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Schiff bases carrying dipicolylamine groups for selective determination of metal ions in aqueous media. A phenanthrene-based fluorescent sensor for Hg^{2+} determination

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Abstract

Four new dipicolylamine compounds carrying anthracene, naphthalene, pyrene and phenanthrene groups were synthesized, and their ion sensor properties were studied by means of emission spectrometry in ethanol-water mixture (1:1). It was disclosed that among a series of studied anions and cations, only with Cd^{2+}, Zn^{2+}, Cu^{2+} and Hg^{2+} cations, ligands formed complexes selectively. With spectrofluorimetric measurements, the complexation stoichiometries and the complex stability constants of the formed complexes were determined. A linear range from 0.1 µg L^{-1} to 150.00 µg L^{-1} where the fluorescence intensity of the phenanthrene derivative compound showed a regular decrease with the increase of the Hg^{2+} ion concentration was obtained. The method developed for the determination of Hg^{2+} was applied to tap water samples. In order to eliminate the matrix effect, a modified standard addition method was used. Detection and quantification limits were 9.0 µg L^{-1} and 27.0 µg L^{-1}, respectively. The recovery rate was above 94.6%. The precision as relative standard deviation (RSD%) was determined as 2.21 for the intra-day measurements while inter-day precision was 3.31.

Keywords: Ion sensor, Hg^{2+} determination, dipicolylamine, fluorescence

1. Introduction

The significance of metal ions in daily life is a well-known subject. Some metal ions are known to be essential for the human body; their lack or exceed may cause a diversity of diseases whereas others are completely toxic therefore must be out of the scope of human consumption. For example, the effects of Zn^{2+}, Cu^{2+} and Hg^{2+} ions on the nervous system are made a subject of research many times [1-2]. Hg^{2+} ion is one of the most dangerous of those ions. Acceptable concentrations of Hg^{2+} ion are determined by law, especially in water resources. Therefore, the detection and determination of this toxic metal cation in environmental systems are significant.

Generally, metal ions are determined with atomic methods. However, these methods are expensive and they usually require pre-treatment and enrichment processes before determination [3-6]. These processes extend the determination period and are disadvantageous when compared to analytical methods based on molecular absorption [7-9]. Therefore, there is a constant need for faster and more economic methods.

Molecular fluorescence methods are selective and sensitive by their nature and they provide simple and quick measurements. With those advantages, they gather attention as an alternative method for metal determination based on atomic absorption. Therefore, many fluorescent sensors were synthesized and recommended for metal determination lately [10].

It is known from the literature that dipicolylamine (DPA) groups tend to form complexes selectively especially with Zn^{2+}, Cu^{2+}, Hg^{2+}

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ions [11-14]. The metal complexes of the ligands carrying this group were also recommended for the determination of anions with great biological importance such as pyrophosphate and phosphate [15-20]. Moreover, fluorescent DPA ligands were proposed as fluorescent sensors for the determination of metal ions [21-23]. However, there is a lack of reports based on fluorescent DPA ligands to determine metal ions in real samples.

Recently, we have been focusing on the synthesis of new fluorescent DPA ligands in order to determine the effect of the fluorophore group on the ionsensor properties of the Shiff base ligands containing anthracene, naphthalene, phenanthrene, and pyrene groups. We came to the realization that among the ligands presented in these studies, the one carrying the phenanthrene group was allowing the selective and sensitive determination of Cu^{2+} in aqueous media [24]. In the fluoroionophore compounds from the stated study, as donor atoms, oxygen donor atoms were present as an addition to the nitrogen atoms of the DPA group. In the presented study, only nitrogen donor atoms of DPA group are present as cation binders. Our purpose was to disclose the effect of the lack of oxygen donors in their build on similar ion sensor properties of ligands. Thus, four new DPA Schiff base ligands were synthesized and characterized. Among the presented ligands, it has been yet again reported that only the compound carrying the phenanthrene group can be used for the determination of the Hg^{2+} ion in aqueous media, and the proposed spectrofluorimetric method was applied to tap water.

2. Experimental

2.1. Chemicals

All of the solvents used in the absorption and fluorescence measurements were at spectroscopic purity and purchased from Merck. The 1000 mg L^{-1} standard solvents of all cations and NO_3^-, SO_4^{2-} and PO_4^{3-} ions were purchased from Merck and used after proper dilution with deionized water. Sodium salts of ammonium acetate, hydrazine hydrate (%100) and other standard anion solutions were also purchased from Merck (Darmstadt, Germany). Stock solutions of the salts were prepared, then those prepared solutions were diluted and turned into working solutions. All aldehyde compounds were purchased from Sigma-Aldrich (Buch, Switzerland).

2.2. Apparatus

For the characterization of new ligands, a FT-IR spectrometer (Perkin Elmer 1600), an NMR spectrometer (Bruker AVANCE III 400 MHz), and an LC-MS spectrometer are used. ^1H NMR spectra were recorded by $CDCl_3$ with TMS as the internal reference. Deionized water was obtained from a Sartorius Milli-Q system (arium® 611UV). The absorption spectra of the solutions were recorded by Analytic Jena Specord 210 spectrophotometer. A PTI spectrofluorimeter (QM-4/2006) was used for all of the fluorescence measurements.

2.3. Measurements

Absorption spectra of the ligands in different solvents containing 10 molar equivalents of Cu^{2+}, Co^{2+}, Hg^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Pb^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}, Ag^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, I^-, Br^-, Cl^-, F^-, CH_3COO^-, NO_3^-, CN^-, SO_4^{2-}, HSO_4^-, CO_3^{2-}, HCO_3^-, PO_4^{3-}, $P_2O_7^{4-}$ were recorded by using 1-cm absorption cell. Fluorescence spectra under the same conditions were recorded by using a 1-cm quartz cell with a slit width of 1 nm in the range of 380-600 nm. Spectrofluorimetric titration experiments were carried out in the ethanol-water mixture (1:1).

The complex compositions were determined by using the molar ratio graphs from the spectrofluorimetric titrations data. The stability constants were calculated according to the method in the literature [25].

A kind of standard addition method was utilized to determine Hg^{2+} ion in tap water samples. The similar approach has already been reported for Hg^{2+} and Fe^{3+} determination with other fluorescent ligands [26-29]. The proposed method for the determination of Hg^{2+} was applied to the spiked tap water samples.

2.4. Synthesis of the ligands

Synthetic pathways for the ligands are given in Scheme 1. Compound **(1)** was synthesized according to the literature [30]. The characterization data of the white solid were consistent with the report in the literature [30].

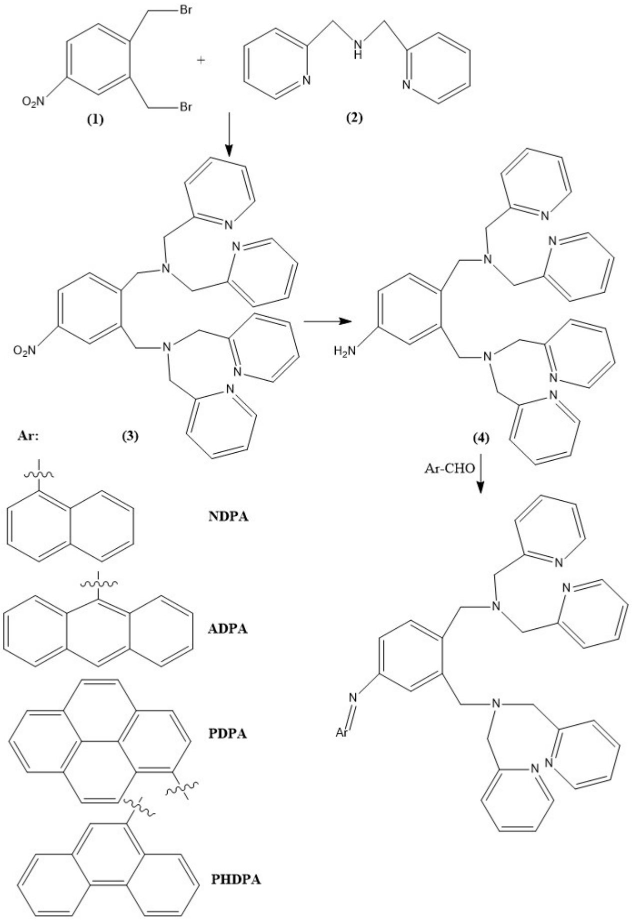
2.4.1. *Synthesis of* **(3)**

The nitro compound **(3)** was synthesized according to a similar procedure in the literature [24]. The yield of the brown oil product was 86%. IR (cm^{-1}): 3051, 3008 (Ar-H), 2928-2822 (C-H), ^1H-NMR

($CDCl_3$): (δ) 8.49-8.55 (m, 4H, Ar-H), 7.12-7.64 (m, 15H, Ar-H), 3.86 (s, 6H, CH_2), 3.98 (s, 6H, CH_2).

2.4.2. Synthesis of ***(4)***

The amine compound **(4)** was prepared by reduction of the nitro compound **(3)** by using hydrazine hydrate (100%) in n-butanol according to a similar procedure in the literature [24]. The product was obtained as yellow oil (yield, 42%). IR (cm^{-1}): 3309-3186 (NH_2), 3054-3009 (Ar-H), 2922-2848 (C-H), ^1H-NMR ($CDCl_3$): (δ) 8.49-8.52 (m, 4H, Ar-H), 7.08-7.60 (m, 15H, Ar-H), 5.88 (s, 2H, NH_2), 3.85 (s, 6H, CH_2), 3.94 (s, 6H, CH_2).



Scheme 1. The ligands and their synthetic pathways.

2.4.3. Synthesis of Schiff bases

An equivalent amount of aldehyde and amine compound (4) was refluxed in methanol for about 5 hours. The Schiff bases were purified by column chromatography on silica gel using chloroform as an eluent to afford the oil product.

Spectral data: NDPA: Brown oil; IR (cm^{-1}): 3050-3008 (Ar-H), 2918-2849 (C-H), 1687 (C=N), ^1H-NMR ($CDCl_3$): (δ) 9.53 (s, 1H, HC=N), 7.18-9.06 (m, 26H, Ar-H), 3.95 (s, 12H, CH_2). ADPA: Brown oil; IR (cm^{-1}): 3054-3010 (Ar-H), 2925-2849 (C-H), 1668 (C=N), ^1H-NMR ($CDCl_3$): (δ) 9.53 (s, 1H, HC=N), 7.18-9.06 (m, 28H, Ar-H), 3.97 (s, 12H, CH_2). MS: m/z 701 $[M-2]^+$. PDPA: Brown oil; IR (cm^{-1}): 3048-3011 (Ar-H), 2919-2850 (C-H), 1673 (C=N), ^1H-NMR ($CDCl_3$): (δ) 8.59 (s, 1H, HC=N), 7.22-7.89 (m, 28H, Ar-H), 4.10 (s, 4H, CH_2), 4.05 (s, 8H, CH_2). PHDPA: Brown oil; IR (cm^{-1}): 3055-3008 (Ar-H), 2958-2868 (C-H), 1685 (C=N), ^1H-NMR ($CDCl_3$): (δ) 8.60 (s, 1H, HC=N), 7.28-8.70 (m, 28H, Ar-H), 3.95 (s, 12H, CH_2). MS: m/z 701 $[M-2]^+$.

3. Results and discussion

3.1. Absorption measurements

The effect of the solvent on the absorption spectra of the ligands was investigated. Many organic solvents were tested as ligand solvent. Ethanol, among the others, gave the highest absorbance values. Therefore, the effect of various ions on the absorption spectra of the ligands was investigated in ethanol: water mixture (1:1). However, with these ions, it was not possible to detect a significant changing in the absorption spectra. Therefore the study was continued with fluorescence measurements.

3.2. Emission measurement

Many organic solvents as a ligand solvent were tested to predict the effect of ions on the emission spectra of the ligands. The emission spectra were recorded with excitation wavelength intervals of 10 nm to obtain the maximum emission intensity in different solvents. The ion effects on the emission spectra were remarkable in the case of ethanol between the tested organic solvents as ligand solvent for all ligands. Hence, ethanol was determined as the solvent for the ligands. Eventually, when the solutions containing 10 equivalent ions in ethanol: water mixture (1:1) was investigated, is was proven that no significant chance causing from the tested anions was seen on the ligands' emission spectra (Fig. S1b, Fig. S6b, Fig. S9b, and Fig. S14b). Similar results were obtained for similar dipicolylamine ligands [24].

All the cations investigated caused fluorescence quenching in the emission spectra of ADPA (Fig. S1a). A remarkable quenching was detected especially at the wavelength of 395 and 421 nm. This quenching was the most in the case of Cu^{2+} and Hg^{2+} ions.

Fluorometric titration experiments were made with the cations by using ADPA to monitor the complex formation. The stable complexes were observed with Cu^{2+}, Hg^{2+}, Cd^{2+} and Zn^{2+} cations. The effect of increasing Cd^{2+} and Zn^{2+} concentration on the emission spectra of ADPA is similar to regular fluorescence enhancements (Fig. S2 and Fig. S3, respectively).

It showed regular emission increase at 418 nm until [M]/[L]=1 during the complexation with Cd^{2+} and after that, a plateau was observed. Hence, the 1:1 complex stoichiometry was detected from the molar ratio graph. The inflection point was 1.0 ([M]/[L]) in the molar ratio graph (Fig. S2 inset above). The similar spectrofluorimetric titration curve was obtained for Zn^{2+} with ADPA (Fig. S3). The complex composition was also 1:1 for this cation (Fig. S3, inset above).

Different from the Cd^{2+} and Zn^{2+} ions, for $Cu^{2+}$and Hg^{2+} ions, fluorescence quenching was obtained at 395, 420 and 442 nm in the spectrofluorimetric titrations with ADPA (Fig. S4 ve Fig. S5). For these cations too, the complex composition was 1:1 (Fig. S4 and S5 insets above).

In the conclusion, even though the spectrofluorimetric titration data disclosed stable 1:1 complexes of ADPA with Cu^{2+}, Hg^{2+}, Cd^{2+}, and Zn^{2+} cations, the results show that the effect of Cu^{2+} and Hg^{2+} on the fluorescence mechanism of the ligand are different from that of Cd^{2+} and Zn^{2+}.

All of the fluorescence studies of ADPA were made with other ligands. It is determined that all cations cause quenching in the fluorescence spectra of NDPA (Fig. S6a). The most quenching was determined for Cu^{2+} and Hg^{2+} ions. The studies showed that among the tested cations, only with these ions NDPA formed stable 1:1 complexes (Fig. S7 and Fig. S8, insets above).

Fig. S9a represents the effect of the cations on the fluorescence spectra of PDPA. All cations, unlike ADPA and NDPA, cause an increase in PDPA's fluorescence intensity. The spectrofluorometric titrations showed that only with Cu^{2+}, Hg^{2+}, Cd^{2+}, and Zn^{2+} ions form stable 1:1 complexes with PDPA (Fig. S10, Fig. S11, Fig. S12 and Fig. S13 insets above).

The effect of cations on the fluorescence spectra of PHDPA is shown in Fig. S14a. Similarly to ADPA and NDPA's spectra, all of the cations cause fluorescence quenching. However, only Hg^{2+} ion among the tested cations forms the stable complex with PHDPA as concluded from the fluorescence quenching at 421 nm (Fig. 1 inset above).

To determine the complex stability constants, the ratio of $F_0/(F-F_0)$ or $F_0/(F_0-F)$ was plotted versus $1/[M]$ and obtained a good straight line. F_0 and F represent the fluorescence intensity of the free ligand solution and the solution containing the ion, respectively. The ratio intercept/slope gives the complex stability constant [25]. The corresponding graphs were given in Fig. S2-5, Fig. S7-8, Fig. S10-13 and, Fig. 1 (inset below).

The stability constants were stated as log K, as seen from Table 1. The most stable complex is ADPA-Hg^{2+} with log K 6.27. The less stable complex was ADPA-Cd^{2+} complex with log K of 4.99.

Table 1 shows that PHDPA compound only forms a stable complex with Hg^{2+} ion among Cu^{2+}, Cd^{2+}, Zn^{2+} and Hg^{2+} ions, thus it acts as a selective compound for the Hg^{2+} ion. Therefore, the sensor ability of the PHDPA was investigated and detected that it is a suitable ligand to determine Hg^{2+} ion in tap water samples, which has convenient Hg^{2+} content.

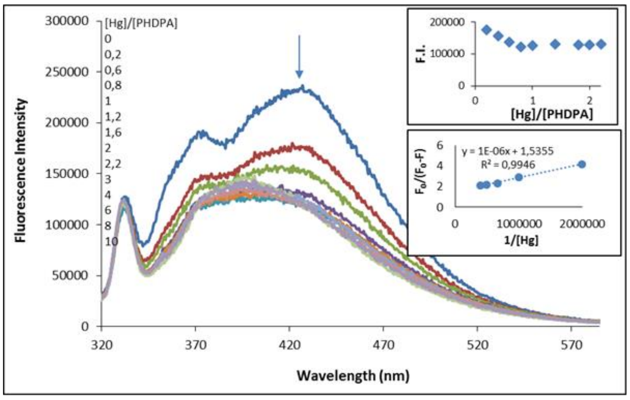


Figure 1. The variation of the emission of the ligand (PHDPA) with the concentration of Hg^{2+}, added as 0-10 equivalents of Hg^{2+} in ethanol-water mixture (1:1). Ligand concentration= 2.5×10^{-6} M. Excitation at 300 nm. Insets: Measurements were carried out at 421 nm.

3.3. Method optimization for Hg^{2+} determination

Non-toxic ethanol was preferred among many tested organic solvents as ligand solvent because it provided high fluorescence intensity. Excitation at 300 nm of PHDPA gave a maximum emission band at 421 nm in ethanol: water mixture (1:1).

Spectrofluorimetric titrations were carried out by using the ligand solutions in the range of 5.0×10^{-5} to 1.0×10^{-6} M with increasing concentrations of Hg^{2+}. The values of fluorescence intensity at 421 nm were plotted against Hg^{2+} concentration. The highest R^2

value was obtained for a ligand concentration of 2.5×10^{-6} M. Therefore, this concentration was selected for further works.

Table 1 The complex stability constant values (Log K) in ethanol-water mixture (1:1), (N=3).

Cation	ADPA	NDPA	PDPA	PHDPA
Cd^{2+}	4.99 ± 0.32	-	5.63 ± 0.24	-
Zn^{2+}	5.72 ± 0.14	-	5.05 ± 0.17	-
Cu^{2+}	5.25 ± 0.22	5.74 ± 0.16	5.04 ± 0.25	-
Hg^{2+}	6.27 ± 0.35	6.00 ± 0.12	5.03 ± 0.28	6.18 ± 0.31

An external calibration line based on fluorescence quenching of 2.5×10^{-6} M ligand showed linearity within the concentration range from 0.1 μg L^{-1} to 150.00 μg L^{-1}. However, recovery was not good in the Hg^{2+} determination in samples using the external calibration graph. Therefore, a modified standard addition method [26-29] was used in the Hg^{2+} determination. The analytical performance data for the proposed method are given in Table 2.

The acceptable recovery results were obtained with the measurements at 421 nm. To optimize the constant Hg^{2+} concentration, various constant Hg^{2+} concentrations (10-50 μg L^{-1}) were tested in the modified standard addition method. The optimum constant Hg^{2+} concentration was found at 30.0 μg L^{-1}.

Table 2 Analytical performance data for the Hg^{2+} determination method.

Excitation wavelength	300 nm
Emission wavelength	421 nm
LOD	9.0 μg L^{-1}
LOQ	27.0 μg L^{-1}
Linear range	10-150 (μg L^{-1} - μg L^{-1})
Correlation coefficient (R^2)	0.9771

3.4. The proposed method for Hg^{2+} determination

A kind of standard addition method proposed by our research group was used to determine Hg^{2+} ion [26-29]. In this study, the constant Hg^{2+} concentration and the ligand concentration were 0.03 mg L^{-1} and 2.5×10^{-6} mol L^{-1}, respectively. The total volume was 4 mL, the waiting time before the measurement was 1-2 min. Fig. 2 shows the calibration graph for the determination of Hg^{2+} (40.0 μg L^{-1}) in the spiked water sample.

3.5. Method validation

A linear fluorescence response as a function of Hg^{2+} concentration at 421 nm was obtained in the range of 0.1 μg L^{-1} - 150.00 μg L^{-1}. The R^2 value was 0.9771 (Fig. 2). The LOD and LOQ values were determined by the standard deviation of eleven measurements of the blank response and the slope of the calibration line according to the IUPAC recommendations. The LOD and LOQ were calculated as $3\times S_d/m$ and $9\times S_d/m$, respectively. S_d was the standard deviation of the blank responses and m was the slope of the calibration line. The LOD and LOQ values were 9.0 μg L^{-1} and 27.0 μg L^{-1}, respectively. The accuracy of the proposed method was tested by recovery measurements. A modified standard addition method was applied to tap water samples of KTU campus in Trabzon. The Hg^{2+} concentration of 40.0 μg L^{-1} was provided in three tap water samples in spiking processes. The recovery rate was above 94.6 %. The tap water samples were diluted in various proportions. But the acceptable recovery results in the tap water samples were obtained at 1/4 dilution. Therefore, the tap water samples were diluted in a ratio of 1/4 before spiking to obtain the acceptable recovery results. The results showed that the proposed method can be applied for the determination of mercury in water samples, which has convenient Hg^{2+} content. The intra-day and inter-day precision were estimated by analysing three spiked tap water samples. The precision as relative standard deviation (RSD %) was determined as 2.21 for the intra-day measurements while inter-day precision was 3.31.

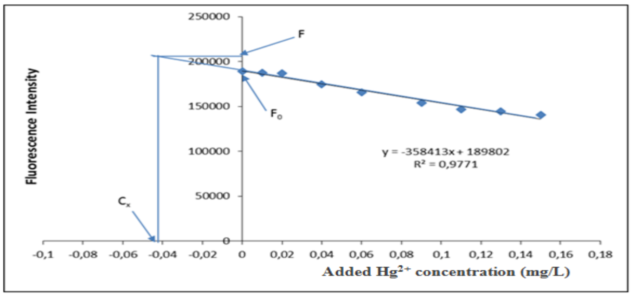


Figure 2. Modified standard addition plot to determine Hg^{2+} with PHDPA. Ligand concentration= 2.5×10^{-6} M. Excitation at 300 nm. Measurement was carried out at 421 nm.

3.6. Quenching mechanism

The Stern-Volmer relationship [31] was utilized to determine the efficiency of the quenching of a fluorophore by a quencher (Equation 1).

$$F_0 / F = 1 + K_{sv}[Q] \quad (1)$$

In Eq. 1, K_{sv} is the Stern-Volmer quenching constant and [Q] is the concentration of the quencher. F_0 and F represent the fluorescence intensity in the absence and the presence of the quencher, respectively. When the system obeys the Stern-Volmer equation, a plot of F_0/F versus molar concentration of the quencher has given a straight line with a slope of K_{sv} and a y-axis intercept of 1.

Fig. 3 shows the Stern-Volmer analysis based on steady-state emission for the complexation of Hg^{2+} by PHDPA. F_0/F term linearly increased with increasing Hg^{2+} concentration until 40.0 μg L^{-1}. As seen in Fig. 3, y-axis intercept is about 1. The Stern-Volmer relationship is obtained in the case of both dynamic and static quenching [31]. It is well known, static quenching results from the formation of the ground state complex [31]. In this study, the 1:1 complex formation with Hg^{2+} was determined. Therefore, it is concluded that the observed quenching should be a static quenching.

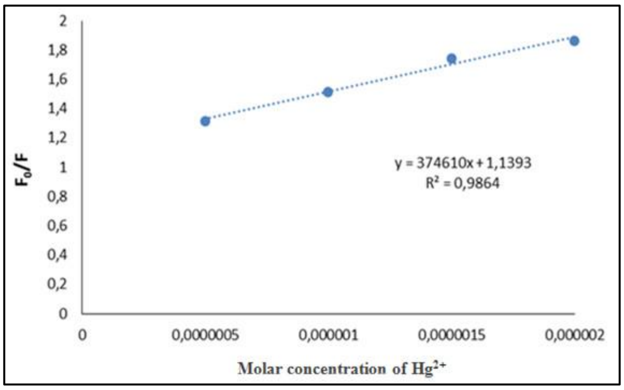


Figure 3. Stern-Volmer plot for the quenching of **PHDPA** by Hg^{2+}.

4. Conclusions

New fluorescent Schiff base ligands carrying dipicolylamine groups were synthesized from the aldehyde compounds having pyrene, naphthalene, anthracene, and phenanthrene groups. The fluorescent Schiff base carrying phenanthrene group PHDPA showed selectivity for Hg^{2+} ion among many metal ions. Therefore, it was used to develop a new Hg^{2+} determination method in aqueous media. To show the accuracy of the proposed method, the spiked tap water samples were analyzed. Recovery values were acceptable. These results suggest that the new Schiff base carrying phenanthrene group (PHDPA) can be used as an analytical ligand for the determination of Hg^{2+} in water samples. The proposed method is relatively economical, time-saving and simpler with respect to convenient atomic methods.

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