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Synthesis and Sensing Properties of Triphenylamine Based Dye Sensor

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We have designed and synthesized a triphenylamine-based new dye sensor and corresponding selective and sensitive detection functions for heavy metal ions were investigated. The complex potentials for heavy metal ions were characterized by the measurements of optical properties using UV-Vis spectrophotometer and spectrofluorophotometer. Furthermore, the molecular energy levels of the designed dye sensors were also computationally optimized and calculated by the density function theory (DFT) with exchange correction functional of local density approximation (LDA) based on the Perdew-Wang (PWC) set and cyclic voltammetry.

Keywords: Dye Sensor, Triphenylamine Derivatives, Mercury Ion, Complex Ability, Molecular Energy Levels.

1. INTRODUCTION

The research development of selective, sensitive and simple chemosensor using dye chromophores toward heavy metal ions is an important topic in dye molecular chemistry due to its fundamental roles in chemical, biological, and environmental systems.[1–4] Since the initial findings was reported in chemosensors such as crown ether, many research efforts have been focused on the design, synthesis and detection of heavy metal ions due to their toxic impacts.[5]

Thus, the concerns over highly noxious heavy and transition metal ions such as mercury (Hg^{2+}), copper (Cu^{2+}) and zinc (Zn^{2+}) are of topical interests because they are considered as highly toxic environmental pollutants. As well known, mercury and copper are considered to be highly dangerous heavy metals in the human body and play an important role in the physiologic process due to their severe toxic effects. In addition, zinc is reported to be related to the etiology of Alzheimer's disease because of the formation of β-amyloid.[1,6,7]

In this context, we have designed and synthesized the dye chromophores based on triphenylamine derivative as a chemosensor for heavy metal ions. The metal ion detection properties of these dyes were examined and determined. The levels of metal ion detection were discussed with UV-Vis absorption and fluorescent emission measurements in details. In addition to metal ion detection properties, the molecular energy potentials (HOMO and LUMO energy levels) of the dye chemosensor based on triphenylamine derivatives were also calculated and determined.

2. EXPERIMENTAL DETAILS

2.1. Materials and Measurements

All reagents and solvents used for synthesis of triphenylamine-based dye chemosensor were purchased from Aldrich and used without further purification. The spectroscopic characteristics and the fluorescent properties of these dyes were examined and determined using Agilent 8453 UV-Vis spectrophotometer and Shimadzu RF-5301 spectrofluorophotometer, respectively. ^1H NMR spectra and elemental analyses were recorded with a JNM-AL400 spectrometer operated at 400 MHz NMR and a Carlo Elba Model 1106 analyzer, respectively. The electrochemistry properties of these dyes were examined with a VersaSTAT3 using a platinum wire served as a working electrode, an Ag/Ag^+ electrode served as a reference electrode and a carbon served as a counter electrode. The scan rate was 100 mV/s. The optimized geometry structure and molecular energy potentials were calculated with Materials studio 4.2.

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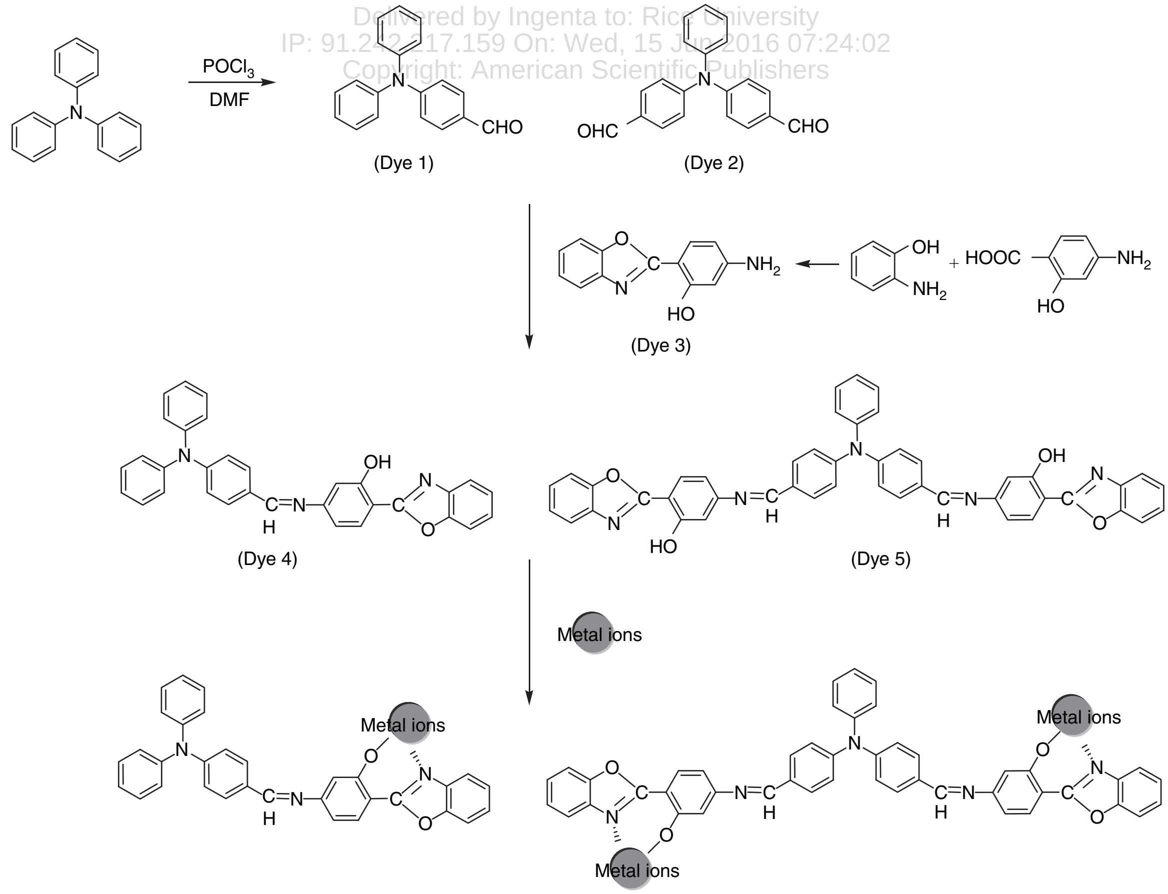
2.2. Synthesis and Characterization of Triphenylamine-Based Dye Sensor (Scheme 1)

To the mixture of 4 g (16.3 mmol) triphenylamine and 8 ml *N*,*N*-dimethylformamide, 7.6 ml phosphorus oxychloride was added at 0 °C and the mixture was then refluxed for 2 h at 45 °C (dye 1) and 4 hrs at 95 °C (dye 2). The reaction was cooled to room temperature and the mixture was quenched into 150 ml ice water. The formed precipitate solution was adjusted to the neutral pH condition using 4 M sodium hydroxide solution. The solid was filtered and purified by column chromatography by eluting with hexane/ethyl acetate.[8,9] Dye 1, Yield: 61.07% (2.72 g); Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.532; N, 5.12. Found: C, 83.42; H, 5.50; N, 4.995. ^1H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, 2H), 7.19–7.25 (m, 6H), 7.38 (t, 4H), 7.7.2 (d, 2H), 9.85 (s, 1H). Dye 2, Yield: 68.27% (2.52 g); Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.65; H, 5.07; N, 4.65. ^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (m, 6H), 7.40 (t, 2H), 7.76–7.78 (d, 4H), 9.89 (s, 2H).

The signal unit dye 3 was prepared by condensing *p*-aminosalicylic acid 0.998 g (6.52 mmol) and *o*-aminophenol 0.711 g (6.52 mmol). 20 g of polyphosphoric acid was added and heated at 200 °C with constant stirring. After 3 h, the reaction was quenched into the ice water and being stirred for 24 h. The formed precipitate solution was adjusted to the neutral pH condition using 1% sodium carbonate solution. After 3 h, the mixture was filtrated with distilled water at several times and dried in oven at 40 °C.[10–12] Dye 3, Yield: 23.03% (0.34 g); Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38: found; C, 69.16; H, 4.16; N, 12.81. ^1H NMR (400 MHz, $CDCl_3$): δ 4.00 (s, 2H), 6.24 (d, 1H), 6.28 (d, 1H), 7.18–7.32 (m, 2H), 7.42–7.50 (m, 1H), 7.52–7.62 (m, 1H), 7.30 (d, 1H), 11.47 (s, 1H).

For next step synthesis, the chemosensor dyes 4 and 5 were obtained from the prepared intermediates 2 and 3. 0.045 g and 0.090 g (0.2 mmol, 0.4 mmol) of Dye 1 were mixed with dyes 2 and 3 (0.2 mmol, 0.054 g, 0.06 g), respectively. The reaction mixture was dissolved in 15 ml of benzene. 5~6 drops of piperidine was added dropwise during the reaction and the mixture was then refluxed for 48 h. The reaction product was filtered using benzene and dried (dyes 4 and 5).[13] Dye 4, Yield: 53.37% (0.052 g); Anal. Calcd for $C_{32}H_{23}N_3O_2$: C, 79.81; H, 4.81; N, 8.73. Found: C, 79.26; H, 4.56; N, 8.25. ^1H NMR (400 MHz, DMSO-d_6): δ 6.07 (s, 4H), 6.26–6.29 (m, 2H), 6.86–6.88 (m, 2H), 7.07–7.19 (m, 1H), 7.32–7.33 (m, 5H), 7.69–7.70 (m, 7H), 9.75 (s, 1H). Dye 5, Yield: 35.81% (0.052 g);



Scheme 1. Synthesic routes for designed dye sensor.

Anal. Calcd for $C_{46}H_{31}N_5O_4$: C, 76.97; H, 4.35; N, 9.76. Found: C, 76.94; H, 4.70; N, 10.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29–6.34 (t, 4H), 6.29 (s, 4H), 7.52–7.54 (d, 1H), 7.60–7.64 (m, 4H), 7.71–7.78 (m, 8H), 7.86 (s, 2H), 8.03–8.05 (d, 2H), 8.43 (s, 2H), 9.87–9.89 (d, 2H), 11.58 (s, 2H).

2.3. Absorption and Fluorescence Measurements

UV-Vis absorption and fluorescence spectra were performed by the addition from 0 to 2 equiv of different metal ions (Hg^{2+}, Cu^{2+} and Zn^{2+}) in 3 ml dye solution (1.0×10^{-4} M).

2.4. Composition of the Metal Complex

The dyes 4, 5 and Hg^{2+} ion solution were mixed in different volume ratio (1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1, 10:0) using a total concentration of 1.0×10^{-4} M. The mixture solutions were characterized at maximum absorption value using spectrophotometer.

3. RESULTS AND DISCUSSION

In this work, the aldehydes of triphenylamine (dyes 1, 2) and benzoxazole intermediate (dye 3) were reacted to

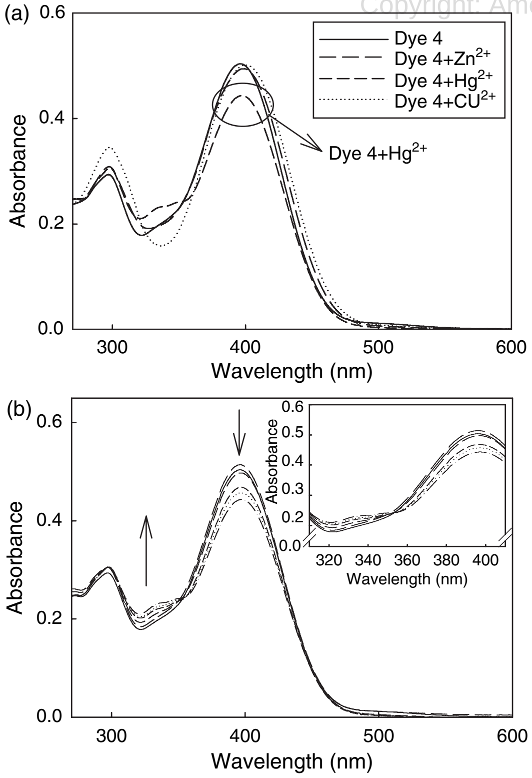


Fig. 1. (a) Absorption spectra of dye 4 (1.0×10^{-4} M, chloroform) in the addition of 2 equiv. of metal ions (Zn^{2+}, Hg^{2+}, Cu^{2+}) and (b) dye 4 titrated selectively with Hg^{2+}.

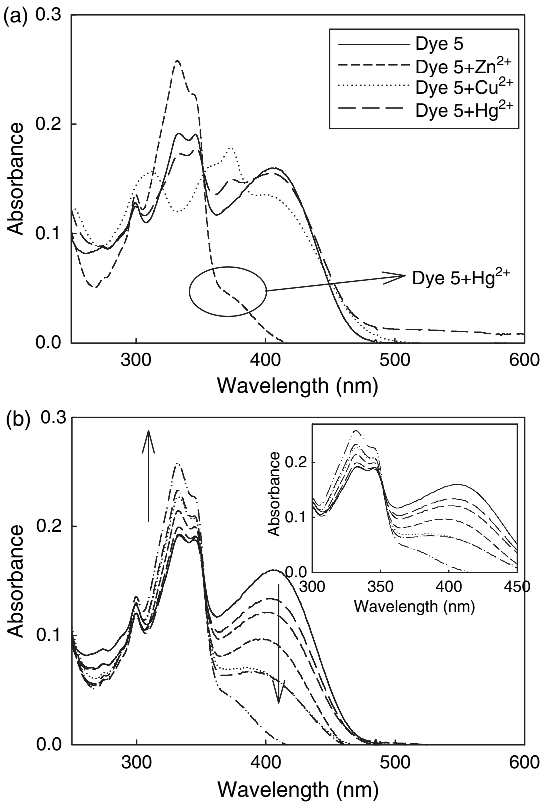


Fig. 2. (a) Absorption spectra of dye 5 (1.0×10^{-4} M, chloroform) in the addition of 2 equiv. of metal ions (Zn^{2+}, Hg^{2+}, Cu^{2+}) and (b) dye 5 titrated selectively with Hg^{2+}.

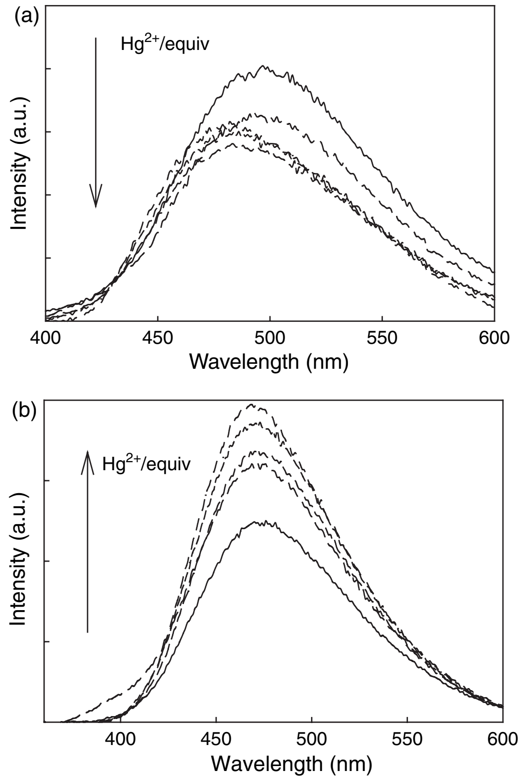


Fig. 3. Fluorescence emission spectra of dye 4 (a) and dye 5 (b) (1.0×10^{-4} M, chloroform) titrated with Hg^{2+}.

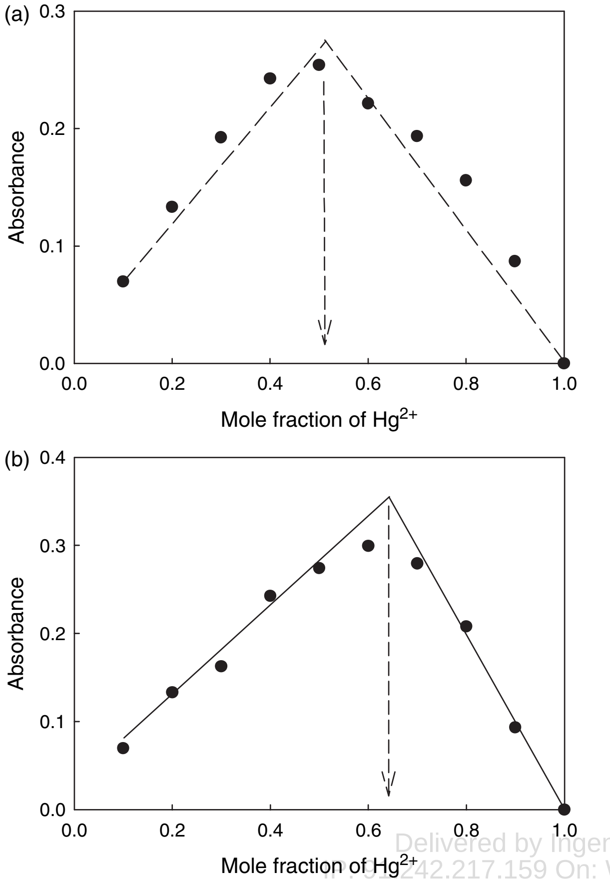


Fig. 4. Job's method for the addition of Hg^{2+}: dye 4 complex (a) and dye 5 complex (b).

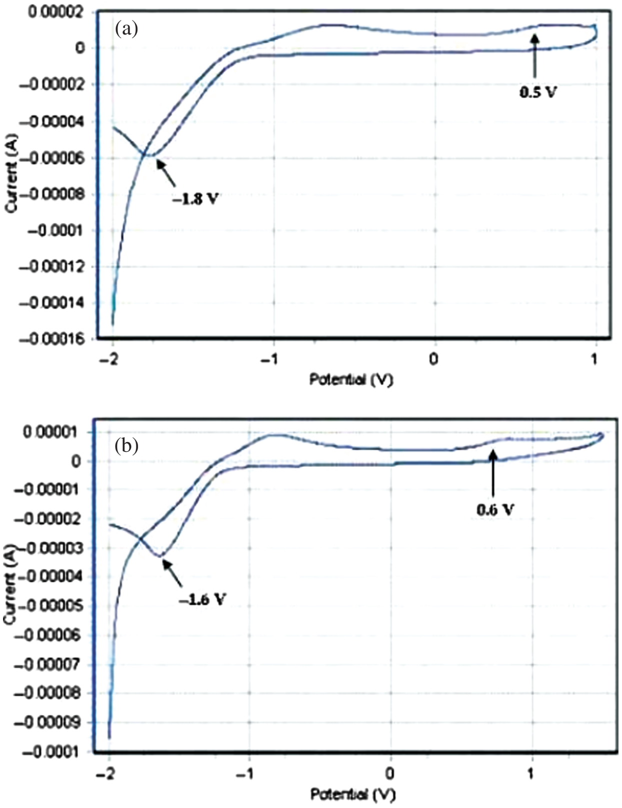


Fig. 6. Cyclic Voltammetry diagrams for dyes 4 (a) and 5 (b) in acetonitrile (0.05 M TBAPF6, Ag/Ag^{+} reference electrode and scan rate 100 mV/s).

produce the aimed dyes 4 and 5. Absorption and fluorescence emission spectra were measured to monitor the sensing functions of the designed dyes 4 and 5 toward heavy metal ions (Hg^{2+}, Cu^{2+} and Zn^{2+}). Absorption spectra of dyes 4 and 5 with three metal ions in chloroform are shown in Figures 1 and 2, respectively. The detection properties of dyes 4 and 5 toward three metal ions showed the selective functions, especially to Hg^{2+} ions. The optical characteristics of dyes 4 and 5 displayed the increased behavior around 320 nm and the decreased behavior around 400 nm with increasing concentration of Hg^{2+}. The isobestic point at 350 nm was clearly observed. This sensing behavior occurred by the metal binding reaction. Figure 3 shows that fluorescence spectra of dyes 4 and 5 with addition of Hg^{2+} ions. With addition of Hg^{2+} to dye 4, the maximum emission band at 500 nm was decreased with increasing concentration

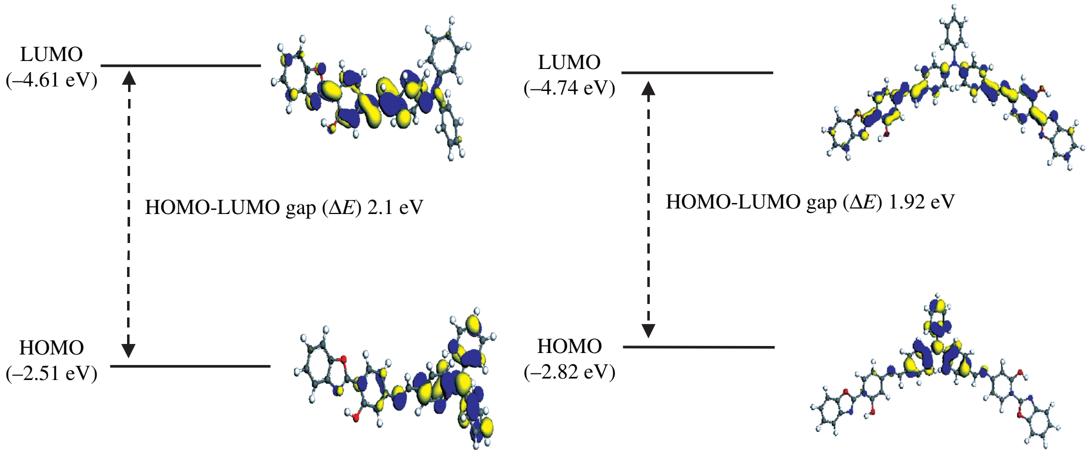


Fig. 5. Geometrical optimization of dyes 4, 5 and HOMO and LUMO energy levels.

Table I. HOMO/LUMO values of dye sensor 4 and 5.

	Computationally calculated			Determined with cyclic voltammograms		
Dye sensor	HOMO	LUMO	ΔE	HOMO	LUMO	ΔE
4	−4.61	−2.51	2.1	−4.88	−2.58	2.3
5	−4.74	−2.82	1.92	−4.98	−2.78	2.2

of Hg^{2+}. However, in the case of dye 5, the maximum emission band at 500 nm was increased with increasing concentration of Hg^{2+}. This optical changing behavior was explained by MLCT, namely "metal to ligand charge transfer." When the metal binding reaction occurred, it shows the clear optical emission property changes. These sensing properties provide the easy way to determine the metal ion detection properties with naked eyes.

The Job's method is widely used to determine the complex composition of the host-guest interaction. The relationship of maximum absorption peak versus mole fraction of the metal ion is shown in Figure 4. From the results of dyes 4 and 5, it is showed that the mole fraction was close to 50% and 65%. This finding confirms that dyes 4 and 5 make a formation of 1:1 and 1:2 binding complexes with the added Hg^{2+} ion, respectively.

The optimization of the molecular geometrical structure and the molecular energy potential of dye sensor 4 and 5 were computationally calculated with the DFT with exchange correction functional of LDA based on the PWC set employing Materials studio 4.2. Figure 5 shows that electron density of dye sensor 4 and 5 was distributed in triphenylamine moiety in HOMO states and was localized in benzoxazole moiety in LUMO states after excited. From the findings, HOMO and LUMO energy levels were calculated by −4.61 eV and −2.51 eV (dye sensor 4) and −4.74 eV and −2.82 eV (dye sensor 5). Cyclic-voltammetry measurements of these dyes were also carried out using a conventional three-electrode system. The oxidation and reduction potential values were also used to determine the potential of HOMO and LUMO energy levels. Figure 6 shows the redox potential characteristics of dye sensor 4 and 5, respectively. From the redox potentials, HOMO and LUMO energy levels of dye sensors were determined and compared (Table I). The HOMO and LUMO energy levels were calculated using the following formula,[14]

$$\text{HOMO (or LUMO) (eV)} = -4.8 - (E_{\text{peak potential}} - E_{1/2(\text{Ferrocene})})$$

where, $E_{\text{peak potential}}$ and $E_{1/2(\text{Ferrocene})}$ is the maximum, minimum peak potential and half-wave potential of Ferrocene (0.42 V).

4. CONCLUSIONS

In this work, we have developed new dye chemosensor 4 and 5 based on triphenylamine. The dye chemosensor clearly showed the selective detection properties of absorption and fluorescence emission intensities toward Hg^{2+}. A stable binding functions of dyes 4 and 5 formed 1:1 and 1:2 complexes with Hg^{2+} ion, which was determined by Job's method. The molecular energy levels were calculated using computational optimization and cyclic voltammetry. The synthesized dye sensor 4 and 5 could be utilized as selective good chemosensors for Hg^{2+} ions in chemical, environmental and biological systems.

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