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Research Article

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Two Schiff Base Compounds Derived from 5-Aminoisophthalic Acid: Chemsensors Properties for Sensing of Metal Ions and Nitroaromatic Compounds

5-Aminoisoftalik Asitten Türetilen İki Schiff Bazı Bileşiği: Metal İyonları ve Nitroaromatic Bileşiklerin Saptanması İçin Sensör Özellikleri

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ABSTRACT

In this work, two Schiff base ligands Z_{2a} and Z_{2b} derived from 5-aminoisophthalic acid were synthesized and their structures were characterized by FTIR, $^{1}H(^{13}C)$ NMR and mass spectrometries. The compounds were investigated for their chemosensor properties towards metal ions [Na^{+}, K^{+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2}+, Cd^{2+}, Hg^{2+} and Pb^{2+}] were examined using colorimetric and spectrophotometric methods (UV-Vis absorption and florescence spectroscopy). Both compounds showed similar sensing properties towards metal ions and they have shown selective sensory properties for Fe^{+3} and Hg^{+2} ions. Moreover, the compounds were examined for their fluorimetric sensing abilities for nitroaromatic compounds [4-nitrofenol (NP), nitrobenzene (NB), 2,4-dinitrofenol (DNP), 1,3,5-trinitrophenol (TNP)]. Both compounds showed higher sensitivities for DNP and TNP than NP and NB. Compound Z_{2b} showed the highest sensitivity for DNP with K_{sv} value of 2.4×10^{4} M^{-1}. Limit of detections for nitroaromatic compounds were calculated and both compounds showed LOD values in micromolar levels. Compound Z_{2b} has shown the lowest LOD value for DNP with 2.77 µM.

Key Words

Schiff base, 5-aminoisophthalic acid, chemosensor, fluorimetric sensor, metal ions, nitroaromatic compounds.

ÖZ

Bu çalışmada, 5-aminoizoftalik asitten türetilen iki Schiff bazı ligandı Z_{2a} ve Z_{2b} sentezlenmiş ve yapıları FTIR, $^{1}H(^{13}C)$ NMR ve kütle spektrometrileri ile karakterize edilmiştir. Bileşiklerin metal iyonlarına [Na^{+}, K^{+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} ve Pb^{2+}] karşı kemosensör özellikleri kolorimetrik ve spektrofotometrik yöntemler (UV-Vis absorpsiyon ve floresans spektroskopisi) kullanılarak incelenmiştir. Her iki bileşikte metal iyonlarına karşı benzer algılama özellikleri göstermiş ve Fe^{+3} ve Hg^{+2} iyonları için seçici sensör özellikler göstermiştir. Ayrıca, bileşiklerin nitroaromatik bileşikler [4-nitrofenol (NP), nitrobenzen (NB), 2,4-dinitrofenol (DNP), 1,3,5-trinitrofenol (TNP)] için florimetrik saptama yetenekleri incelenmiştir. Her iki bileşikte DNP ve TNP için NP ve NB'den daha yüksek duyarlılık göstermiştir. Z_{2b} bileşiği, 2.4×10^{4} M^{-1} K_{sv} değeriyle DNP için en yüksek hassasiyeti göstermiştir. Nitroaromatik bileşikler için tespit limiti hesaplandı ve her iki bileşik de mikromolar seviyelerde LOD değerleri göstermiştir. Z_{2b} bileşiği, 2.77 µM ile DNP için en düşük LOD değerini göstermiştir.

Anahtar Kelimeler

Schiff bazı, 5-aminoizoftalik asit, kemosensör, florimetrik sensör, metal iyonları, nitroaromatik bileşikler.

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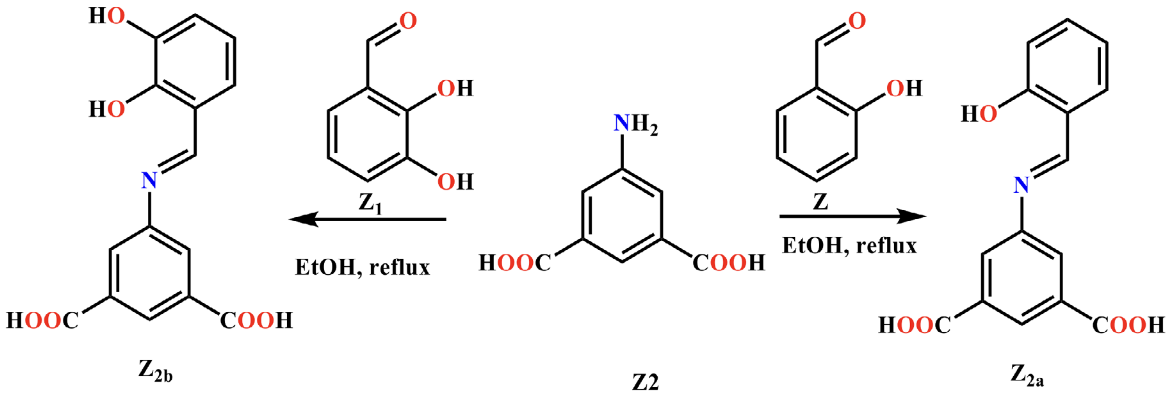
INTRODUCTION

Schiff base compounds are nitrogen analogues of aldehydes or ketones and are obtained by the condensation reaction of aldehydes or ketones with primary amines [1]. Schiff base compounds are widely used in pigments, catalysts, intermediates in organic synthesis, polymer stabilizers, dyes, biological activity, molecular memory storage, imaging systems, pharmaceutical and agro-industrial chemistry [2]. Since Schiff base compounds have the ability to form stable complexes with metal ions, they are used in molecular recognition and in the development of fluorescence sensors [3]. Schiff base derivatives with nitrogen-oxygen-rich coordination as a receptor site provide a powerful platform for detectable color change and fluorescence detection. In real samples, sensor structures containing Schiff base and capable of detecting metal ions by various mechanisms attract attention [4]. Schiff base compounds exhibit characteristic photophysical (absorption and emission) properties, have various binding sites, and are easy to synthesize, and these compounds are preferred in designing chemosensors as in many areas [5]. For example, a simply prepared quinoline hydroxyl derivative was used for selectively fluorescent “Off-On” recognition of Ag^+ in aqueous medium [6].

Nitroaromatic compounds such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) are primary military explosives and also major components of unexploded landmines around the world [7]. The highest-energy explosives are nitro-substituted (nitrated) compounds that have the highest priority for detection and are therefore the focus of current investigation. The widespread use of military explosives also raises concerns about environmental pollution where they are produced and stored [8]. Major public health threat such as anemia, carcinogenicity, abnormal liver function, cataract development and skin irritation can occur to both animals and humans through short-term or long-term exposure to nitroaromatic explosives [9]. Detection of explosives in aqueous solution is of great importance due to the spread of terrorist activities from land to sea, the protection of underwater mines and the characterization of soil groundwater pollution [10]. Commercially available methods for detecting explosives are trained dogs, metal detectors, and ion mobility spectrometry (IMS) [11]. Therefore, there is an urgent need for innovative detection strategies that are not only cost-effective and convenient, but also highly sensitive and selective [12]. Explosive detection of optical sensors including absorbance (colorimetric) and fluorescence spectroscopy has begun to be used [13]. In addition, the source and detector of the fluorescent method can be easily incorporated into a hand-held device for field detection of explosives. Therefore, the fluorescence-based method has an important field of use in the rapid, sensitive and selective detection of explosives. Polyaromatic conjugated structures are widely used as fluorescent-based explosive sensors [14–16].

In this work, we prepared two Schiff base ligands derived from 5-aminoisophthalic acid (Scheme 1) and characterized their structures by spectroscopic and analytical methods. Sensing ability of the compounds toward metal ions and nitroaromatic compounds were investigated.



Scheme 1. Synthesis of Z_{2a} and Z_{2b}.

MATERIALS and METHODS

Materials and Instrumentation

All reagents and solvents were provided from commercial sources (Aldrich or Merck) and were used as received without further purification. A Perkin-Elmer FT-IR spectrometer (Spectrum 400) equipped with an ATR was used to record infrared spectra. $^1H(^{13}C)$ NMR spectra were obtained in d_6-DMSO solvent on a Bruker 400 MHz equipment and TMS was utilized as an internal standard. The Hitachi U3900H Spectrophotometer was used to measure UV-Vis absorption spectra.

Synthesis of Z_{2a} and Z_{2b}

5-aminoisophthalic acid (0.905 g, 5 mmol) was dissolved in ethanol (30 mL). To this solution, salicylaldehyde (0.610 g, 5 mmol) for Z_{2a} or 2,3-dihydroxybenzaldehyde (0.690 g, 5 mmol) for Z_{2b} dissolved in ethanol (20 mL) was added. The solution colours changed to orange with the addition of aldehyde. The reaction mixtures were refluxed for 24 hours. The consumption of the aldehydes in the reactions are followed by TLC [17]. After completion of reactions, the mixtures are cooled to the room temperature. The orange-coloured precipitates were filtered and dried in air.

Z_{2a}: Molecular Formula: $C_{15}H_{11}NO_5$. Molecular weight: 285.26 g/mol. Yield: 86%. Colour: Orange. m.p.: >300 °C (decomposed). FTIR (ATR, cm^{-1}): 3198, 3070, 1721, 1695, 1627, 1595, 1572, 1499, 1447, 1405, 1374, 1276, 1192, 1153, 1131, 970, 896, 788, 749, 726, 679, 662, 603, 568, 503. Elemental analysis found (calculated for $C_{15}H_{11}NO_5$) %: C, 62.96 (63.16); H, 3.72 (3.89); N, 4.78 (4.91). ^1H NMR (ppm, DMSO-d_6): δ 12.65 (1H, b, -COOH), 10.73 (1H, b, -OH), 8.39 (1H, s, CH=N_{imine}), 8.13 (2H, s, $CH_{aromatic}$), 7.76 (1H, d, $CH_{aromatic}$), 7.54 (1H, d, $CH_{aromatic}$), 7.50-7.44(1H, t, $CH_{aromatic}$), 7.37(1H, s, $CH_{aromatic}$), 6.99-6.94 (1H, t, $CH_{aromatic}$). ^{13}C NMR (ppm, DMSO-d_6): δ 192.41 ($\underline{C}$OOH), 167.53 ($\underline{C}$=N_{imine}), 166.84, 160.60, 149.23, 136.07, 131.92, 129.73, 126.34, 123.27, 119.77, 117.68. ESI-Q-TOF (m/z): 286.0748 $[M + H]^+$, 318.1734 $[M + CH_3OH + Na]^+$.

Z_{2b}: Molecular Formula: $C_{15}H_{11}NO_6$. Molecular weight: 301.25 g/mol. Yield: %83. Colour: Orange. m.p.: 256-260 °C (decomposed). FTIR (ATR, cm^{-1}): 3190, 2887, 1723, 1695, 1644, 1616, 1548, 1462, 1361, 1283, 1198, 1220, 1027, 969, 911, 855, 775, 724, 675, 609, 500. Elemental analysis found (calculated for $C_{15}H_{11}NO_6.C_2H_5OH$) %: C, 58.65 (58.79); H, 4.83 (4.93); N, 3.95 (4.03). ^1H NMR (ppm, DMSO-d_6): δ 12.76 (1H, b, -COOH), 10.21(1H, b, -OH), 9.07(1H, s, $CH_{aromatic}$), 8.39(1H, s, CH=N_{imine}), 8.12(2H, s, $CH_{aromatic}$), 7.65(1H, d, $CH_{aromatic}$), 7.20(1H, d, $CH_{aromatic}$), 6.84(1H, t, $CH_{aromatic}$), 3.47-4.43(2H, q, -$CH_{2ethanol}$), 0.99(3H, t, -$CH_{3ethanol}$). ^{13}C NMR (ppm, DMSO-d_6): δ 193.19 ($\underline{C}$OOH), 167.68 ($\underline{C}$=N_{imine}), 166.66 ($\underline{C}$-O), 166.35 ($\underline{C}$-O), 149.56, 146.48, 133.28, 131.81, 127.95, 126.31, 123.51, 117.38, 56.13 (-$\underline{C}H_2$-$O_{ethanol}$), 19.08 ($\underline{C}H_3$-$_{ethanol}$). ESI-Q-TOF (m/z): 353.2715 $[M + CH_3OH + H_2O + H]^+$, 381.3046 $[M + 2CH_3OH + H_2O]^+$.

RESULTS and DISCUSSION

In the context of this study, we have prepared two Schiff base ligands (Z_{2a} and Z_{2b}) by condensation reaction of 5-aminoisophthalic acid with salicylaldehyde (Z_{2a}) or 2,3-dihydroxybenzaldehyde (Z_{2b}) (Scheme 1). The compounds were obtained in high yield and purity [18]. The structural characterizations of the compounds were done by FT-IR, $^1H/^{13}C$ NMR and mass spectral analysis. The compounds were tested for their sensing abilities towards metal ions and nitroaromatic compounds [19].

FTIR spectra of Schiff base compounds (Z_{2a} and Z_{2b}) were taken in order to address the characteristic bond stretching's in the structures. FTIR spectral data were given in the experimental section and spectra of the compounds were provided in the supplementary documents (Figs. S1 and S2). The characteristic imine bond (C=N) stretching's were observed at 1627 and 1616 cm^{-1}, respectively [20–23]. The sharp peaks observed in 1721 and 1695 cm^{-1} for Z_{2a}, 1723 and 1695 cm^{-1} for Z_{2b} are assigned to the carboxy group stretching's n(COO) [24] . Observing carboxyl group stretching's n(C=O) peaks as two separate peaks was interpreted as the co-existence of the solid form phenol-imine tautomeric form and the keto-amin/zwitter ion form for these compounds. Peaks observed in FTIR spectrums of Z_{2a}-Z_{2b} compounds are in harmony with similar compound spectrums found in the literature [24].

In order to characterize the synthesized Schiff base compounds, their $^1H(^{13}C)$ NMR spectra were taken in d_6-DMSO. The $^1H(^{13}C)$ NMR spectra of the compounds are given in Figures 1&2.

In the ^1H NMR spectra of Z_{2a} and Z_{2b}, the carboxyl group protons (-COOH) were observed as peaks at 12.65 and 12.76 ppm, respectively [24–26]. The phenolic group protons were observed at 10.73 and 10.21 ppm respectively [21, 27]. A singlet peak at 8.39 ppm for both

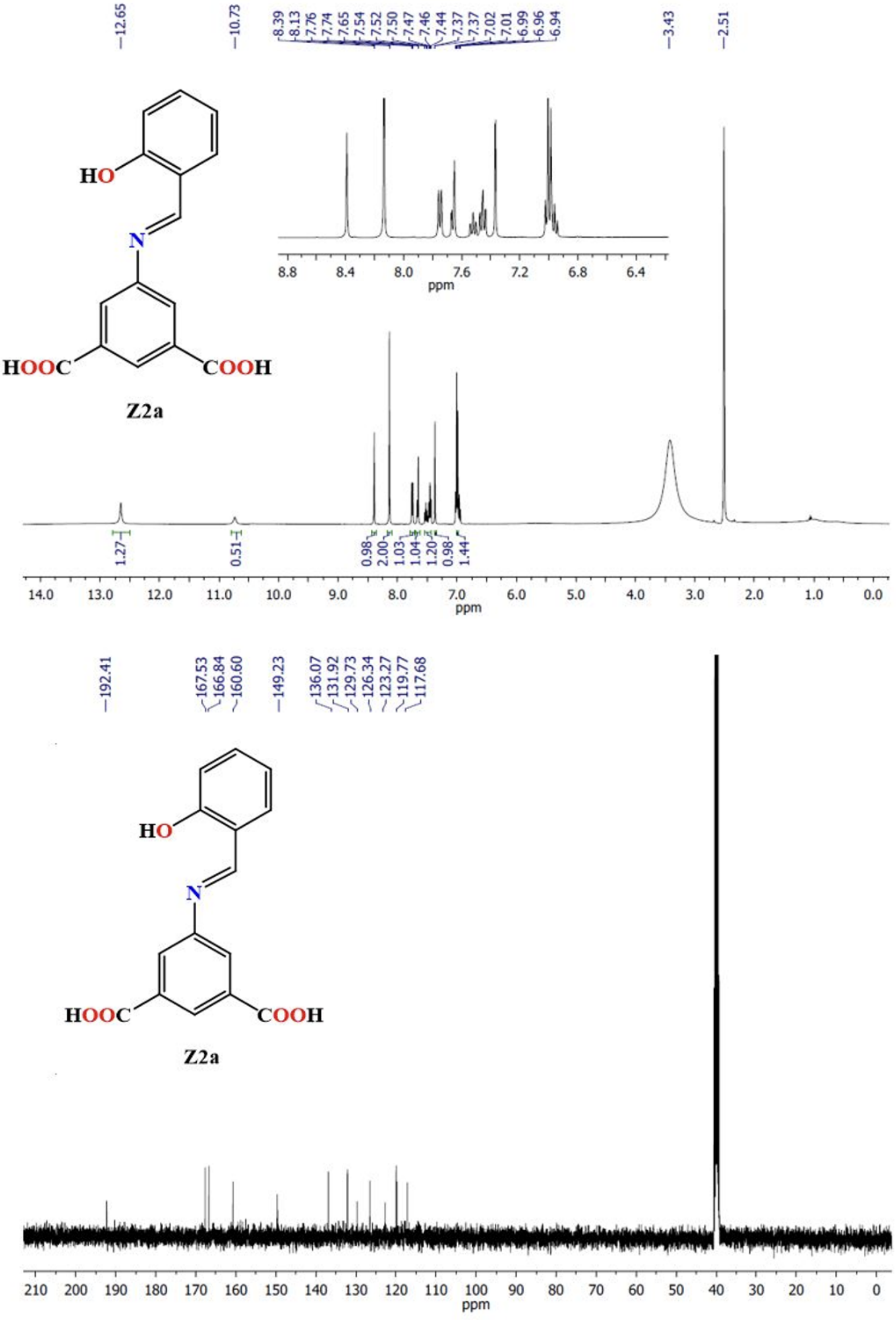


Figure 1. ^{1}H(^{13}C) NMR spectra of Z_{2a}.

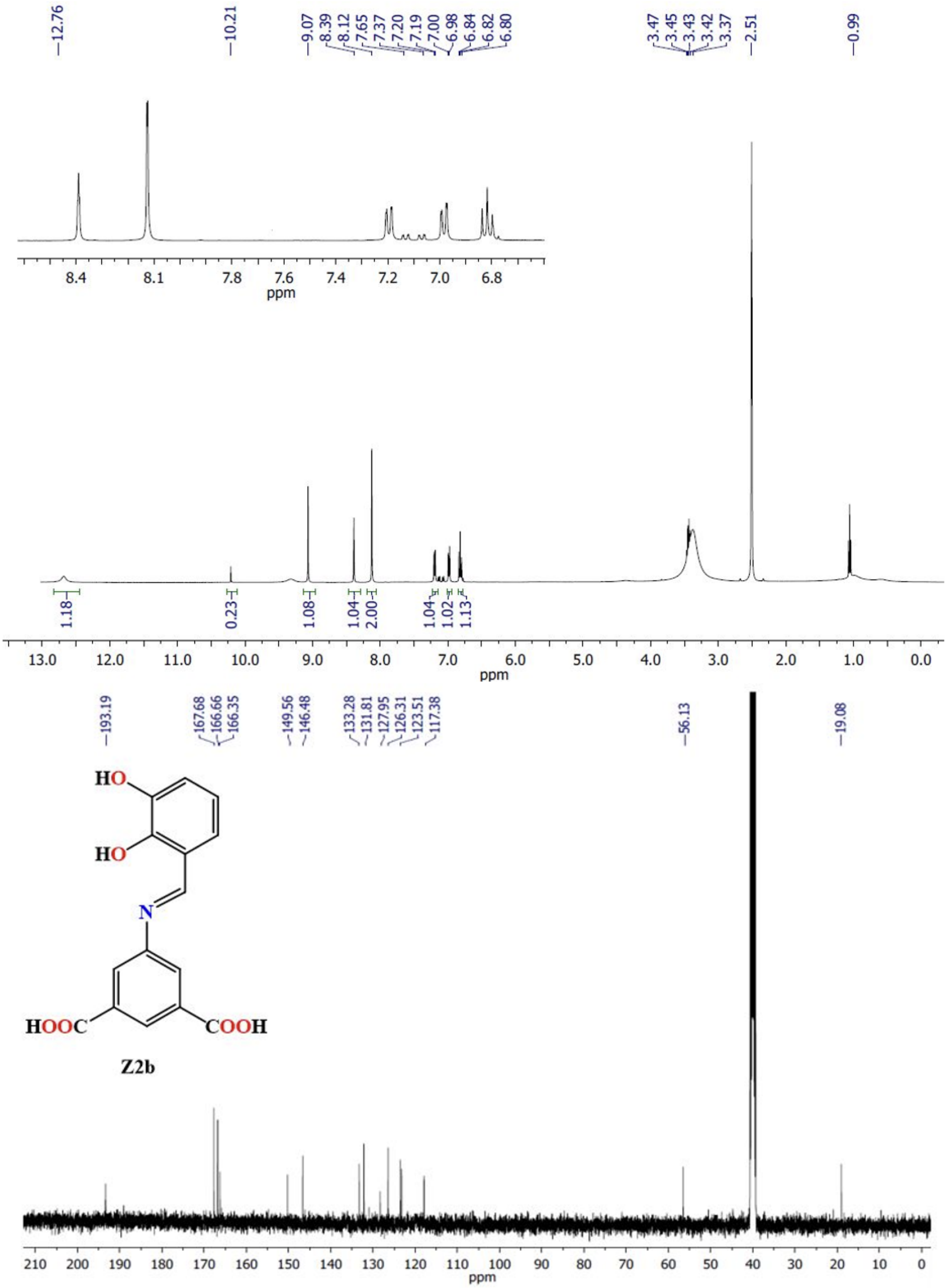


Figure 2. ^{1}H(^{13}C) NMR spectra of Z_{2b}.

ligands were assigned to the imine group protons. Aromatic proton signals in the range of 8.13-6.84 ppm were observed in the spectrums of both compounds. In the spectrum of Z_{2b}, two multiplet peaks at 4.43 and 0.99 ppm are due to the proton signals of ethanol solvent and integration values suggest that there is one ethanol solvent per molecule in the compound sample. The integration values for proton assignments were in good agreement with their proposed structure.

When the ^{13}C NMR spectrums of the compounds were examined, carbon atomic signals observed at 192.41 (Z_{2a}) and 193.19 (Z_{2b}) ppm were caused by the carboxyl (-COOH) group [24]. The peaks at 167.53 for Z_{2a} and 167.68 for Z_{2b} ppm are attributed to the bond of imine group carbon atom (C=N) [28, 29]. In the spectra of the compounds, aromatic carbon atom signals were observed in the range of 166.84-117.38 ppm. It has been observed that the compounds are compatible with peak numbers structures observed in the ^{13}C NMR spectra. The two signals observed at 56.13 and 19.08 ppm in the ^{13}C NMR spectrum of Z_{2b} are carbon atom signals from the ethanol solvent found in the sample.

The structure of the compounds was further characterized by ESI-Q-TOF mass spectral analysis and molecular ion peaks were observed for both compounds. ESI-Q-TOF mass spectra of the compounds were given in Figure 3. In the spectrum of Z_{2a}, peaks at m/z 286.0748 and 318.1734 were assigned to the molecular ions

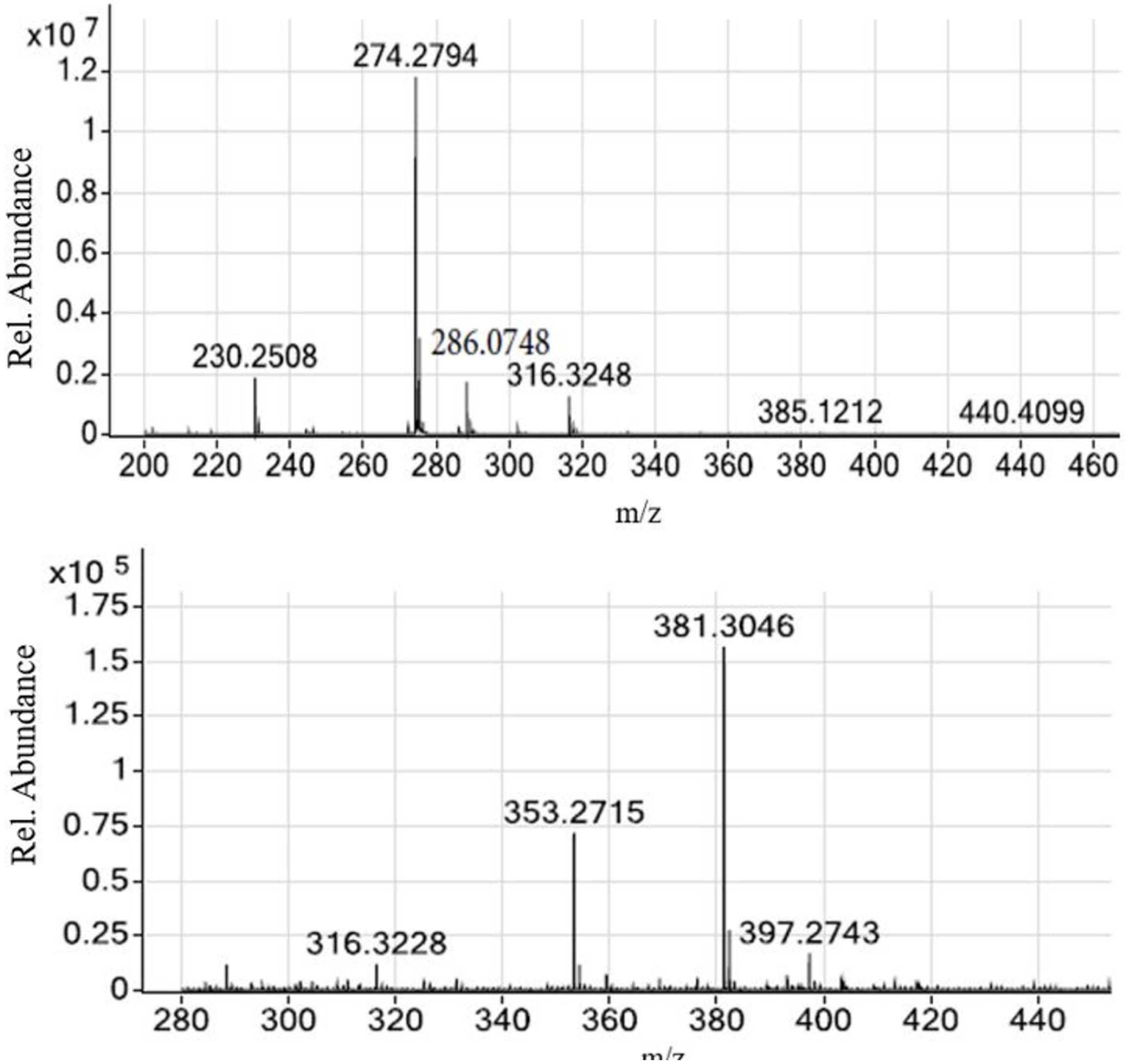


Figure 3. ESI-Q-TOF spectra of Z_{2a} (top) and Z_{2b}(bottom).

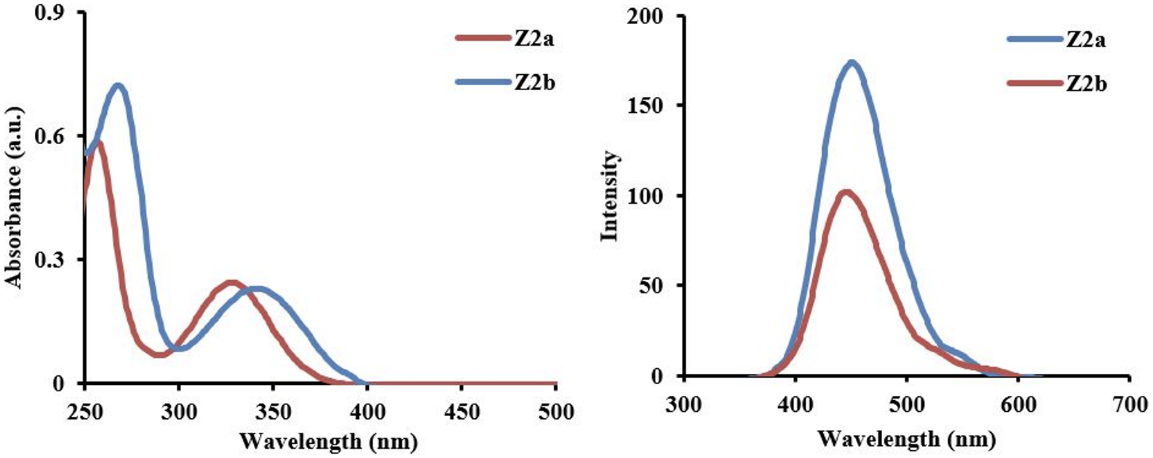


Figure 4. UV-Vis absorption (up) and emission spectra (down) of Z_{2a} and Z_{2b} in DMSO (10^{-5} M).

$[M+H]^+$ and $[M+Na]^+$, respectively. In the spectrum of Z_{2b}, two peaks at m/z 353.2715 and 381.3046 were assigned to the positively charged molecular ions species $[M+CH_3OH, H]^+$ and $[M+2CH_3OH, H]^+$, respectively.

UV-Vis absorption and photoluminescence properties of the Schiff base were investigated compounds in DMSO (10^{-5} M). UV-Vis absorption and photoluminescence spectra of Z_{2a} are shown in Figure 4. The spectra of Z_{2b} are provided in the supplementary documents. In the UV-Vis absorption spectra of the compounds Z_{2a} and Z_{2b}, there are two absorption bands in the range of 250-380 nm [26, 28]. The first band was observed at 250-300 nm range and this absorption band was assigned to the π-π* electronic transitions of π-electrons in the structures. The second absorption band was seen at 300-380 nm with lower absorption values. This absorption band can be attributed to the n-π* electronic transitions. The compounds are also emissive when excited in the UV region. Both compounds gave emission maximums in the blue region (400-500 nm) when they were excited in the range of 250-274 nm. Although emission wavelengths are similar for both compounds, the emission intensity of Z_{2a} are considerably higher than that of Z_{2b}. This may be due to the second hydroxyl group in Z_{2b} which may cause energy transfer in the excited state.

Sensor properties towards metal ions

The chemosensory properties of Z_{2a} and Z_{2b} against metal cations were investigated colorimetric and spectrophotometric methods. Color changes of ligands in the presence of metal ions (1:1 ratio) were investigated under daylight, 254 (short wavelength) and 365 nm (long wavelength) light. Color changes of the DMSO solution (10^{-5} M) of the compounds Z_{2a} and Z_{2b} in the presence of various metal ions are given in Figure 5. DMSO solutions (10^{-5} M) of both the Z_{2a} and Z_{2b} are yellow in under daylight. With the addition of Fe^{3+}, the color of both ligands has turned to yellow-brown. The addition of Hg^{2+} turns Z_{2a}'s solution color slightly yellow, while the solution color of Z_{2b} is noticeably brown. No noticeable change in the solution colors of both ligands was observed in the presence of other metal ions. Under short wavelength light (254 nm), the Z_{2a} and Z_{2b} compounds showed blue fluorescence. While there was a slight dampening of blue fluorescence in the presence of Fe^{+3} and Hg^{+2} ions, no color change was observed in the presence of other metal ions. Under long wavelength light (365 nm), both ligands showed blue-turquoise fluorescence. Na^+, K^+, Al^{3+}, Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{+2} and Pb^{2+} ions were observed with turquoise fluorescence and no noticeable color changes were observed. In the presence of Fe^{3+} and Hg^{2+} ions, quenching of fluorescence characteristics of both compounds was detected. Fluorescence quenching in the presence of Fe^{3+} and Hg^{2+} ions was also observed in emission spectra.

When the UV-Vis spectra of receptor compounds were examined in the presence of metal ions, no significant change was observed in the wavelengths of the absorption bands of the receptor compounds. In the presence of Fe^{3+} and Hg^{2+} ions, a significant increase in the absorbance values of the absorption bands of the ligand was observed. The emission spectral changes of Z_{2a} and Z_{2b} solutions in the range of 400-550 nm (excited at 256 nm for Z_{2a} and 269 nm for Z_{2b}) with the addition of metal ions were investigated. In the presence of all metal ions, the emission intensities of

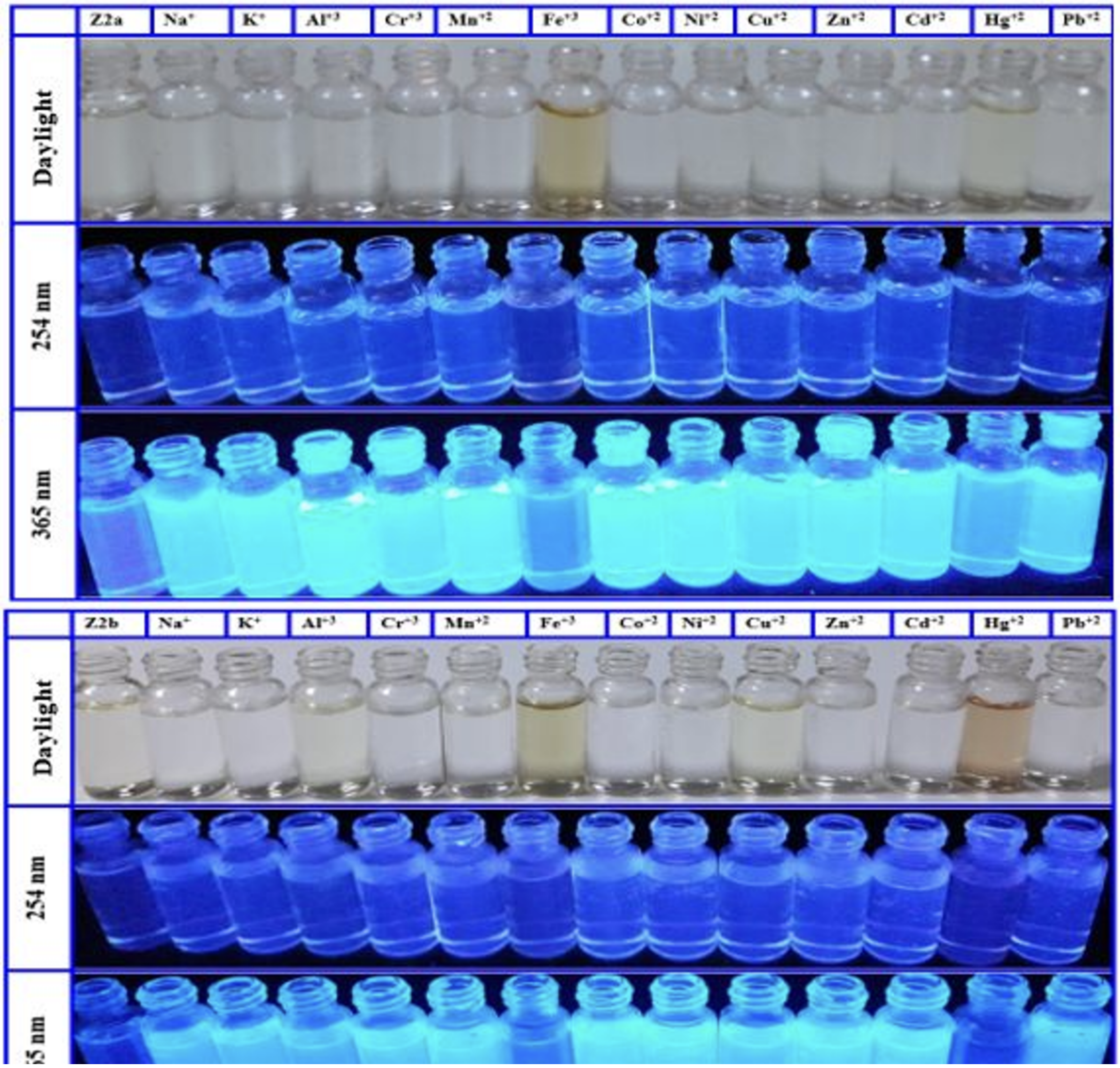


Figure 5. Color changes of Z_{2a} and Z_{2b} in the presence of metal ions under day light and UV-lamp (254 and 365 nm).

Z_{2a} and Z_{2b} decreased. However, in the presence of Fe^{3+} and Hg^{2+} ions, the emission of Z_{2b} is almost turned off. Z_{2b} compounds showed colorimetric and fluorimetric sensor properties against Fe^{3+} and Hg^{2+} ions in solution environment.

Fluorimetric sensing of nitro-aromatic compounds

Fluorescent quenching-based fluorimetric sensing are one of the selective and sensitive methods that have been frequently studied in recent years for the detection of nitro-aromatic explosives [30]. The quenching effect occurs in the emission band mainly due to the interaction of the fluorescence sensor with the nitroaromatic compounds [31]. Usually hydrogen bonding and π-π interactions occur between the fluorimetric sensor and the analyte. Monomers, polymers and metal-organic frameworks with highly conjugated π-electrons are often used for the detection of nitroaromatic compounds. There are many reported fluorescence quenching-based fluorimetric sensors for the detection of nitroaromatic compounds in the literature [31]. However, they have several drawbacks such as high cost, multi-step synthesis, reusability, lack of selectivity, and low sensitivity. The fluorimetric sensing properties of the Schiff base-based compounds that were synthesized within the scope of the work were investigated by fluorescence spectroscopy in the detection of nitroaromatic compounds. DMSO solutions of nitroaromatic compounds were added to the DMSO solution of the compounds (keeping the ligand concentration constant). The emission spectra of the obtained mixtures were taken

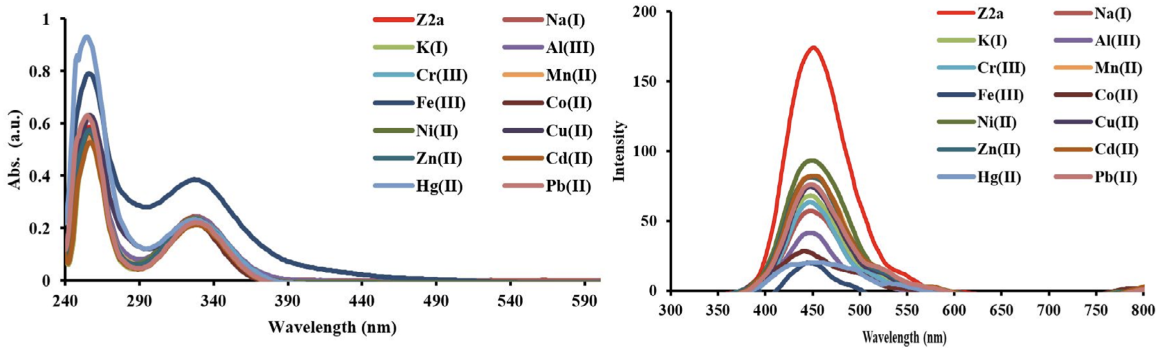


Figure 6. Absorbance and emission spectra changes of Z_{2a} in the presence of metal ions.

Table 1. Figure-of-merit (FOM) calculation of the sensor at different glycerol concentrations (FWHM represents full width at half maximum of the curves).

		K_{sv} M^{-1} (R^2)		
Compound	NB	NP	DNP	TNP
Z_{2a}	$8.30\times10^3(0.9897)$	$1.80\times10^3(0.9900)$	$1.84\times10^4(0.9906)$	1.66×10^4 (0.9835)
Z_{2b}	$3.09\times10^3(0.9868)$	$3.40\times10^3(0.9928)$	$2.4\times10^4(0.9892)$	1.93×10^4 (0.9970)
		Limit of detections (LOD, µM)		
	NB	NP	DNP	TNP
Z_{2a}	16.89	66.42	10.16	15.75
Z_{2b}	3.84	25.72	2.77	7.25

at the excitation wavelength of the fluorescent compound, and fluorometric titrations in the presence of incremental addition of nitroaromatic compounds were performed. In this study, nitrobenzene (NB), 4-nitrophenol (NP), 2,4-dinitrophenol (DNP) and 1,3,5-trinitrophenol (TNP) available in our laboratory were selected as nitroaromatic compounds. The emission band of the ligands decreased with gradual addition of nitroaromatic compounds. The nitroaromatic compounds caused a quenching effect in the emission spectra. It was observed that this decrease was linear for all nitroaromatic compounds.

In order to examine the quenching efficiency of the compounds for sensitivities towards nitroaromatic compounds, Stern-Volmer plots (I_0/I vs [A]) were drawn and quenching constants (K_{sv}) were obtained. The obtained K_{sv} values are given in Table 1.

When the obtained K_{sv} values were examined, it can be seen that both compounds showed higher sensitivities to DNP and TNP than the other nitroaromatics. Compound Z_{2b} showed better sensitivity towards DNP and TNP than compound Z_{2a}. Emission spectral change, Stern-Volmer plot (I_0/I vs [A]) and emission quenching percentages of compound Z_{2b} in the presence of 5-100 mM TNP are given in Figure 7. As the TNP concentration increased, there was a linear decrease in the emission intensity of compound Z_{2b}. Emission intensity at 435 nm decreased by 10% in the presence of 5 µM TNP. Addition of 100 µM TNP, the emission intensity decreased by 70%. Compound Z_{2b} exhibit the highest sensitivity for DNP amongst the studied nitroaromatic compounds. The higher sensitivity of the compounds towards DNP can be explained better energy transfer in the excited state between the florescent receptor compounds (Z_{2a} and Z_{2b}) and DNP. Based on the fluorescence titration data in the presence of nitroaromatic compounds, we also calculated the limit of detections (LOD) for nitroaromatic compounds and LOD values are given in Table 1. The compound Z_{2a} and Z_{2b} showed LOD in micromolar levels. Compound Z_{2b} showed lower LOD values for studied nitroaromatic compounds than compound Z_{2a}. Compound Z_{2b} showed the lowest LOD value for DNP (LOD: 2.77 mM). Compound Z_{2b} showed best sensitivity and lowest LOD for DNP.

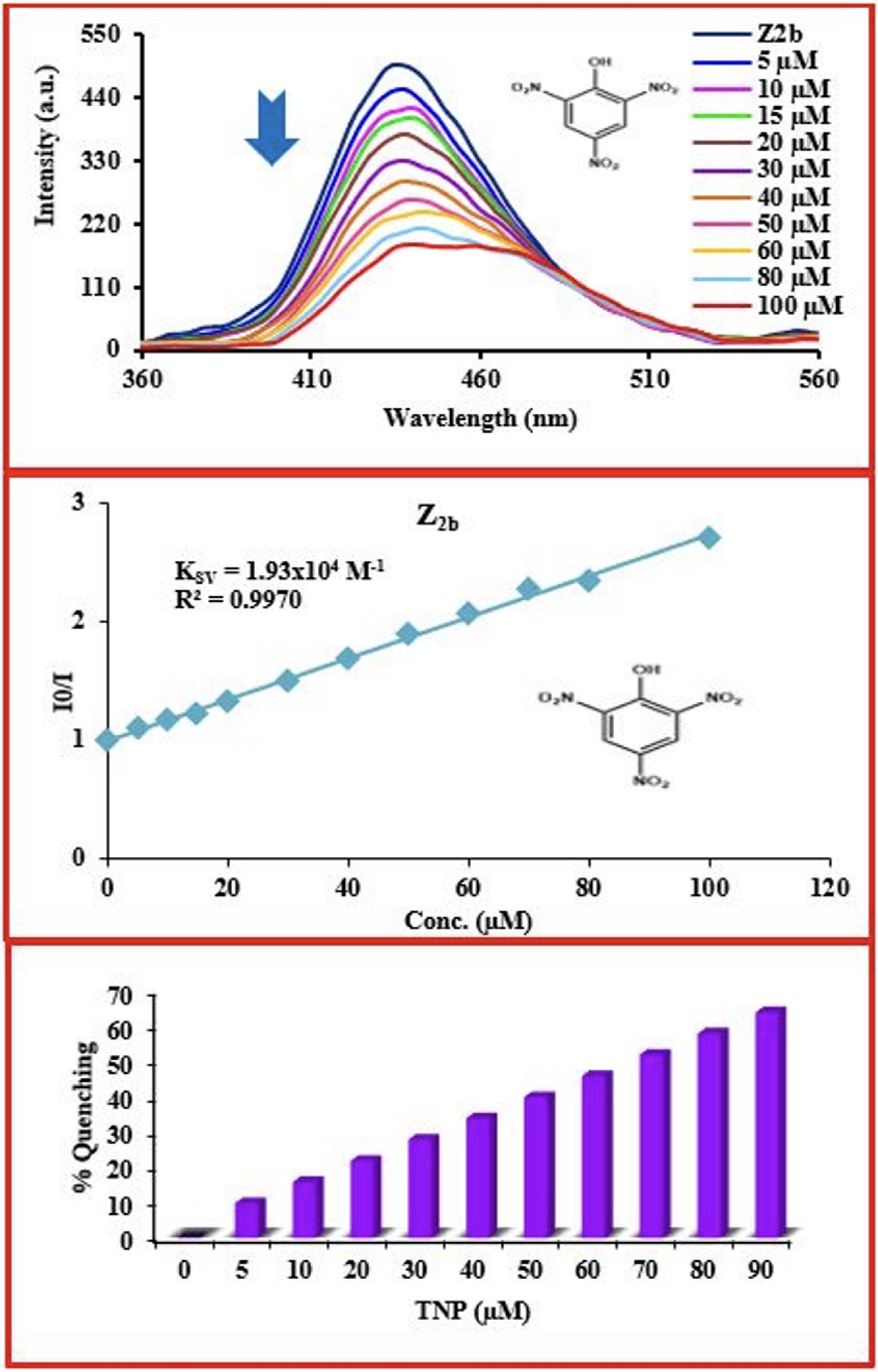


Figure 7. a) Emission spectra change of Z_{2b} upon incremental addition of TNP. b) Stern-Volmer plot (I0/I vs [A] c) Emission quenching percentage upon increased amount of TNP.

CONCLUSIONS

In this work, we prepared two Schiff base ligands from the reaction 5-aminoisophthalic acid and salicylaldehyde (Z_{2a}) or 2,3-dihydroxybenzaldehyde (Z_{2b}). The compounds were characterized by elementel analysis, FTIR, $^1H/^{13}C$ NMR and mass spectral studies. The compounds were screened for their sensing properties towards cations and nitroaromatic compounds. Colorimetric and fluorimetric studies revealed that both compounds (Z_{2a} and Z_{2b}) have selective sensing abilities towards Fe^{3+} and Hg^{2+} ions. Both Fe^{3+} and Hg^{2+} ions caused quenching of emission band of the free ligands. Fluorimetric sensing properties of the synthesized compounds towards nitroaromatic compounds [nitrobenzene (NB), 4-nitrophenol (NP), 2,4-dinitrophenol (DNP) and 1,3,5-trinitrophenol (TNP)] have also been investigated and data showed that compound Z_{2b} showed the best sensitivity and lowest LOD values for DNP. Compound Z_{2b} showed the lowest LOD value for DNP (LOD: 2.77 mM).

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