and six methoxy end-groups (III) was also synthesized as a comparison (Fig. 7). This was to prove that the oxygen atoms of the ethoxy side-groups did not involve in the metal-binding phenomenon, and picolinamide units really played an important role in the Cu(II)-binding process. This molecule emitted light in blue region  $(\lambda_{em(max)}=446 \text{ nm})$  with a quantum efficiency ( $\phi$ ) of 0.7 in acetonitrile. The absorption and emission spectra of the molecule in acetonitrile were shown in Fig. 8.



Fig. 7. Ethoxy-phenylene vinylene (III).



Fig. 8. Absorption and emission spectra of ethoxy-phenylene vinylene (III) in acetonitrile.

The metal-sensing experiments were done at the same protocol as the other two PV molecules. The solution of ethoxy-PV ( $1.5 \times 10^{-6}$  M) was prepared in acetonitrile and mixed with each metal ion solution ( $1.5 \times 10^{-4}$  M) at 1:1 ratio.

From the results in Fig. 9, the fluorescent quenching by metal ions can be divided into two groups. The first group described the metal ions those did not quench or scarcely quenched the emission intensity of the ethoxy-PV, which included Cd(II), Cu(I), Co(II), Mn (II) and Zn(II). The other group was the metals those can somewhat quench the emission intensity of the ethoxy-PV, which were Cu(II), Ni(II) and Pb(II). However, when compared these results with the picolinamide-PV experiments, it can be concluded that this ethoxy-PV did not interact very well with all the metal ions used in the experiments.



Fig. 9. Responses of III towards metal ions.

The results confirmed the hypothesis that the two oxygen atoms of the ethoxy side-groups were not the dominant sites for the metal-binding process.

From the experiments on the three phenylene vinylene derivatives, it can be interpreted that the phenylene vinylene main chain cannot show a practical metal-sensing property without the picolinamide side-groups. In order to confirm the crucial role of the picolinamide side-groups, theoretical calculations have been introduced in the next section.

# 2.2. Theoretical calculation

2.2.1. Free molecule. The HOMO and LUMO orbitals of the picolinamide-PV sensing molecule are provided in Fig. 10 and Table 1. The obtained HOMO and LUMO levels were mainly localized on the HOMO $\rightarrow$ LUMO transition of the fluorescent molecule with an oscillator strength of 1.7146, and HOMO-2→LUMO, HOMO- $1 \rightarrow$  LUMO with an oscillator strength of 0.1932; whereas the LUMO+4 spread out over the picolinamide moiety. In addition, the sensing molecule was divided into two parts, the fluorophore (phenylene vinylene skeleton) and the receptor (picolinamide moiety), in the calculations for a better understanding of the fluorescent mechanisms. The HOMO and LUMO orbitals of the fluorophore are illustrated as localized electrons on the skeleton as shown in Fig. 11, and the calculated molecular orbitals are shown in Table 2. The HOMO and LUMO orbitals of the receptor moiety are provided in Fig. 12 and Table 3. The majority of electrons were located within the picolinamide moiety but some electrons of the HOMO orbital were confined between the linker and the picolinamide unit.

*2.2.2.* Cu(II)-bound molecule. The sensing molecule was expected to bind divalent or trivalent metal ions where the picolinamide



Fig. 10. Molecular orbitals (MOs) of the picolinamide-PV (I).

#### Table 1

Calculated excitation energy, oscillator strengths and molecular orbitals (MOs) involved in the excitation of the picolinamide-PV (I), using B3LYP/6-311G(d)

Energy (eV)	$\lambda_{abs} (nm)$	Oscillator strength	MOs
2.7699 3.4729	447.62 357.00	1.7146 0.1932	HOMO→LUMO (99%) HOMO-2→LUMO (27%) HOMO-1→LUMO (68%)



Fig. 11. Molecular orbitals (MOs) of molecule II.

#### Table 2

Calculated excitation energy, oscillator strengths and molecular orbitals (MOs) involved in the excitation of molecule **II**, using B3LYP/6-311G(d)

Energy (eV)	$\lambda_{abs} (nm)$	Oscillator strength	MOs
2.984	415.49	2.1342	HOMO→LUMO (85%)

Table 3	
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Calculated excitation energy, oscillator strengths and molecular orbitals (MOs) involved in the excitation of the picolinamide moiety, using B3LYP/6-311G(d)

Energy (eV)	$\lambda_{abs} (nm)$	Oscillator strength	MOs
4.9533	250.30	0.0831	HOMO-3→LUMO (19%) HOMO-1→LUMO (12%) HOMO→LUMO (51%)

units were proposed as recognition sites that bind to the ions. When the binding occurred, the HOMO and LUMO levels of the picolinamide-PV changed and a fluorescent process was altered. Theoretical calculation with fully optimized structure of Cu(II)-bound picolinamide-PV suggested that the nitrogen atom of the picolinamide unit and one oxygen atom of a methoxy group involved in the metal-binding process. The geometry-optimized structure, selected bond distances and selected atomic charges were shown in Fig. 13. The computed binding energy (*BE*) of bound state was -6.65 eV as defined by

BE(eV) = E(bound state) - [E(unbound state) + E(metal ion)]

where E(bound state) is the energy of Cu(II)-bound picolinamide-PV; and E(unbound state) and E(metal ion) are the energies of picolinamide-PV and Cu(II) ion, respectively.

The perturbation of electrons in the HOMO and LUMO of the Cu(II)-bound picolinamide-PV was shown in Fig. 14. In the unbound state, all its electron pairs presented as a closed shell, whereas in the bound state, the complex became an open shell in which  $\alpha$  and



Fig. 12. Molecular orbitals (MOs) of the picolinamide moiety.



Fig. 13. Geometry-optimized structure, selected bond distances and selected atomic charges of Cu(II)-bound molecule.



Fig. 14. Molecular orbitals (MOs) of the Cu(II) bound sensing molecule.

β electrons were investigated. The energies of the HOMO and LUMO of the free molecule, and the metal-bound molecule were calculated and compared. The excited state of the Cu(II)-bound sensing molecule composed of the transitions from HOMO(α)→LUMO(α), HOMO(β)→LUMO(β) and HOMO-2(β)→LUMO(β) with an oscillation strength of 0.3757 (Table 4). The transitions of HOMO(α)→LUMO(α) and HOMO(β)→LUMO(β) were considered to be charge-transfer processes within the fluorophore skeleton, whereas HOMO-2(β)→LUMO(β) was a charge-transfer process from the metal-binding site to the phenylene vinylene skeleton. This process suggested that the fluorescent efficiency of the molecule will be reduced.

Table 4

Calculated excitation energy, oscillator strengths and molecular orbitals (MOs) involved in the excitation of the Cu(II)-bound PV, using B3LYP/6-311G(d)

Energy (eV)	$\lambda_{abs}$ (nm)	Oscillator strength	MOs
1.0537	1176.65	0.3757	HOMO(β)→LUMO(β) (91%) HOMO(α)→LUMO(α) (5%) HOMO-2(β)→LUMO(β) (4%)

# 3. Conclusion

Picolinamide-PV (I) was synthesized as a metal ion-capturing molecule. The molecule contained phenylene vinylene core as a fluorescent-reporting unit and methoxy groups as solubilizing groups. Picolinamide moieties were attached in order to interact with metal ions. The molecule was tested to be specifically quenched by Cu(II) ion in solution. The crucial role of picolinamide groups was confirmed by using oligo-PV **II** and oligo-PV **III** as comparisons. Moreover, theoretical calculations suggested that the nitrogen atom at the picolinamide moiety and one oxygen atom of a methoxy group were involved in the metal-binding process. In the Cu(II)-bound state, the fluorescent signal of the compound was predicted to be quenched by a charge-transfer process from the metal-binding site to the phenylene vinylene main chain [HOMO- $2(\beta) \rightarrow \text{LUMO}(\beta)$ ].

## 4. Experimental

#### 4.1. General

All chemicals were purchased and used as received. Solvents for syntheses were anhydrous reagent grade. The synthesis of amino-functionalized phenylene vinylene (amino-PV) was previously reported elsewhere.<sup>26</sup> UV–vis spectra and fluorescent emission spectra were recorded by Perkin–Elmer Lambda 650 and Perkin–Elmer LS 55 spectrometers, respectively. <sup>1</sup>H NMR spectra were obtained using Bruker 500 MHz spectrometer.

### 4.2. Synthesis of picolinamide-PV (I) (Scheme 1)

In a dry flask, picolinic acid (0.96 mmol, 0.118 g) and triphenylphosphine (1.44 mmol, 0.378 g) were dissolved in dichloromethane (2 mL) at 0 °C. A solution of carbon tetrabromide (1.44 mmol, 0.378 g) in dichloromethane was slowly added to the reaction mixture. The mixture was allowed to warm up to room temperature and stirred for 30 min. Next, triethylamine (2.88 mmol, 0.4 mL) and amino-PV (0.1 mmol, 0.058 g) were added subsequently. The mixture was stirred at room temperature for 30 min, washed with solutions of 10% HCl, CaHCO<sub>3</sub> and water and dried over anhydrous MgSO<sub>4</sub>. After evaporation, the residue was purified by column chromatography (silica, hexanes/ethyl acetate, 1:1) to give yellow powder of picolinamide-PV (0.0298 g, 34%).



Scheme 1. Synthetic route of picolinamide-PV (I).

<sup>1</sup>H NMR (500 MHz CDCl<sub>3</sub>): δ 3.86 (s, 18H), 3.95 (m, 4H), 4.26 (m, 4H), 6.76 (s, 4H), 7.04 (d, 2H, *J*=16.5 Hz), 7.13 (s, 2H), 7.36 (m, 4H), 7.81 (t, 2H, *J*=7.5 Hz), 8.15 (d, 2H, *J*=7.5 Hz), 8.35 (d, 2H, *J*=3.6 Hz), 8.54 (m, 2H); LRMS (NaFormate):  $[M+H]^+$ , found 791.33. UV–vis (methanol,  $\lambda_{max}$ ): 388 nm. Photoluminescence (methanol,  $\lambda_{ex}$ =380 nm):  $\lambda$ =440 nm (max), 466 nm (shoulder).

# 4.3. Synthesis of oligo-PV II (Scheme 2)

Into a dry flask under a nitrogen atmosphere, 1,2,3-trimethoxy-5-vinylbenzene (1 mmol, 0.19 g), 1,4-diiodobenzene (0.5 mmol, 0.16 g), tri(*o*-tolyl)phosphine (0.24 mmol, 0.073 g) and palladium diacetate (0.018 mmol, 0.0039 g) were charged. Anhydrous dimethylformamide (6 mL) was added as a solvent. Triethylamine (2.51 mmol, 0.35 mL) was added when the temperature has reached 80 °C. The reaction mixture was then stirred at 100 °C for 3 days. The reaction was allowed to cool, and then evaporated to give crude product. After purification by column chromatography (silica, hexanes/ethyl acetate, 1:1), the product was obtained as brown solid (0.15 g, 66%).



Scheme 2. Synthetic route of oligo-PV II.

<sup>1</sup>H NMR (500 MHz CDCl<sub>3</sub>):  $\delta$  3.86 (s, 6H), 3.91 (s, 12H), 6.73 (s, 4H), 7.01–7.03 (dd, 4H), 7.49 (s, 4H); LRMS (NaFormate): [M+H]<sup>+</sup>, found 463.21. UV–vis (acetonitrile,  $\lambda_{max}$ ): 368 nm. Photoluminescence (acetonitrile,  $\lambda_{ex}$ =365 nm):  $\lambda$ =448 nm (max), 478 nm (shoulder).

#### 4.4. Synthesis of ethoxy-PV (III) (Scheme 3)

1,4-Diethoxybenzene (**A**): In a dry flask, a solution of hydroquinone (6.00 mmol, 0.661 g) and bromoethane (14.4 mmol, 1.57 g) in 60 mL of DMF was stirred and heated to 90 °C. A powder of  $K_2CO_3$  (14.4 mmol, 1.99 g) was slowly added into the reaction mixture. After that, the solution was stirred at 90 °C overnight. The resulting mixture was allowed to cool and then cold water was added. The resulting brown precipitate was collected by filtration. The product was collected and dried to give light brown crystals (0.318 g, 32%).



Scheme 3. Synthetic route of ethoxy-PV III.

1,4-Diethoxy-2,5-diiodobenzene (**B**): 1,4-Diethoxybenzene (0.29 mmol, 1.75 g) was added into a flask followed by water (0.29 mL), glacial acetic acid (8.75 mL) and sulfuric acid (96%) (0.12 mL). The mixture was stirred, then potassium iodate (0.88 mmol, 0.187 g) and iodine (resublimed) (2.1 mmol, 0.533 g) were added. The reaction was stirred and heated to reflux for 18 h. Next, the reaction was allowed to cool and ice water (5 mL) was added. The precipitate was collected by filtration and dried. The crude product was redissolved in chloroform and washed with a solution of Na<sub>2</sub>O<sub>3</sub>S<sub>2</sub>. Afterwards, the organic layer was separated and dried to give product as brown oil (0.716 g, 98%).

*Compound* **III**: Into a dry flask under a nitrogen atmosphere, 3,4,5-trimethoxystyrene (2.00 mmol, 0.39 g), 1,4-diethoxy-2,5-diiodobenzene (1.00 mmol, 0.39 g), tri(*o*-tolyl)phosphine (0.48 mmol, 0.15 g) and palladium diacetate (0.035 mmol, 0.0078 g) were added. Anhydrous dimethylformamide (12.5 mL) was added as a solvent. Triethylamine (5.02 mmol, 0.7 mL) was added when the temperature has reached 80 °C. The reaction mixture was then stirred at 100 °C for 2 days. The reaction was allowed to cool, and then poured into water. The precipitate was collected by filtration and further purified by column chromatography to yield a yellow powder (0.069 g, 7%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.42 (m, 6H), 3.87 (s, 6H), 3.92 (s, 12H), 4.17 (m, 4H), 6.85 (s, 4H), 6.97 (d, 2H, *J*=16.0 Hz), 7.02 (s, 2H), 7.38 (d, 2H, *J*=16.0 Hz). UV–vis (acetonitrile,  $\lambda_{max}$ ): 390 nm. Photoluminescence (acetonitrile,  $\lambda_{ex}$ =365 nm):  $\lambda$ =446 nm (max), 472 nm (shoulder).

#### 4.5. Metal ion-sensing experiments

Picolinamide-PV solution  $(1.5 \times 10^{-6} \text{ M})$  was prepared in acetonitrile. Metal ions, such as Zn(II), Mn(II), Cu(II), Ni(II), Cu(II), Cu(II), Cd(II) and Pb(II) were also prepared in acetonitrile at a concentration of  $1 \times 10^{-4}$  M. The picolinamide-PV solution was mixed with each metal ion solution at the volume ratio of 1:1. Fluorescence emission spectra of the mixtures were measured to observe the changes. The oligo-PVs **II** and **III** were prepared and mixed at the same manner.

#### 4.6. Quantum chemical calculations

Quantum chemical calculations were performed to gain insight into the electronic properties of picolinamide-PV. The ground state was fully optimized using the B3LYP/6-31G(d) by Gaussian03 program. The calculations of the excitation energies were calculated at the TD-B3LYP/6-31G(d). All calculations were performed with PCM calculation using methanol as the solvent. Moreover, the metalbound molecules were then investigated at different electronic states using B3LYP/6-31G(d) with full geometry optimizations without any constraints. The absorption spectra were obtained using the TD-B3LYP/6-311G(d) basis set with PCM calculation to study the response selectivity.

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