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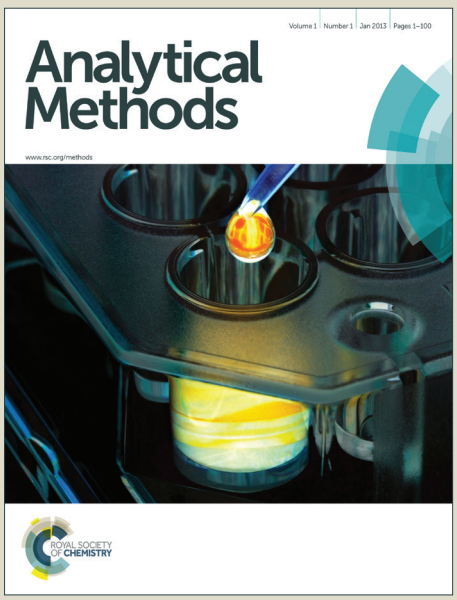

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Azo Schiff bases as colorimetric and fluorescent sensors for selective recognition of F^-, Cd^{+2} and Hg^{+2} ions

Raziyeh Arabahmadi[a], Masoumeh Orojloo[b] and Saeid Amani*[b]

[a]Chemistry Department, Payame Noor University (PNU), Tehran 19395-3697, Iran

[b]Chemistry Department, Faculty of Sciences, Arak University, Dr. Beheshti Ave., Arak 38156-8-8349, Iran

Abstract

The optical and colorimetric sensing properties of H_2L^1 - H_2L^3 for anions were investigated by naked eye and UV–Vis, fluorescence spectroscopy. These chemosensors show visual changes towards anions like F^- and also towards cations such as Hg^{2+} and Cd^{2+} in DMSO. Yet, other anions such as Cl^-, Br^-, NO_3^-, OAc^-, HSO_4^-, $H_2PO_4^-$ and CN^- could not cause any color change. The ligands do not show any significant change on addition of other metal ions like Mn^{2+}, Fe^{+2}, Co^{+2}, Ni^{2+} ,Cu^{+2} and Zn^{2+}. The binding constant (Ka) and stoichiometry of host-guest complex formed were determined by Benesi–Hildebrand (B–H) plot and Job's plot method, respectively. The anion sensing abilities of the receptors toward halide anions were also monitored by electrochemical techniques.

Keywords: Electrochemical study, Chemosensor, Anion recognition, Transition metal ions.

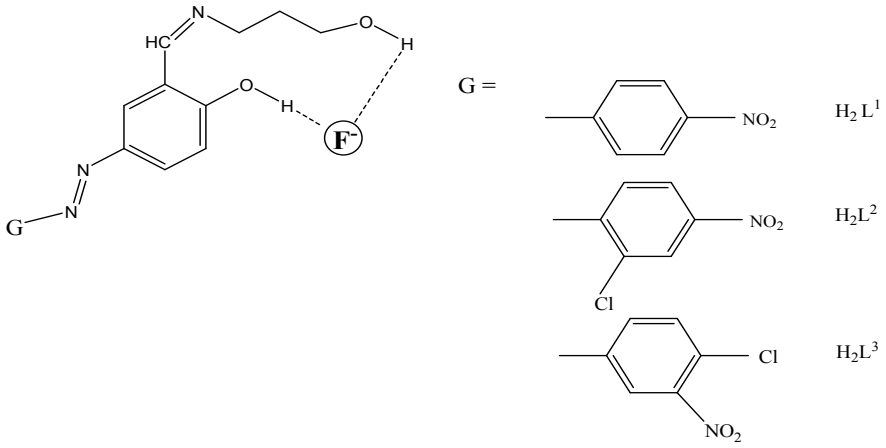
* Author to whom all correspondences should be addressed

E-mail: s-amani@phd.araku.ac.ir, Phone office: +98 8634173415; Fax office: +98 8634173406

1. Introduction

There is an increasing interest in the development of a new generation of molecules for the sensing of target chemical species of environmental or biological interest. Inorganic anionic and cationic species have a huge impact on biology and environment. The anions play an important role in a wide range of chemical and biological processes, and can have deleterious effects on both the environment and the human health, thus justifying the growth in the demand for selective anion receptors and sensors [1–5]. Among the various anions, fluoride is of particular interest due to its established role in preventing dental caries and treatment of osteoporosis [6–8]. Although cation receptors have been studied for more than four decades but the development of anion receptors received less attention. Several reasons why reliable sensing of anions is a particularly challenging area of research are: (i) anions are larger than isoelectronic cations and, therefore, have lower charge-to-radius (surface) ratio, a feature that makes the electrostatic binding of anions to the receptors less effective [9], (ii) anions have a wide range of geometries and are often present in delocalized forms, which results in higher complexity in design and synthesis of receptors and (iii) pH sensitivity. Therefore, to achieve the desired selectivity, the combination of electrostatic attraction, hydrogen bonding and a suitable framework onto which these structural components can be assembled needs to be taken into consideration when designing artificial anionic hosts [10]. Chemosensors are the molecules of abiotic origin that bind selectively and reversibly with the analyte [11]. Hitherto, numerous colorimetric and/or fluorescent chemosensors for anions, cations or neutral molecules have been reported; however, almost all of these are designed to rely upon the same Principles namely, that the functional moiety is covalently (binding site-signalling subunit approach) [12-15] or non-covalently (displacement approach) [16, 17] linked to the signal moiety (eg chromogene, electrochemical group, fluorescent group). Molina et al. used azobenzene dyes for the sensing of fluoride ion via binding constant, color and UV–Vis changes [18, 19]. During the last few years, the fluorescent sensors appear particularly attractive because they offer the potential for high sensitivity at low analyte concentration [20]. Most of the reported receptors upon binding with anions exhibit fluorescence intensity changes on a single wavelength [21]. However, several factors such as phototransformation, receptor concentration and

environmental effects contribute to the fluorescence intensity modulation of a system. [22] Cheng et al. demonstrated that a series of azobenzene dyes receptors showed a selective color change on addition of Cd^{2+} and Hg^{2+} metal ions [23-24]. This paper concerns a novel colorimetric and fluorescent anion comprises a OH- phenolic group (anion binding site) coupled to with a phenylazo group (chromogenic and fluorescence unit). The behavior of this new compound towards anions eg fluoride, was investigated by UV-Vis and fluorescence spectroscopy in DMSO. Just as expected, the sensors H_2L^1 - H_2L^3 could act as a convenient, colorimetric and fluorescent chemosensor for biologically inorganic anions and cations (Scheme1).



Scheme1. Structure of H_2L^1 - H_2L^3 with fluoride ion.

2. Experimental

Electronic spectra of receptors in DMSO were recorded on a Perkin-Elmer Lambda 15 and fluorescence intensity was measured by luminescence spectrophotometer Perkin-Elmer (LS50). The electrochemical experiments were carried out using an Autolab PGSTAT-302 (potentiostat/galvanostat) equipped with a USB electrochemical interface and driven by a NOVA 1.8 software package (Eco Chemie, Utrecht, The Netherlands). All readings were taken using three electrode potentiostatic systems in DMSO with 0.1 mol cm^{-3} tetrabutylammonium perchlorate (TBAP, electrochemical grade) as supporting electrolyte. A three-

electrode assembly composed of a platinum working electrode, a platinum auxiliary electrode, and calomel reference electrode was used with sample concentrations of 1×10^{-3} M.

All anions in the form of tetrabutylammonium salts were purchased from Fluka and used without further purification. All solvents were of reagent grade quality and were purchased from Merck Chemical Company and used as received without further purification. The Mn^{2+}, Fe^{+2}, Co^{+2}, Ni^{2+}, Cu^{+2}, Zn^{2+}, Hg^{2+} and Cd^{2+} were added as chloride salt solutions in DMSO. Azo dyes H_2L^1 - H_2L^3 were synthesized according to the well-known literature procedure [25].

3. Results and Discussion

3.1. Electronic absorption spectra

The electronic absorption spectra of H_2L^1 - H_2L^3, recorded in DMSO at room temperature display mainly three bands, Fig. 1. The first band located at 265–269 nm can be assigned to the moderate energy ($\pi\rightarrow\pi^*$) transition of the aromatic rings while the second band at 403–416 nm is due to low energy ($\pi\rightarrow\pi^*$) transition involving the π-electrons of the azo and azomethine groups [26]. On the other hand, the absorption spectra of H_2L^1 - H_2L^3 display a broad band at 443–470 nm assigned to $n\rightarrow\pi^*$ transition of azo and azomethine chromophores and also intramolecular charge transfer interaction involving the whole molecule of the dye. The intramolecular CT band can be assigned to the existence of tautomeric equilibrium originating from hydroxyl group in o-position of aromatic ring. Examination of the results reported in Table 1, reveals that the position of low energy $\pi\rightarrow\pi^*$ band is influenced by the nature of the para-substituent, R.

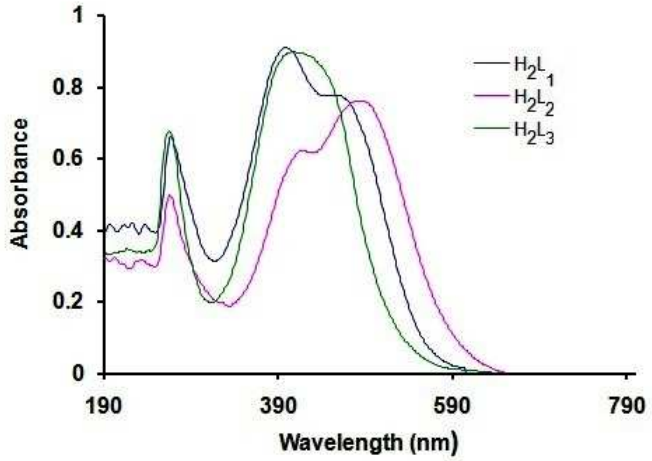


Fig. 1. The absorption spectra of H_2L^1 - H_2L^3 in DMSO.

3.2. Solvent effect on the electronic spectra

It has been accepted that the electronic transitions of azo-azomethine compounds strongly depend on the nature of media [27]. For this purpose, the electronic absorption spectra of 3×10^{-5} M solution of H_2L^1 - H_2L^3 in four organic solvents with different polarity were measured at room temperature. The absorption spectra of H_2L^1 in various solvents are shown in Fig. 2 (for other dyes, see Supporting information, Fig. S1-S2). The influence of solvents for the prepared dyes increases in the order DMSO > DMF > THF > $CHCl_3$. It was found that the absorption band at 443–470 nm generally shows hypsochromic shift (negative solvatochromism) as the polarity of solvent was increased (Table 1), indicating a reduction in the dipole moment upon electronic excitation. The other band at 403–416 nm shows bathochromic shift (positive solvatochromism) upon increasing solvent polarity. This positive solvatochromism exhibited by the dyes may be due to the effect of dipole moment changes of the excited state and/or changes in the hydrogen bonding strength in polar solvents [27].

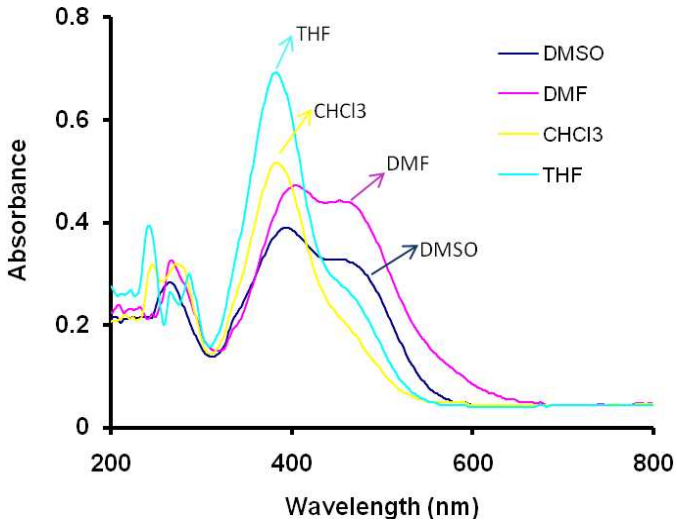


Fig. 2. The absorption spectra of H_2L^1 in solvents with different polarities.

Table 1

Absorption spectral data of H_2L^1 - H_2L^3 in various organic solvents; λ_{max}/nm (ε/dm mol^{-1} cm^{-1}).

Compounds	DMSO	DMF	THF	$CHCl_3$
H_2L^1	269(8996) 406(12453) 460(10926)	268(10640) 399(15323) 462(14696)	239(12687) 253(8503) 282(9470) 385(22403) 463(10576)	242(9980) 262(10070) 386(16636) 465(7970)
H_2L^2	266(14337) 416(17233) 470(23466)	268(7963) 412(11620) 530(16480)	240(15903) 258(11983) 273(10523) 387(20703) 474(13776)	246(10410) 266(11360) 381(19620) 480(12056)
H_2L^3	265(15740) 403(18890) 443(18890)	264(18426) 417(23146) 465(22406)	242(27083) 262(20276) 272(16296) 360(25740) 450(11853)	257(29626) 357(24260) 453(10926)

3.3. Anion sensing

3.3.1. Colorimetric analysis

The analyte recognition via hydrogen-bonding interactions could be easily followed by the naked-eye or by monitoring the changes in the UV–vis absorption spectra of the receptors H_2L^1 - H_2L^3. Initially, the

qualitative estimation of the affinity of the sensors H_2L^1 - H_2L^3 towards various anions was performed visually. Noticeable color changes were observed when receptors H_2L^1 - H_2L^3 were treated with 2 equiv. of fluoride anion, while no color changes were observed when the 2 equiv. of other anions of Cl^-, Br^-, NO_3^-, OAc^-, HSO_4^-, $H_2PO_4^-$ and CN^- were added, indicating that H_2L^1 - H_2L^3 acted as an efficient and selective colorimetric sensors for fluoride anion (see Fig. 3). It is noteworthy that, for H_2L^1 - H_2L^3, the naked-eye color changes were fully reversible upon addition of water, which presumably competed with the anions for the binding site [24]. The result indicated that the color changes were most probably owing to the formation of the new H_2L^1 - H_2L^3 anion complexed species with different electronic properties from that of the receptors H_2L^1 - H_2L^3 and therefore, new colors were observed.

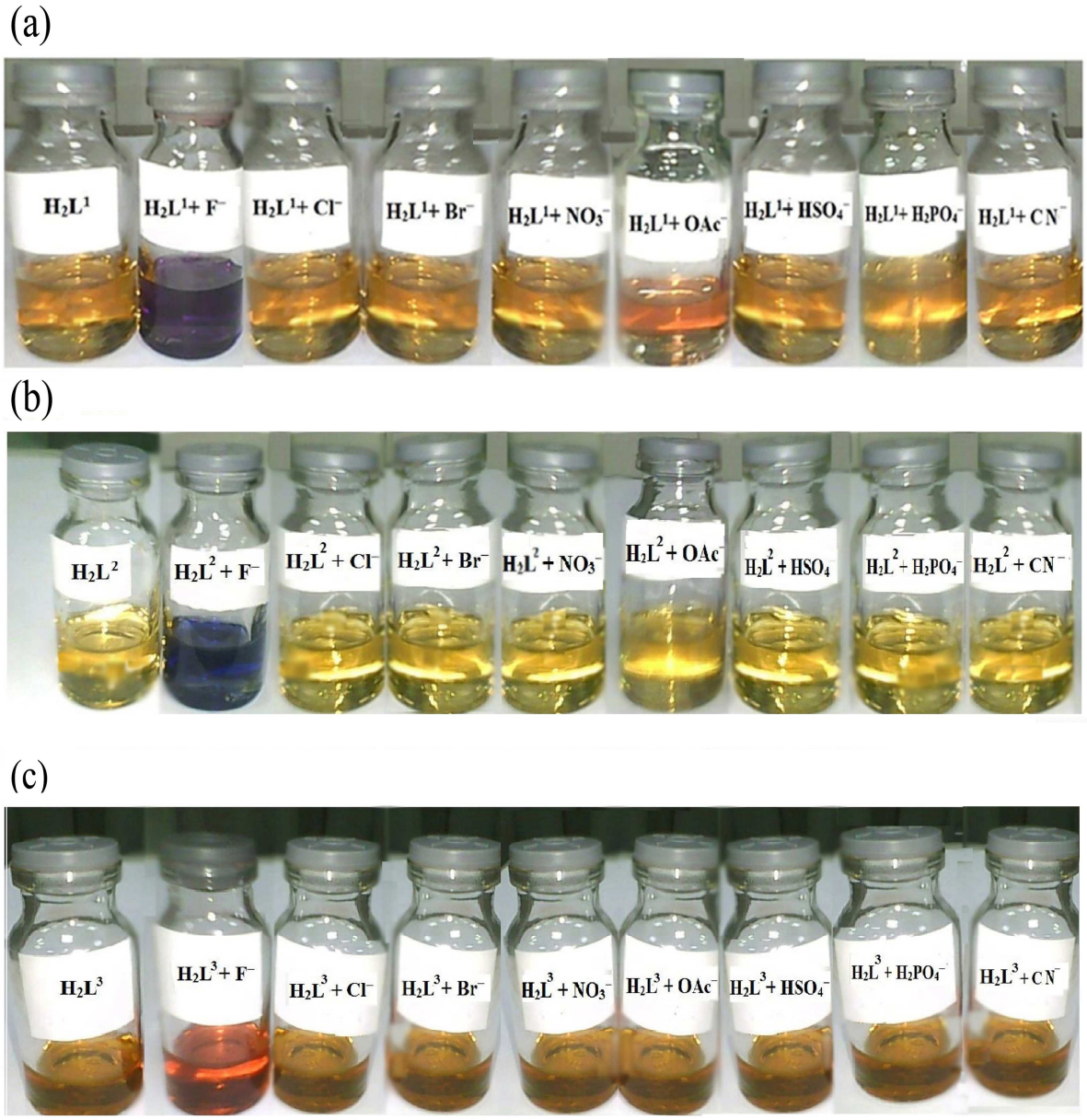


Fig. 3. (a) Color changes of H_2L^1 in DMSO (4×10^{-5} M) before and after the addition of 2 equiv. of respective anions (5×10^{-4} M) (From the left to right H_2L^1, $H_2L^1 + F^-$, $H_2L^1 + Cl^-$, $H_2L^1 + Br^-$, $H_2L^1 + NO_3^-$, $H_2L^1 + OAc^-$, $H_2L^1 + HSO_4^-$, $H_2L^1 + H_2PO_4^-$ and $H_2L^1 + CN^-$). (b) Color changes of H_2L^2 in DMSO (4×10^{-5} M) before and after the addition of 2 equiv. of respective anions (5×10^{-4} M) (From the left to right H_2L^2, $H_2L^2 + F^-$, $H_2L^2 + Cl^-$, $H_2L^2 + Br^-$, $H_2L^2 + NO_3^-$, $H_2L^2 + OAc^-$, $H_2L^2 + HSO_4^-$, $H_2L^2 + H_2PO_4^-$ and $H_2L^2 + CN^-$). (c) Color changes of H_2L^3 in DMSO (4×10^{-5} M) before and after the addition of 2 equiv. of

respective anions (5×10^{-4} M) (From the left to right H_2L^3, $H_2L^3 + F^-$, $H_2L^3 + Cl^-$, $H_2L^3 + Br^-$, $H_2L^3 + NO_3^-$, $H_2L^3 + OAc^-$, $H_2L^3 + HSO_4^-$, $H_2L^3 + H_2PO_4^-$ and $H_2L^3 + CN^-$).

3.3.2. UV–Vis spectroscopic studies

The change in optoelectronic properties of azo-linked salicylaldimine Schiff base ligands in the presence of fluoride anion was investigated by UV–Vis spectroscopic methods. The titrations were carried out in DMSO medium at 4.0×10^{-5} M concentrations of receptors H_2L^1 - H_2L^3 upon the addition of incremental amounts of (5.0×10^{-4} M) of tetrabutylammonium fluoride, the spectra of the receptors are shown in Fig. 4a–d. When increasing the concentration of F^-, in all these receptors H_2L^1 - H_2L^3, a new red shifted absorption band at 553, 580 and 449 nm were gradually enhanced, while the intensity of absorption at 406, 470 and 403 nm were decreased correspondingly. A clear isosbestic points were observed at 504, 529 and 459 nm for H_2L^1 -H_2L^3 respectively. The appearance of a single isosbestic point indicates the presence of only two species, neutral host and its anion in the solution. The inset of Fig. 4a shows the absorbance changes at both 406 and 553 nm for H_2L^1 versus the concentrations of F^-. The results obtained demonstrated the H-bond interactions between the host and the anionic guests affected the electronic properties of the chromophore. Nevertheless, the receptors H_2L^1 - H_2L^3 were insensitive to addition of excess equiv Cl^-, Br^-, NO_3^-, OAc^-, HSO_4^-, $H_2PO_4^-$ and CN^- ions in DMSO (Fig. 4d). So, it corroborates the fact that the receptors provides selectivity for F^- ion which is solely based up on its deprotonation and is related to the factors (a) intrinsic acidity of the receptor, (b) basicity of the anion, and (c) polarity of the solvent [28]. The similar phenomena were observed for sensors H_2L^1 - H_2L^3 with TBA-OH in. The formation of these hydrogen bonds affects the electronic properties of the chromophore, resulting in a color change with a subsequent new intraligand or internal charge transfer (ICT) band involving between the F^--bound hydroxyl group and electron deficient azo moiety. However, a full understanding of the principles that govern anion recognition has not been achieved. It became clear early on that multiple hydrogen-bonding interactions are necessary in high-affinity anion binding sites. Charge and shape complementarity between the host and the anionic guests are also extremely important. Here receptors

H_2L^1 - $H_2L^3$was able to bind fluoride ion more strongly than other anions as phenolic OH moiety being particularly appropriate for effective binding of the smaller anion.

The host–guest interaction was analyzed according to following equations for spectroscopic UV–Vis titration (Eq. (1)) [29].

$$\frac{b}{\Delta A} = \frac{1}{S_t K_a \Delta\varepsilon} \times \frac{1}{[L]} + \frac{1}{S_t \Delta\varepsilon} \qquad \textbf{(1)}$$

The binding constant for the fluoride complexes of receptors H_2L^1 - H_2L^3 were obtained from the variation in the absorbance at 553, 580 and 499 nm, respectively. The binding constant of the receptors with the corresponding anions is summarized in the Table 2. The bonding constant for azo Schiff bases were reported as 2.52×10^3 mol L^{-1} and 6.2×10^3 mol L^{-1} by other research groups [18]. Receptor H_2L^1 (nitro substituent) shows a higher binding constant than the others. This may be due to the presence of the electron-withdrawing group, which results in strong hydrogen bond interactions with fluoride. Judging from the titrations, the strong binding of fluoride allowed the Job's plot method to be used in the determination of the binding stoichiometry, which was found to be a 1:1 host-to-anion complexation. The detection limitation of sensors toward F^- was obtained according to UV–Vis titration. The fluorimetric LOD of H_2L^1 - H_2L^3 was found to be 1.03×10^{-6}, 1.01×10^{-6} and 1.00×10^{-6} mol L^{-1} respectively. The calculated detection limit for azobenzene dyes was found to be 1.03×10^{-6} mol L^{-1} by other studies [19].

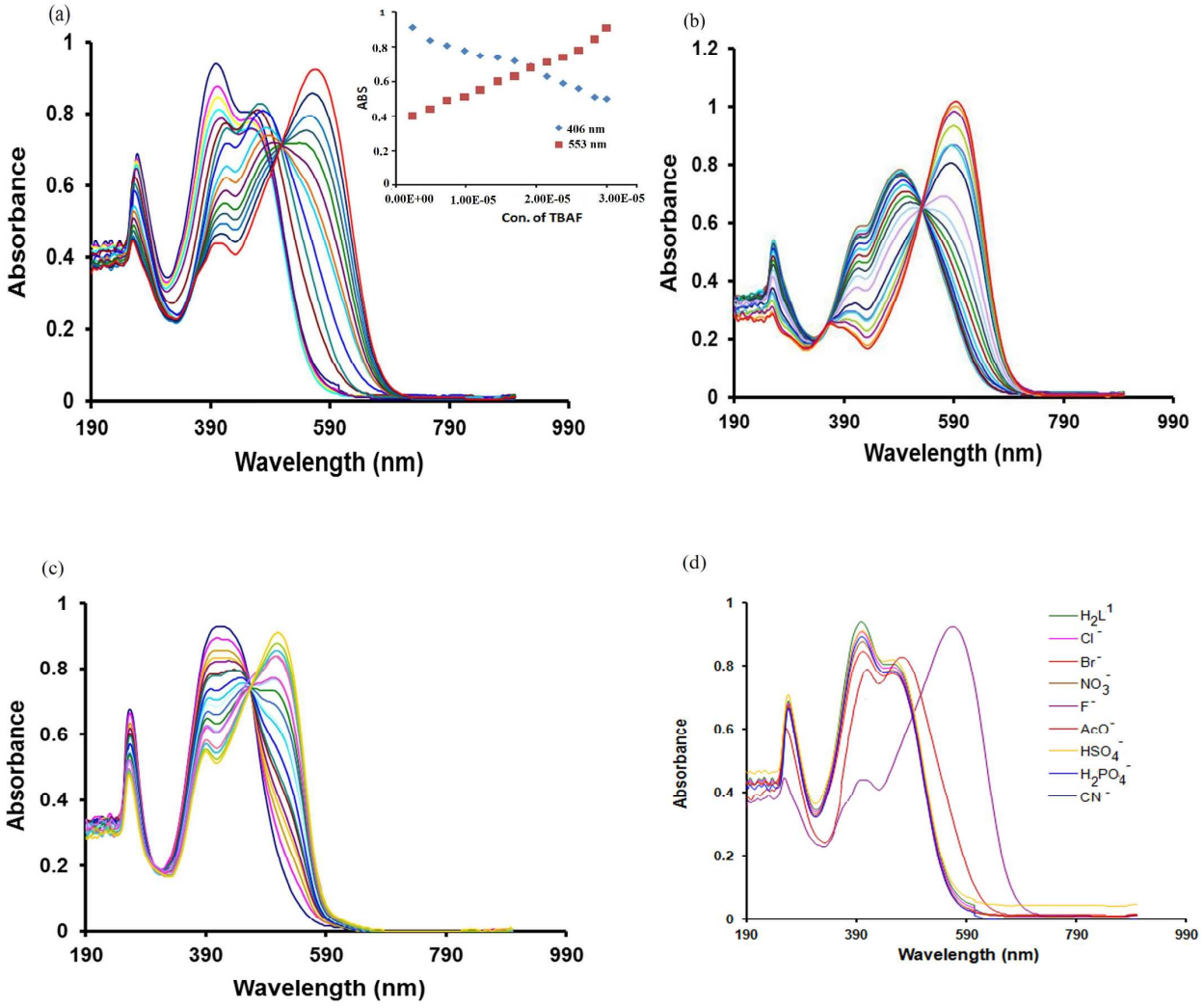


Fig. 4. Absorption spectra of the receptors H_2L^1 - H_2L^3 (a, b and c, respectively) recorded in DMSO after addition of 0–2 equiv. of tetrabutylammonium fluoride. (d) UV–Vis absorption spectra of H_2L^1 upon addition of a particular anion salt, respectively.

Table 2

Data obtained from the UV–vis spectra upon titration of receptors (**H_2L^1 - H_2L^3**) with n-$Bu_4N^+F^-$ in DMSO

Receptor	Receptor, λ_{max} (nm)	Complex, λ_{max} (nm)	Bathochromic shift, $\Delta\lambda_{max}$ (nm)	Isosbestic point (nm)	$K_a(M^{-1})$
H_2L^1	406	553	164	504	7.603×10^3
H_2L^2	470	580	110	529	4.731×10^3
H_2L^3	403	499	107	459	2.463×10^3

3.3.3. Fluorescence properties

In order to learn more about the sensing ability of the receptors, fluorescence measurements were carried out similar to UV–visible measurements. The fluorescent spectral properties of receptors H_2L^1 - H_2L^3 (2×10^{-5} M) were determined in CH_3CN solvent which shows a weak fluorescence at 531-551 nm with a shoulder at 554, 555 nm (Fig. 5a). The fluorescent emission of receptors H_2L^1 - H_2L^3 did not originate from the azobenzene unit, as it is well known that the azobenzene unit does not exhibit luminescence, but resulted from the Schiff base unit [30, 31]. As seen in Fig. 5b, with the stepwise addition of F^- to a solution of compound H_2L^1, the fluorescence emission intensity of H_2L^1 at 551 nm increased gradually. Two possible reasons for the enhanced fluorescence might be as follows: (1) inhibition of photoinduced electronic transfer (PET) and (2) binding-induced rigidity of the host molecule [32-34]. Firstly, before coordination with F^- ion, the nitrogen atoms of the imine of free H_2L^1 could form an intramolecular hydrogen bond with the hydrogen atom of OH, which resulted in a photoinduced electron transfer, and the de-excitation of the resulting tautomer occurred mainly via a nonradiative pathway. These processes consequently led to the weak fluorescence of H_2L^1. Once H_2L^1 was coordinated with F^- ion, which induced deprotonation of the OH, the electron-transfer process was forbidden. Therefore, an enhancement of the fluorescence emission of H_2L^1 was observed. Secondly, the configuration of free receptor H_2L^1 was flexible and could rotate freely. Upon complexation with F^- ion, the host molecule H_2L^1 was rigidified, which gave birth to a large increase in emission intensity because of inhibiting vibrational and rotational relaxation modes of nonradiative decay. The wavelengths of excitation and emission are reported in Table 3.

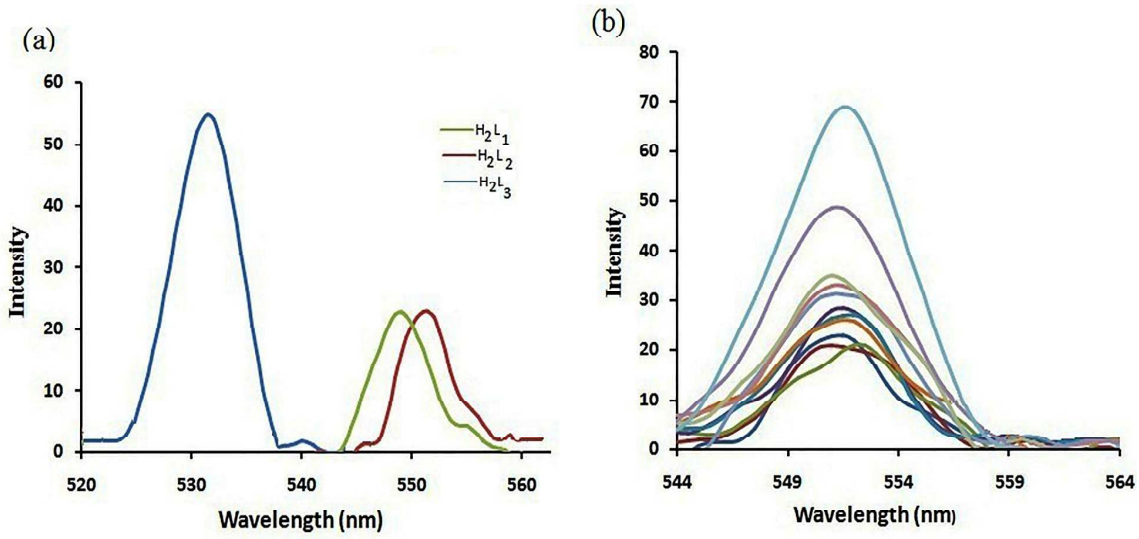


Fig. 5. (a) Fluorescent spectra of receptors H_2L^1 - H_2L^3 in CH_3CN (2×10^{-5} M). (b) Fluorescent titration of receptor H_2L^1 in CH_3CN (2×10^{-5} M) upon addition of F^- ion.

Table 3

Photophysical data receptors H_2L^1 - H_2L^3.

Compound	Excitation (nm)	Emission (nm)
H_2L^1	250	551, 554
H_2L^2	230	549, 555
H_2L^3	221	531

3.3.4. Cyclic voltammetry measurements

The electrochemical properties of the ligands H_2L^1 - H_2L^3 were investigated using cyclic voltammetry. Cyclic voltammetry indicates that azo-linked salicylaldimine Schiff base ligands have quasi-reversible redox behavior and some of the compounds give irreversible and reversible reduction. The redox potentials of azo dyes H_2L^1 - H_2L^3 are measured by the use of cyclic voltammetry in DMSO containing 0.1 M TBAP supporting electrolyte. Representative cyclic voltammograms of receptors H_2L^1 - H_2L^3 in the absence and presence of fluoride are shown in Fig. 6a-d and the corresponding characteristic data are summarized in Table 4. The cyclic voltammogram of compound H_2L^1 exhibits three reversible reduction waves, the first of which is observed at - 0.72 V, the second and third waves were observed at -1.01 V and -1.40 V, respectively. Also, a irreversible oxidation wave is observed for compound H_2L^1 at 0.49 V. The cyclic voltammetry of compound H_2L^2 and H_2L^3 shows two reversible waves, one of which is appeared at

- 0.69 V, and the other is observed at -0.95 V. Also, a irreversible oxidation wave is observed at 0.63 V for compound H_2L^3. The azo-dyes display oxidations at more positive potentials as a consequence of the destabilizing effect of the electron-withdrawing group on the arylazo moiety [35]. The reduction process may be due to the partial reduction of the imine bonds to secondary amines. This process may also be associated with the reduction of the azo bonds. In general, the reduction of imines is believed to occur via two well separated steps and can follow one of two mechanisms [36-37]. However, upon addition of fluoride ion to H_2L^3 a remarkable electrochemical response occurs. Specifically, the addition of fluoride ion yielded a slight cathodic shift of redox wave value. After the addition of 4 equiv of fluoride, large anodic shift, for H_2L^3 was observed. However, to the best of our knowledge, the significant anodic shift is the greatest so far reported for an electrochemical fluoride sensor. For the most common anion sensors, anion binding stabilizes the oxidized state to result in a cathodic shift in the oxidation potential. Other anions were also added to detect oxidation-reduction processes. However, no new peaks appeared.

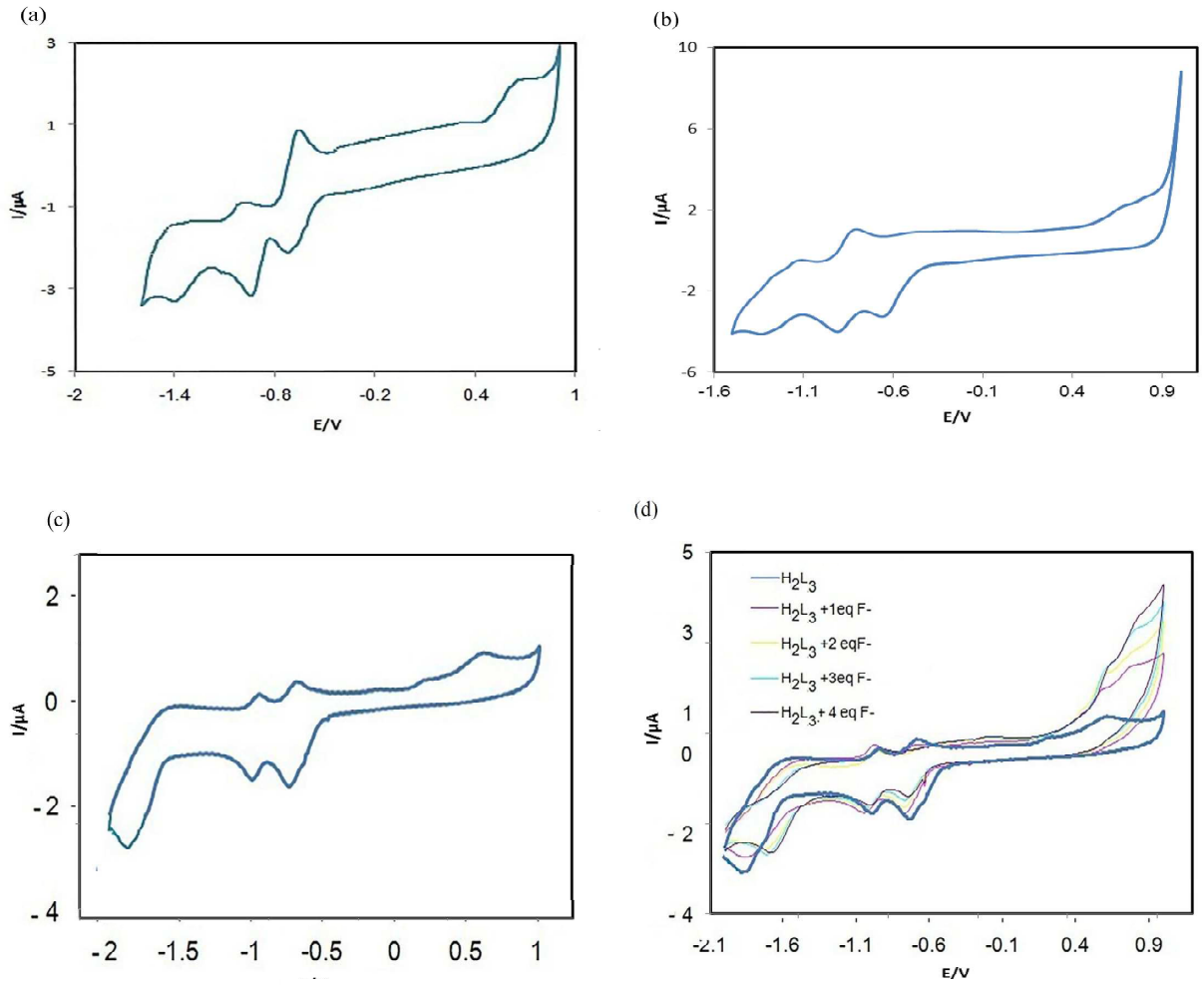


Fig. 6. Cyclic voltammograms of H_2L^1 - H_2L^3 (a, b and c, respectively) DMSO containing 0.1M TBAP. (d) Cyclic voltammograms of H_2L^3 (2×10^{-5} M) recorded in DMSO at 298 K with increasing amounts of F^-, at a scan rate of 100 mV/s.

Table 4

Cyclic voltammetry data for ligands H_2L^1 - H_2L^3.

Compound	E_{red} (V)	E_{ox} (V)
H_2L^1	-0.72, -1.01, -1.40	0.49
H_2L^2	- 0.69, -0.95	-
H_2L^3	- 0.69, -0.95	0.63

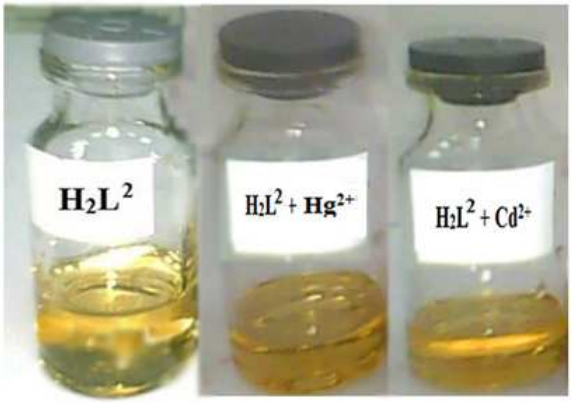
3.4. Cation-sensing properties

We investigated the recognition ability of the receptors H_2L^1 - H_2L^3 by naked-eye colorimetric experiments for transition metal ions such as Mn^{2+}, Fe^{+2}, Co^{+2} Ni^{2+}, Cu^{+2}, Zn^{2+}, Hg^{2+} and Cd^{2+}. When Hg^{2+}

solutions in DMSO were added to the receptors H_2L^1 - H_2L^3 in DMSO, the colors were changed to pale pink, dark yellow and gold respectively. Addition of Cd^{2+} to H_2L^1 - H_2L^3 changed the color to light yellow and gold. We have done the selectivity analysis for Cd^{+2} and Hg^{+2} ions in presence of Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} and found no change in the color of the solution by addition of these transition metal ions as an interfere cation. The addition of other metal ions does not show any visible color changes. The chemosensor behaviour of receptors H_2L^1 - H_2L^3 (2×10^{-5} M in DMSO) with Hg^{2+} (5×10^{-2} M) and Cd^{2+} (5×10^{-2} M) was investigated by UV–vis measurements. A solution of H_2L^1 - H_2L^3 titrated with increasing volume of microlitres of concentrated solution of a given cation. Upon treatment with Hg^{2+} ions the spectrum of H_2L^2 underwent obvious changes which implied that H_2L^2 was a good ligand for Hg^{2+}. On the incremental addition of Hg^{2+}, the absorption peaks initially at 416 and 470 nm were gradually decreased along with a hypsochromic shift about 6 nm from 470 nm to 464 nm (Fig. 7a). On successive addition of Cd^{2+}, the spectrum of H_2L^2 shifted from 470 nm to 543 nm and the intensity of the band at 416 nm decreased (Fig. 7b). The selectivity for azobenzene dyes has been reported by the other authors [23-24]. By plotting the changes of H_2L^2 in the absorbance intensity at 464 nm and 543 nm as a function of Hg^{2+} and Cd^{2+} concentration, sigmoidal curves were obtained and are shown in the inset of Fig. 7a-b. These changes in the spectra have been interpreted as a consequence of 1:1 complex formation between the ligand H_2L^2 with Hg^{2+} and Cd^{2+} ions. The stoichiometries of the H_2L^2 complexes were determined by a titration method. In each case, well-defined isosbestic points were also observed during the titration experiments, indicating the presence of a unique complex in equilibrium with the neutral ligand. The similar experiments were also performed for H_2L^1 and H_2L^3. The binding constants and detection limit for the receptors H_2L^1 - H_2L^3 with Hg^{2+} and Cd^{2+} are reported in Table 5. The calculated detection limit for azobenzene based chemodosimeter with Hg^{2+} was found to be 10×10^{-6} mol L^{-1} by other studies [24].

(a)

(b)



(c)

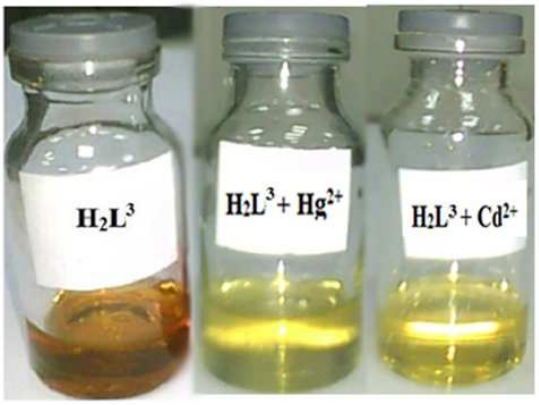


Fig. 7. Color changes of **H_2L^1 - H_2L^3** (a, b and c, respectively) in DMSO (2×10^{-5} M) before and after the addition of 2 equiv. of cations **Hg^{2+}** and **Cd^{2+}** (5×10^{-2} M).

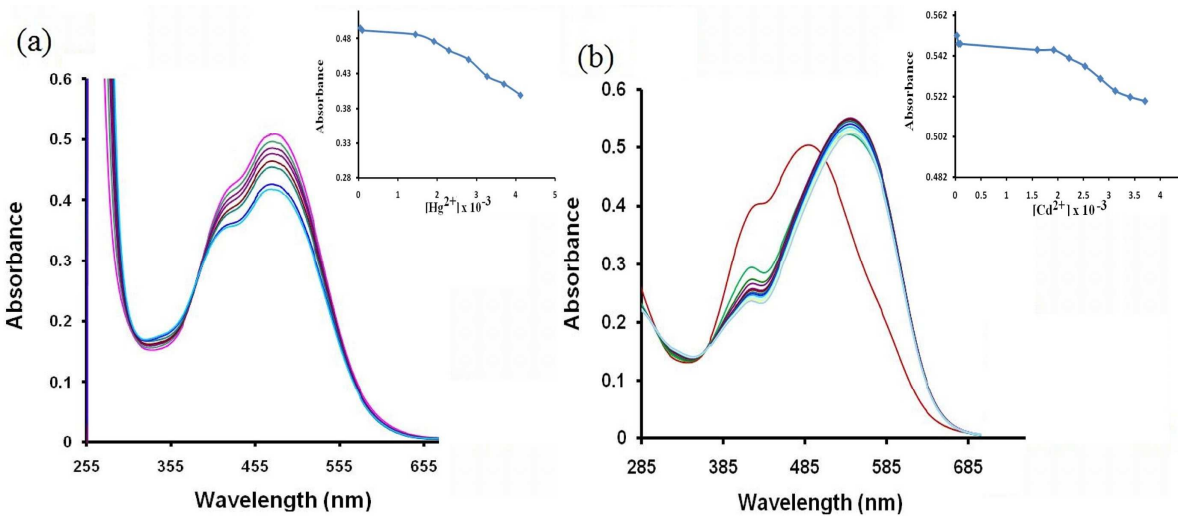


Fig. 8. Changes in the absorption spectra of H_2L^2 (2×10^{-5} M) in DMSO upon addition from 0 to 2 equiv of (a). Hg^{2+} and (b). Cd^{2+} ions. Inset shows plot of absorbance at 464 nm and 543 nm on titration of H_2L^2 with Hg^{2+} and Cd^{2+} ions.

Table 5

Binding constant of the receptors with the corresponding ions.

Receptor+ ions	Binding constant	Detection limit	Receptor+ ions	Binding constant	Detection limit
H_2L^1- Hg^{2+}	6.51×10^3	2.12×10^{-6}	H_2L^1- Cd^{2+}	4.73×10^3	1.03×10^{-6}
H_2L^2- Hg^{2+}	5.33×10^3	4.82×10^{-7}	H_2L^2- Cd^{2+}	3.14×10^3	4.00×10^{-7}
H_2L^3- Hg^{2+}	3.07×10^3	4.00×10^{-7}	H_2L^3- Cd^{2+}	3.04×10^3	3.82×10^{-7}

3.5. Sensing in the presence of competing ions

Since the receptors H_2L^1 - H_2L^3 sense both transition metal ions and anions like F^-. We examined the effect of sensing ability in the presence of competing ions. These experiments have been carried out in two different manners. First, the receptors were treated with 2equivalents of anions and to this, successive addition of cations (20–200 μl) were done and in another set of experiments receptors were first treated with 2 equivalents of cations and to that 20–200 μl of anion was added incrementally. For this dual sensing experiment the Hg^{2+}, Cd^{2+} and F^- ions were chosen.

It is obvious that H_2L^2 -Hg^{2+} and H_2L^2 have different mechanisms of binding anions. The existence of Hg^{2+} in H_2L^2 -Hg^{2+} promoted the intramolecular charge transfer when the metal complex bound with anion, which induced the red shift of the spectra and the color change. It was noted that the selectivity of H_2L^2 -Hg^{2+} for F^- was greatly improved. The absorption titration of H_2L^2 -Hg^{2+} with F^- was performed and the result was presented in Fig. 8a. In the absence of F^-, the maximal wavelength of absorption spectrum centered at 464 nm, whereas upon addition of F^-, the spectra underwent dramatic change in two steps. When the concentration of F^- was lower than 1.0 equiv. of H_2L^2 -Hg^{2+} the spectra red shifted from 464 to 493 nm and the absorbance increase. While the concentration increased to more than 1.0 equiv., the absorbance at 493 nm decreased. The color of the solution changed which was easily observed via naked eyes. It was assumed that ternary complex of H_2L^2 -Hg^{2+} -F^- was formed. The effect of the addition order on the spectral change was also studied (shown in fig. 8b). Upon addition of Hg^{2+} into the mixture of H_2L^2

and F^-, the new peak at 493 nm was also observed implicating the ternary complex formation. However, when the amount of Hg^{2+} was increased the absorbance at long wavelength decreased.

We also studied the interaction between H_2L^2 -Cd^{2+} and anions (shown in Fig. 8c-d). The results showed the similar spectral change as H_2L^2 -Hg^{2+}. However, H_2L^2 -Cd^{2+} was sensitive to F^-, which indicated that the selectivity of H_2L^2 -Cd^{2+} for F^- was good. To further confirm the mechanism, Hg^{2+} was added into the solution of H_2L^1 .F^- and H_2L^3 .F^-, the spectrum underwent change. Furthermore H_2L^3 -Hg^{2+} and H_2L^1 -Hg^{2+} complexes can selectively sensed fluoride ion.

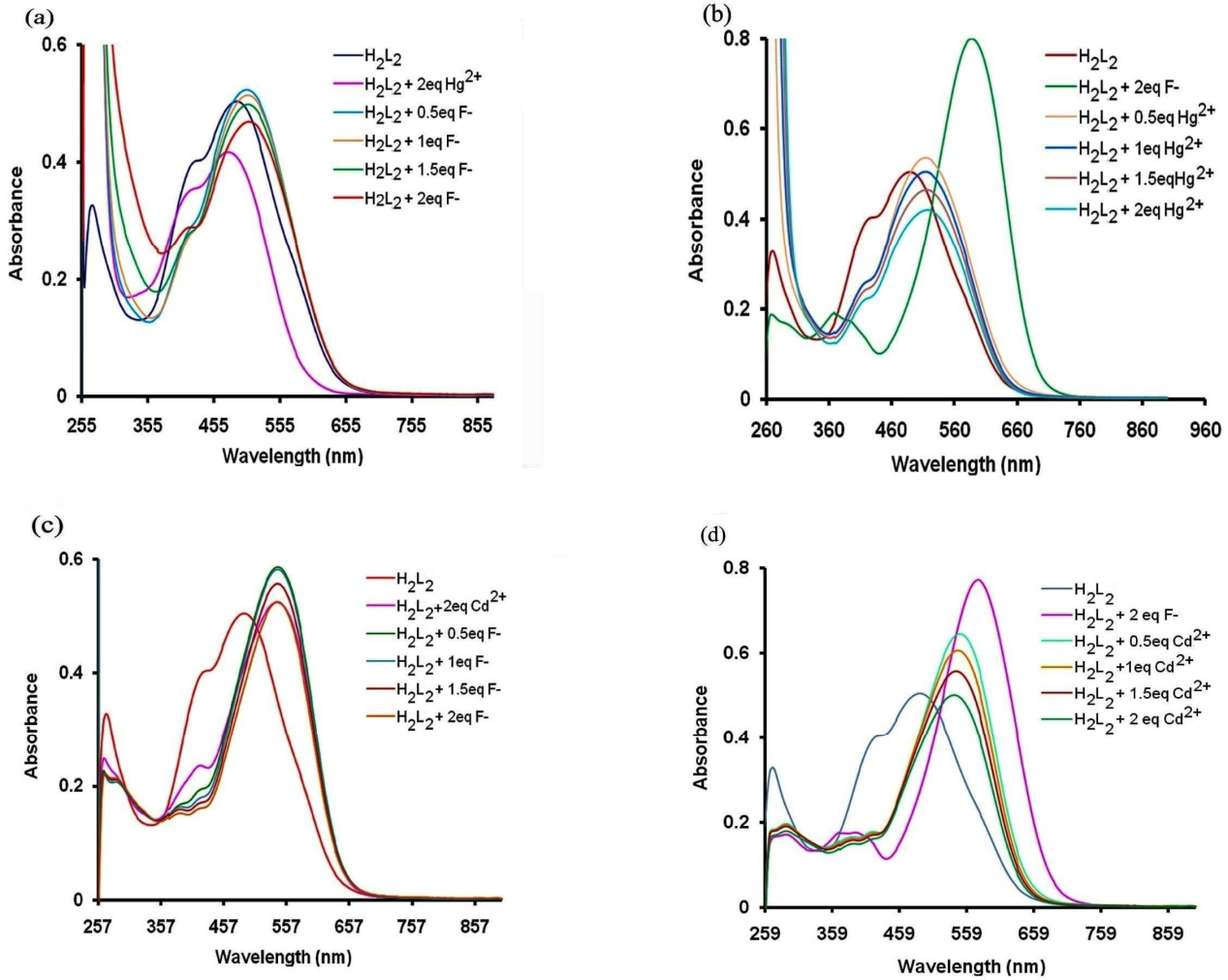


Fig. 9. (a) Absorption spectrum of H_2L^2 on addition of Hg^{2+} (2 equivalents) and then titration with F^-, (b) absorption spectrum of H_2L^2 on addition of F^- (2 equivalents) and then titration with Hg^{2+}, (c) absorption spectrum of H_2L^2 on addition of Cd^{2+} (2 equivalents) and then titra

tion with F^-, (d) absorption spectrum of H_2L^2 on addition of F^- (2equivalents) and then titration with Cd^{2+}.

4. Conclusion

In conclusion, we have studied highly selective and sensitive H_2L^1 - H_2L^3 chemosensor for the detection of Hg^{2+}, Cd^{2+} and F^-. These chemosensors can be utilized for the detection of Hg^{2+}, Cd^{2+} in the presence of other competing metal ions and for the detection of F^- in the presence of other halide ions in DMSO by both selective coloration and change in the absorption spectra. Among them, the receptor H_2L^1 has higher sensitive for the fluoride and there is a more prominent color change that can be observed by the naked-eyes.

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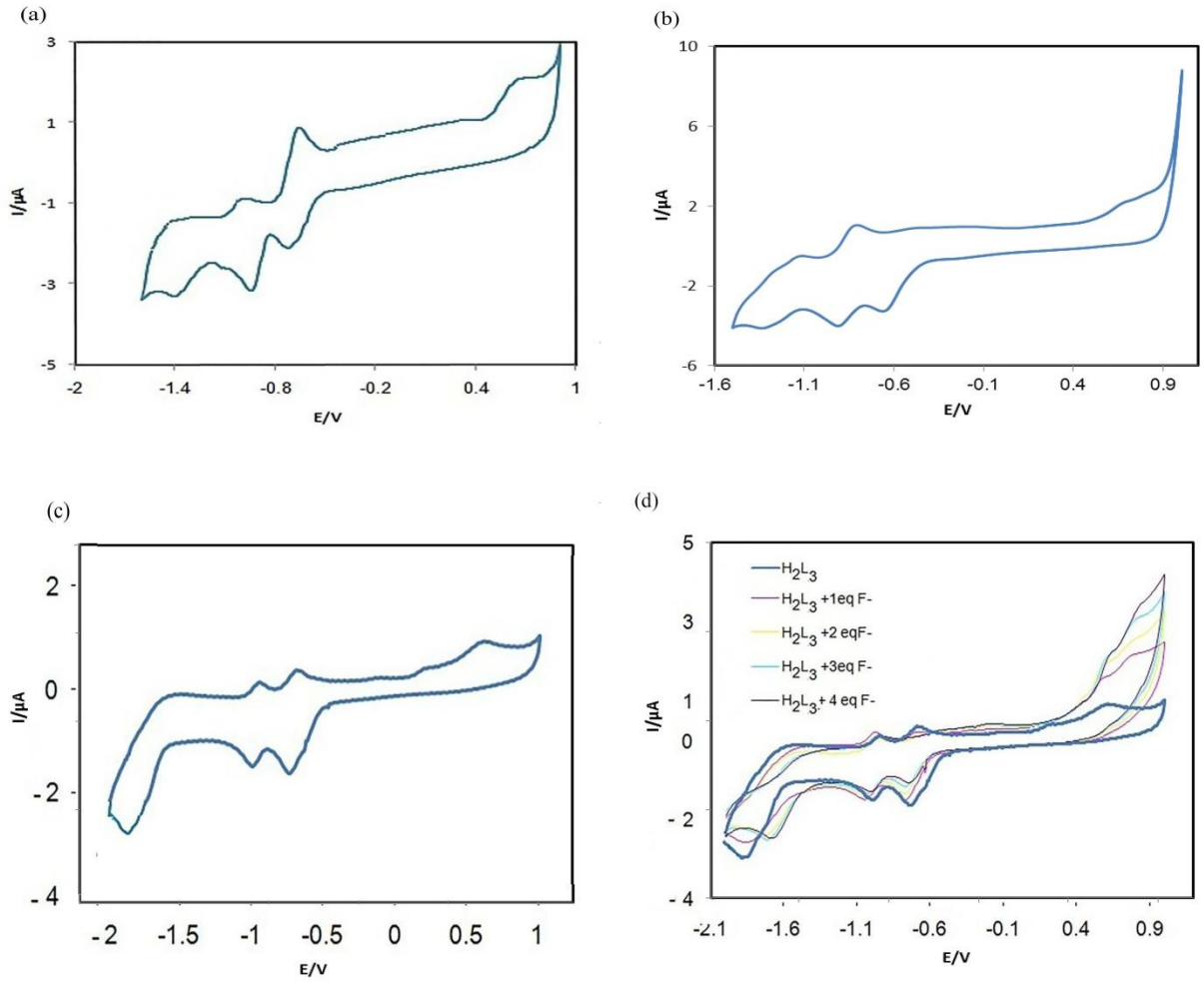

Fig. 6. Cyclic voltammograms of H_2L^1 - H_2L^3 (a, b and c, respectively) DMSO containing 0.1M TBAP. (d) Cyclic voltammograms of H_2L^3 (2×10^{-5} M) recorded in DMSO at 298 K with increasing amounts of F^-, at a scan rate of 100 mV/s.