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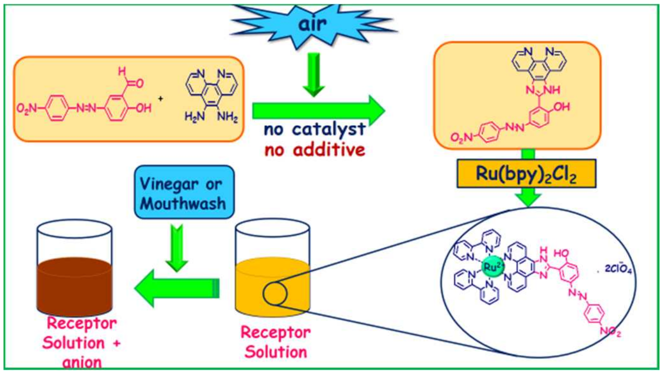

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Cite this: DOI: 10.1039/c0xx00000x

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PAPER

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Catalyst-free approach to a novel imidazo [4,5-*f*][1,10] phenanthroline ligand and its corresponding ruthenium(II) complex: insights into their applications in colorimetric anion sensing

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

We have designed and synthesized a novel imidazo [4,5-*f*][1,10] phenanthroline ligand (**L**) containing azo-coupled salicylaldehyde scaffold for the first time under catalyst-free condition using air as an oxidant. **L** was further utilized to fabricate mixed-ligand monometallic Ru(II) complex of composition $[(bpy)_2Ru(\mathbf{L})](ClO_4)_2$ {bpy=2,2′-bipyridine and **L**= 2-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)-4-((4-nitrophenyl)diazenyl)phenol}. The anion sensing properties of the synthesized complex as well as the parent ligand has been thoroughly explored using absorption, emission and ^{1}H NMR spectral measurements. On the basis of findings, it has been postulated that both synthesized probes act as efficient sensors for colorimetric recognition of F^- among halides and AcO^- and $H_2PO_4^-$ among oxoanions in aqueous media. Significantly, the colorimetric response was considered to be the direct consequence of monoproton transfer from probes to aforementioned anions. It is evident that the introduction of electron withdrawing groups into the backbone of the prepared complex renders the hydrogen-bind donors appreciably acidic. Thus, the sensor is capable of competing with water molecules to detect the trace amount of anions in aqueous environment without any spectroscopic instrumentation. Successfully, the current sensory system could as well be served as practical tool for immediate and qualitative detection of inorganic anions in real samples.

Introduction

Design and also construction of artificial anion probes have been a subject of considerable contemporary research theme for the imperative role played by anions in biological, aquatic, environmental and industrial processes.[1] Among the various kinds of anions, fluoride is the most intriguing target owing to its established roles in treatment of osteoporosis and preventing dental cares. [2a-d] However, its excessive ingestion is accused of skeletal fluorosis, kidney failure and nephrolithiasis. [2e-g] Moreover, the oxyanion, acetate, is a critical component in various metabolic processes and synthetic organic molecules and exhibits vital biochemical behaviours in the enzymes and antibodies.[3] Also, phosphate is of utmost importance. It plays not only a pivotal role in transduction, energy storage and gene construction, but it is also recognized as an essential structural ingredient in teeth and bone matrix.[4] Given this importance, it is not surprising that extensive investigations have been dedicated to the design and fabrication of receptors proficient for sensing biologically functional anions with high affinity. In particular, colorimetric anion probes are increasingly appreciated since naked eye detection without resorting to any spectroscopic instrumentation is low cost and highly favourable for applications in immediate screen processes. [5]

In recent years, a variety of systems containing amide, urea and thiourea, amidourea, phenol, pyrrole, imidazolium and indole that are capable of providing an acidic N-H and/or O-H groups have been well documented.[6] In this context, metal-complexed-based anion sensors have also been studied extensively, mainly owing to their long lifetime compared to the purely organic sensors.[7] Among them, ruthenium polypyridyl complexes are found to be the most investigated chemical systems due to their remarkable chemical stability, unique electrochemical and photophysical properties and also their intense metal-to-ligand charge transfer (MLCT) transitions in the visible region which indeed facilitate the anion recognition by a visually striking colour change. [4a,8]

To date, although myriad of receptors based on ruthenium(II) polypyridyl complexes have been devised, most of them are operational in purely organic media, restricting their applications as anion sensors.[9] For instance, Baitalik *et al.* have developed a new series of heteroleptic bis-tridentate ruthenium(II) complexes

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† Electronic Supplementary Information (ESI) available: Characterization data of all compounds, UV-Vis spectrophotometric titrations, stoichiometric determination by Benesi–Hildebrand method, Job's plot, determination of pK_a values, ^{1}H NMR titrations and fluorescence spectra. See DOI: 10.1039/b000000x/

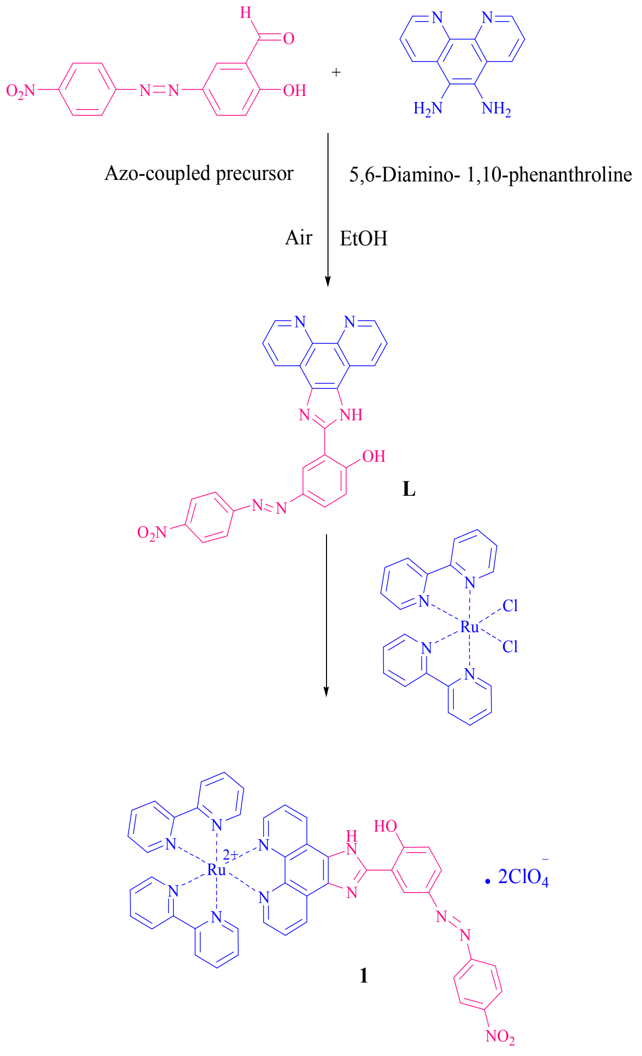
for multi-channel recognition of ions such as F^-, AcO^- and to some extent $H_2PO_4^-$.[10] But, the determination process was carried out in non-aqueous environment which is far away from real-life applications. Thus, development of sensors for direct sensing of anions in aqueous media or even water-organic mixed solvents is an important target. This intriguing approach was reported by Duan and co-workers, in which a remarkably selective Ru-bpy based quinone hydrazone chemosensor allowed detection of F^- in water with the naked eye.[11] However, the F^- sensing in aqueous media was limited to the use of test papers which requires several minutes for the detection process. Then, this strenuous approach was further wielded by Wang and co-workers using Ru(II) polypyridyl complex with a terpyridine/phenylimidazo[4,5-*f*]-phenanthroline hybrid, as highly sensitive and selective luminescence sensor for $H_2PO_4^-$ in CH_3CN-H_2O solution.[4a] Although, the colour changes of receptor in the presence of anions were very marginal to the naked eye.

With these considerations in mind, our current interest manifests the synthesis, characterization and detailed anion binding studies of an unprecedented azo-coupled salicylaldehyde/imidazo[4,5-*f*][1,10]phenanthroline hybrid (**L**) and its monometallic Ru(II) complex. To do this, first, **L** was synthesized from very green and practical protocol under catalyst and additive free condition using air as an oxidant. Then, the reaction of **L** with bis-bipyridine ruthenium(II) dichloride gave appropriate complex of composition $[(bpy)_2Ru(\mathbf{L})](ClO_4)_2$, **1**, Scheme 1. Interestingly, the introduction of transition-metal element along with electron withdrawing NO_2 substituent into the framework of sensing molecule greatly augments the acidity of active sites and also detecting limit. Therefore, the designed sensor can compete with water for naked eye detection of F^- among halides and AcO^- and $H_2PO_4^-$ among oxoanions in aqueous environment.

Results and discussion

Synthesis and characterization

In the past decades, a number of synthetic methodologies have been subsequently developed to construct imidazoles. Generally, the coupling of *o*-diamines and carboxylic acids or their derivatives (nitriles, imidates or orthoesters) which often requires harsh and strong acidic conditions or microwave irradiation, has been extensively utilized.[12] To further simplify the situation, the synthesis of imidazole from aldehydes instead of carboxylic acids or their derivatives under oxidative condition turned out to be the most facile and effective method.[13] Despite the advances of this methodology, in some cases, using excess amount of oxidants, drastic reaction condition, low yield, employing noble transition metal catalyst and operational difficulty restrict their application.[14] To overcome the previous drawbacks, we continued our research interest to seek for a more efficient and green method. Inspired by Jiao and co-workers[15], we have presented a catalyst and additive free method to synthesize **L**. For this aim, **L** has been straightforwardly prepared through very green and practical procedure in excellent yield by the reaction of 5,6-Diamino-1,10-phenanthroline and 1-(3-formyl-4-hydroxyphenylazo)-4-nitrobenzene in ethanol using air as oxidant. Meanwhile, the plausible mechanism has been reported in literature.[15] Then, the target metal monometallic complex was obtained by reacting **L** with bis-bipyridine ruthenium(II) dichloride. Subsequently, treatment of the complex with $NaClO_4$, afforded $[(bpy)_2Ru(\mathbf{L})](ClO_4)_2$, **1**, Scheme 1. The desired compounds have been thoroughly characterized by elemental (C, H and N) analyses, MALDI-TOF mass, IR, UV-Vis and ^1H NMR spectroscopic measurements (ESI†). Exemplary, the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of **1** is displayed in Fig. 1 as well. The characteristic $[M\text{-}ClO_4]^+$ and $[M\text{-}2ClO_4^-\text{-}H]^+$ peaks of obtained complex are seen at *m/z*=974.2 and 874.3 which are in excellent agreement with calculated values of *m/z*=974.11 and 874.16, respectively, based on the molecular formula of complex. Also, the isotopic pattern of the original peak is in good accord with the calculated one.



Scheme 1. Synthesis of sensor **1**.

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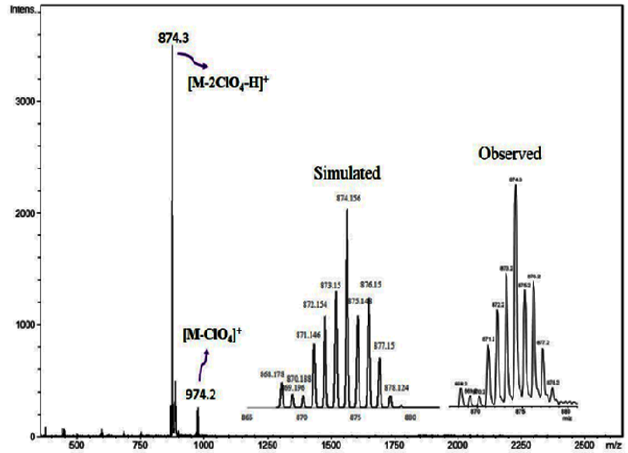

Fig. 1 MALDI-TOF mass spectrum of compound **1**; the insets show the isotope patterns for the dominant peak.

Colorimetric signaling

The colorimetric sensing ability of **L** and its mixed-ligand monometallic Ru(II) complex, **1**, has been investigated on a qualitative basis by visual examination of the anion-induced colour changes in DMSO (2×10^{-5} mol L^{-1}) before and after the addition of the anions such as F^-, Cl^-, Br^-, AcO^-, I^-, $H_2PO_4^-$, ClO_4^-, N_3^-, NO_2^-, NO_3^- and HSO_4^- as their tetrabutylammonium (TBA) salts. The photographs in Fig. 2 indicate vivid changes in colour in the case of fluoride, acetate and dihydrogenphosphate, suggesting strong interaction between the receptors with relatively basic anions. Conversely, the addition of other examined anions failed to cause any conspicuous colour changes.

Absorption spectral studies

To provide fundamental insights to the suitability **1** and **L**, as chromogenic anion sensors, the anion sensing behaviour was initially explored by monitoring the UV-Vis spectral changes in DMSO, upon the addition of various anions as their TBA salts. Detailed spectroscopic studies disclosed that the basic anions like F^-, AcO^- and $H_2PO_4^-$ had a profound effect on the electronic spectra of receptors. However, there were no significant changes in the absorption behaviour in the presence of weakly basic anions.

As an initial test, the anion sensing properties of the sensors (2×10^{-5} mol L^{-1}) were assessed by UV-Vis spectroscopy in DMSO via addition of 5 equiv. of different anions. As shown in Fig. 3, the UV-Vis absorption spectrum of $[(bpy)_2Ru(\mathbf{L})](ClO_4)_2$ in DMSO gives rise to an intense band at 289 nm, attributed to the π→π* transition of bipyridine, higher wavelength absorption band centred at 355 nm due to the π→π* transition of **L** and also less intense absorption shoulder appearing at 461 nm assigned to the metal-to-ligand charge transfer (MLCT) transition. Upon the addition of relatively basic anions (F^-, AcO^- and $H_2PO_4^-$), the intensity of the bands at 289 and 355 nm decreased and new band at *ca.* 560 nm generated accompanied with dramatic colour change from light orange to dark brown. No significant spectral and colour changes were observed for other anions.

Fig. 2 Colour changes seen for receptors (a) **1** and (b) **L** (2×10^{-5} mol L^{-1} in DMSO) after addition of 5 equiv. of various anions. From left to right: none, F^-, Cl^-, Br^-, I^-, ClO_4^-, AcO^-, NO_3^-, HSO_4^-, N_3^-, NO_2^- and $H_2PO_4^-$ (TBA$^+$ salts).

To gain a deeper insight into the binding characteristics of the prepared sensors, we performed UV-Vis spectroscopic titrations upon the addition of standard solutions of F^-, AcO^- and $H_2PO_4^-$ to the dry DMSO solution of **1** (2×10^{-5} mol L^{-1}). As shown in Fig. 4, on incremental increase of either F^- or AcO^-, the absorption bands at 289 and 355 nm decreased gradually and a new tailing absorption band appeared at *ca.* 560 nm and was intensified, indicating strong interaction between anions and receptor. Analogous investigation was carried out for addition of TBA salt of $H_2PO_4^-$ to the solution of **1** in dry DMSO (Fig. S8, ESI†). Furthermore, the definite stoichiometric ratio between **1** and aforementioned anions was determined to be 1:1 from UV-Vis spectral changes with the help of Benesi–Hildebrand method[16] and also Job's plot experiments (Fig. S9 and Fig. S10, ESI†). For practical aim, the detection limits of sensors were calculated on the basis of UV-Vis measurements. Moreover, the deprotonation constants for designed sensors with F^-, AcO^- and $H_2PO_4^-$ were evaluated from Benesi–Hildebrand equation. A summary of the characteristics of the obtained sensor are presented in Table 1.

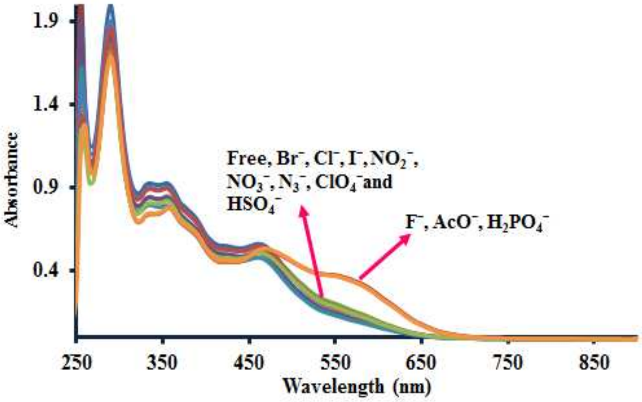

Fig. 3 UV-Vis absorption spectra of **1** (2×10^{-5} mol L^{-1} in DMSO) in the presence of 5 equiv. of various anions.

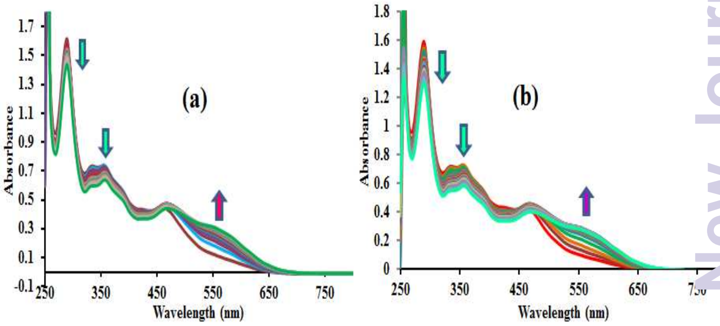

Fig. 4 UV-Vis titrations of **1** (2×10^{-5} mol L^{-1}) in dry DMSO with incremental addition of standard solution of (a) TBAF and (b) TBAOAc (0-5 equiv.).

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Table 1 Data determined from the UV–Vis spectra upon titration of **L** and **1** with F^-, AcO^- and $H_2PO_4^-$ in DMSO.

	L		**1**	
	K, M	LOD,M^{-1}	K, M	LOD, M^{-1}
F^-	6.57×10^4	1.56×10^{-6}	2.66×10^5	1.55×10^{-6}
AcO^-	8.20×10^4	1.77×10^{-6}	1.04×10^5	1.27×10^{-6}
$H_2PO_4^-$	6.79×10^4	1.90×10^{-6}	1.78×10^5	2.27×10^{-6}

From the viewpoint of the practical applications of anion sensors, it is crucial that the receptors can be operational in water-containing media. Indeed, water is highly competitive solvent and interferes in sensing process of anions by mediating interaction between partners. Consequently, anions are strongly solvated and interactions between targeted anions and molecular sensors are drastically attenuated.[17] This is the reason why the direct sensing of inorganic anions in water constitutes to be a quite difficult task. However, this hindrance could be overcome utilizing the sensor decorated by electron withdrawing moieties (metal centre and NO_2 substituent) to recognize anions with high affinity.

To explore the applicability of sensor in aqueous environment, further UV-Vis spectrophotometric titrations were performed in 9:1 DMSO-water solutions upon addition of F^-, AcO^- and $H_2PO_4^-$ as their n-Bu_4N^+ salts. Interestingly, titration of **1** with anions afforded similar spectral and colour changes to that observed in organic media (Fig. S11, ESI†). Moreover, it is worth mentioning that on all occasions, the number of equivalents required to reach plateau were exactly the same as those required in DMSO, verifying that the interaction stoichiometry between receptor and anions is not affected by the presence of competitive water molecules.

To corroborate, the 1:1 ratio between **1** and anions, Benesi–Hildebrand method was executed (Fig. S12, ESI†). Accordingly, the detection limits determined from the UV-Vis measurements and deprotonation constants are summerized in Table 2.

It would be of interest to compare anion sensing ability of free ligand with its monometallic Ru(II) complex. To do so, UV-Vis spectroscopic experiments were performed in DMSO and 9:1 DMSO-water solution upon the addition of standard solutions of F^-, AcO^- and $H_2PO_4^-$ as their TBA salts. Fig. 5 depicts the spectra taken over the course of the titration of **L** (2×10^{-5} mol L^{-1}) with TBAF in DMSO. On addition of increasing concentration of TBAF, the band at 356 nm, attributed to the π→π* transition of chromophore, decreased and simultaneously the band at 552 nm, assigned to the n→π* transition and also intramolecular charge transfer, developed remarkably with distinct isosbestic point at 456 nm. These observations were in accordance with discernable colour change from light purple to deep purple. It has to be noted that AcO^- and $H_2PO_4^-$ induced similar colour change and spectral pattern (Fig. S13, ESI†). Moreover, the Benesi–Hildebrand plot of $1/[A\text{-}A_0]$ *vs.* $1/[F^-]$ for titration of **L** with TBAF provided a straight line (Fig. 6), supporting the 1:1 stoichiometry ratio. The 1:1 stoichiometry was also substantiated by Job's plot (Fig. S15, ESI†). Furthermore, the resulting values containing deprotonation constants and detection limits are collected in Table 1 and 2. A further insight into Tables reveals that appending electron withdrawing metal centre can indeed be used to augment anion affinities relative to the free ligand. In fact, the introduction of metal centre along with NO_2 group can decrease the electron density on active sites and also render the hydrogen-bind donors more acidic, thereby promoting the anion affinitiy.[18]

Important to note that the titration curves of both sensors reach to plateau at higher equiv. of $H_2PO_4^-$ than F^- and AcO^-, presumably regarding to the lower basicity of dihydrogenphosphate compared to fluoride and acetate ions. Evidently, the requirement of a higher equivalents of less basic $H_2PO_4^-$ suggests the anion induced deprotonation phenomenon.[1g] Additionally, this hypothesis was further strengthened by titration of **1** and **L** with standard solution of tetrabutylammonium hydroxide (TBAOH) in DMSO. Fig. 7 indicates the OH^- induced spectral changes of **1** and **L**. The close resemblance of the spectral patterns obtained with OH^- to those observed for other basic anions, proved the deprotonation mechanism.[19] Moreover, the pK_a values were determined to be 10.25 and 8.33 for **L** and **1**, respectively, from spectroscopic pH titrations (Fig. S18, ESI†). These results clearly exhibit that molecular sensors can be deprotonated by basic anions. In according to previous study reported by Eseola and co-workers for similar 1*H*-imidazo[4,5-*f*][1,10]phenanthroline frameworks, all phenolic compounds give lower pK_a values than non-phenolic ones, indicating the observed anionic states for imidazole compounds bearing hydroxyl group is attributed to the phenolic proton abstraction.[20] In particular, the introduction of electron withdrawing NO_2 substituent into the backbone of our designed sensors, renders the phenolic OH group

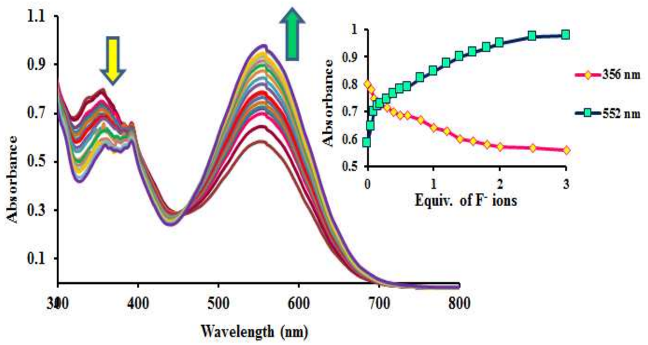

Fig. 5 UV-Vis absorption spectra of sensor **L** (2×10^{-5} mol L^{-1}) in dry DMSO upon the addition of TBAF (0-5 equiv.). Inset showing the binding isotherm at selected wavelengths in DMSO.

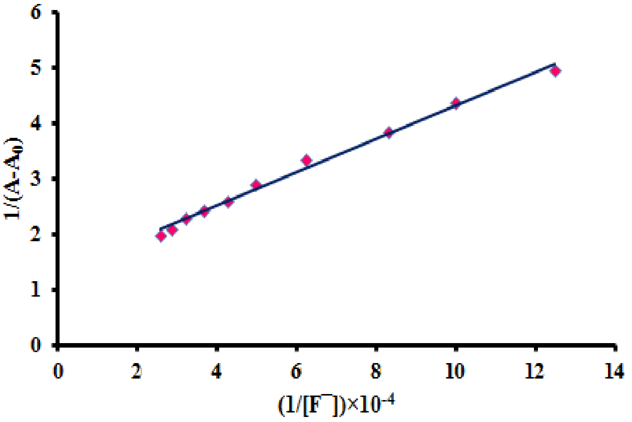

Fig. 6 Benesi–Hildebrand plot of sensor **L** binding with F^- anion associated with absorbance change at 552 nm in DMSO.

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Table 2 Data determined from the UV–Vis spectra upon titration of **L** and **1** with F^-, AcO^- and $H_2PO_4^-$ in 9:1 DMSO-water.

	L		**1**	
	K, M	LOD,M^{-1}	K, M	LOD, M^{-1}
F^-	8.55×10^4	3.17×10^{-6}	2.55×10^5	4.09×10^{-6}
AcO^-	8.50×10^4	1.89×10^{-6}	3.09×10^5	3.43×10^{-6}
$H_2PO_4^-$	8.93×10^4	2.03×10^{-6}	3.14×10^5	1.98×10^{-6}

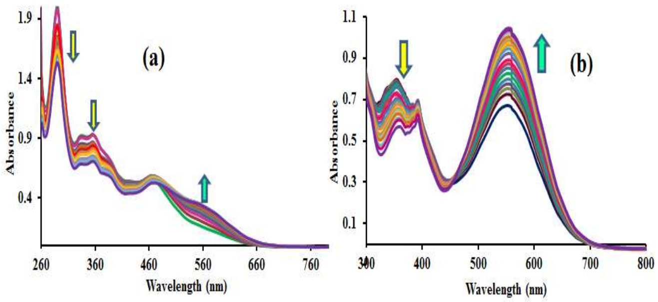
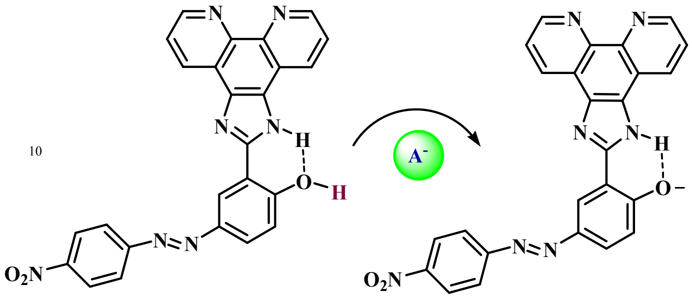


Fig. 7 UV-Vis titrations of (a) **1** and (b) **L** (2×10^{-5} mol L^{-1}) in dry DMSO with incremental addition of standard solution of TBAOH (0-5 equiv.).



Scheme 2. Proposed interaction modes of sensors **L** and **1** with anion.

more acidic. Also, it is worth to note that observation of the second deprotonation (imidazole NH deprotonation) did not happen, possibly due to the stability of the intramolecular H-bonding (Scheme 2).[21]

Proton NMR spectra

To shed light on the nature of the interaction between synthesized sensors and anions, ^1H NMR spectroscopy was applied. Fig. 8 illustrates the ^1H NMR spectra of **1** and **L** in the absence and presence of TBAF in DMSO-d_6. It should be noted that the ^1H NMR spectra present the broad signal at 14.67 and 14.43 ppm, assigned to the OH and NH protons of **1** and **L**, respectively, as was authenticated by D_2O exchange experiment. The OH and NH signals are too broad to be observed due to the rapid proton exchange and intramolecular hydrogen-bonding interactions.[8e] Interestingly, for both receptors, upon the addition of 1 equiv. of F^-, the broad signal attributed to the OH and NH protons, got thoroughly vanished and simultaneously, the aromatic proton signals underwent upfield shift. However, the chemical shifts for the bpy protons are far less affected. The upfield shift is attributed to the considerable augmentation of electron density onto the π-conjugated framework, causing shielding effect.[22] The evidence observed above precisely reflects the neat deprotonation. Importantly, more than 1 equiv. of F^- did not induce further upfield shift. This phenomenon confirms that the stoichiometry of the interaction between probes and F^- is 1:1 and only one proton was transferred to the anion (Scheme 2). Almost similar shift patterns were observed in the ^1H NMR spectra of **L** and **1** with AcO^- and $H_2PO_4^-$ (Fig. S19 and Fig. S20, ESI†).

Fluorescence signaling

The anion recognition properties of the synthesized sensors were further explored by fluorescence spectroscopy in DMSO at room temperature. In solution, the synthesized probes are weak emitters {quantum yields (Φ)= 0.056 for **L** and 2.70×10^{-5} for **1**}. The observation of emissions with low intensity has been ascribed to the well-known photoinduced electron transfer (PET) phenomenon, which comes into play due to availability of the lone pairs of OH and NH groups.[23]

Interestingly, excitation of **L** and **1** at 355 and 460 nm, respectively, resulted in enhancement of emission intensity at *ca.* 420 nm for **L** and 735 nm for **1** upon addition of F^-, AcO^- and $H_2PO_4^-$ anions, Fig. 9, (for free ligand see Fig. S21, ESI†). The acidity of phenolic OH proton is drastically increased upon photoexcitation, meanwhile, the potential excited state intermolecular proton transfer (ESPT) channel based on excitation-collision-deprotonation mechanism could be opened which is in accord with previously reported literature.[9c,24] Then, proton abstraction from the OH group by aforementioned anions generates phenoxide anion which will be stabilized via intramolecular hydrogen bonding to the NH group facilitating augmented fluorescence signal (Scheme 2).[25] In contrast, it is worth noting that the emission intensity of sensors underwent nominal changes with addition of Cl^-, Br^-, I^-, ClO_4^-, N_3^-, NO_2^-, NO_3^- and HSO_4^-. Apparently, these observations were consistent with those of the absorption spectral studies and ^1H NMR technique.

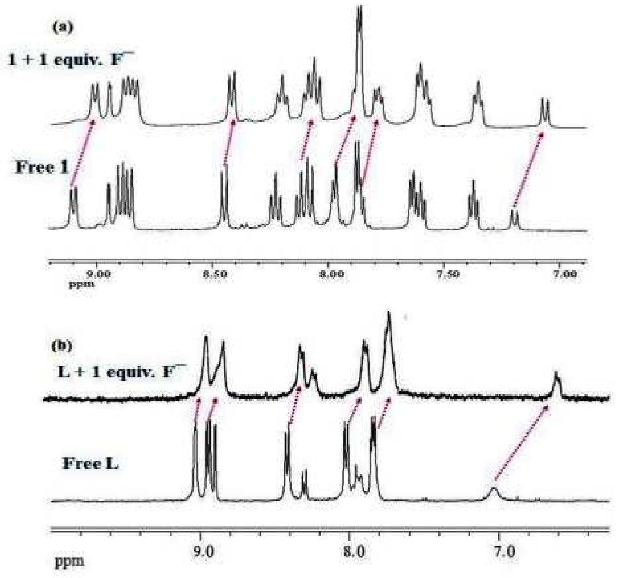


Fig. 8 ^1H NMR spectra of (a) **1** and (b) **L** in DMSO-d_6 (2×10^{-2} mol L^{-1}) in the absence and presence of 1 equiv. of F^-.

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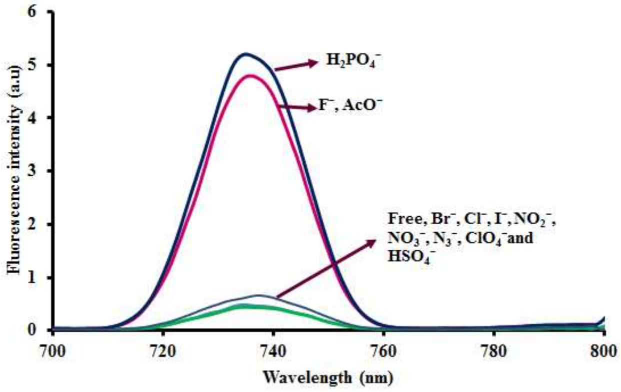

Fig. 9 Fluorescence spectra of complex **1** (2×10^{-5} mol L^{-1} in DMSO) upon addition of 5 equiv. of several different anions.

Practical application

Recently, we were inspired by Hundal and co-workers, who reported qualitative detection of anions in aqueous media.[26] Thus, we wondered if the sensor **1** could be applicable for naked eye sensing of inorganic anions in real samples and water. To achieve this ultimate goal, we extended our work for qualitative detection of F^- and AcO^- anions in commercially available mouthwash and vinegar, respectively. To our delight, addition of one drop of either mouthwash or vinegar to the receptor **1**, caused a conspicuous colour change from light orange to dark brown, indicating **1** is capable of detecting inorganic anions in aqueous media by the naked eyes. The results were also substantiated using UV-Vis spectroscopy. For this purpose, we employed the 2×10^{-5} mol L^{-1} of receptor **1** in 9:1 DMSO-water solution. Very remarkably, as is shown in Fig. 10, addition of 5μL of commercial mouthwash or vinegar caused the appearance of new band at 560 nm. Therefore, the designed monometallic Ru(II) complex can be considered as a highly promising candidate for rapid detection and colorimetric sensing of anions in real samples.

Conclusion

To sum up, we have presented a green and practical method to fabricate the novel azo-coupled salicylaldehyde/imidazo[4,5-*f*][1,10]phenanthroline hybrid and corresponding Ru(II) complex. The catalyst and additive free conditions, using air as an oxidant, makes this protocol very efficient and green. Importantly, the introduction of electron withdrawing metal centre along with NO_2 substituent makes the devised probe as appreciable sensor for immediate sensing and colorimetric detection of anions in water without any spectroscopic instrumentation. The detailed anion binding properties were also explored by absorption, emission and ^1H NMR spectroscopic techniques. The observations made from the above measurements, unequivocally suggest that the prepared sensor got deprotonated in the presence of F^- among halides and AcO^- and $H_2PO_4^-$ among oxoanions, which was evidenced through a colour change from light orange to dark brown. Notably, the sensory system could as well be served as proficient tool for qualitative detection of anions in real samples.

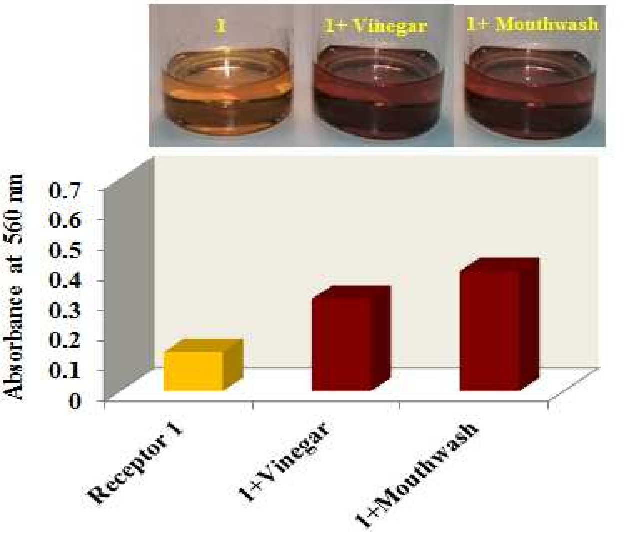

Fig. 10 The proof of concept for detection of acetate and fluoride in vinegar and mouthwash, respectively.

Experimental

General

All chemicals were purchased from Sigma-Aldrich and used without further purification. Bis(2,2′-bipyridine)dichloro ruthenium(II)[27], 1,10-phenanthroline-5,6-diamine[28] and 1-(3-formyl-4-hydroxyphenylazo)-4-nitrobenzene[29] were synthesized according to literature methods. Electronic spectral measurements were carried out using Optizen 3220 UV spectrophotometer in the range of 200-900 nm. FT-IR spectra were recorded as pressed KBr discs, using Unicom Galaxy Series FT-IR 5000 spectrophotometer in the region of 400-4000 cm^{-1}. The fluorescence measurements were performed using a Cary Eclipse Fluorescence Spectrophotometer (Varian, USA) at room temperature. Melting points were determined on Electrothermal 9200 apparatus. NMR spectra were recorded on Bruker AV 300 MHz and Bruker Avance III 400 MHz spectrometers. C. H. N. analyses were performed on a Vario EL III elemental analyzer. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was measured using a Bruker Reflex III spectrometer.

Synthesis of 2-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)-4-((4-nitrophenyl)diazenyl)phenol}(L)

A mixture of 1-(3-formyl-4-hydroxyphenylazo)-4-nitrobenzene (0.27 g, 1 mmol) and 1,10-phenanthroline-5,6-diamine (0.21 g, 1 mmol) in EtOH (60 mL) was heated to reflux for 8 h. The mixture was allowed to cool gradually and stir for 15-20 min at room temperature. Then, the obtained solid was filtered, washed thoroughly with ethanol and dried under vacuum at room temperature. Yield: 81%, m. p.> 270 ºC. ^1H NMR (DMSO-d_6, 400 MHz, ppm): δ 7.03 (s, 1H), 7.84 (m, 3H), 8.02 (d, 2H, J = 8.80 Hz), 8.42 (d, 2H, J = 8.80 Hz), 8.90 (d, 1H, J = 2.40 Hz), 8.94 (d, 2H, J = 7.40 Hz), 9.03 (d, 2H, J = 3.60 Hz), 14.43 (br,

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2H, NH+OH). IR (KBr, cm^{-1}); 3360, 3068, 1649, 1601, 1587 (phenol ring), 1518 (NO_2), 1493 (N=N), 1342 (NO_2), 1275, 1147, 850, 808 and 738. Anal. Calcd. for $C_{25}H_{15}N_7O_3$: C, 65.07; N, 21.25; H, 3.28. Found: C, 65.28; N, 21.73; H, 2.93 %. λ_{max} (nm) (ε ($M^{-1}cm^{-1}$)): 277 (50500), 356 (33350) and 552 (33100) in DMSO.

Synthesis of $[(bpy)_2Ru(L)](ClO_4)_2$ (1)

L (46.7 mg, 0.1 mmol) and bis(2,2′-bipyridine)dichloro ruthenium(II) monohydrate (48.4 mg, 0.1 mmol) were suspended in DMF (20 ml) and the resultant solution was heated at 140 ºC for 3 h. After cooling to room temperature, most of solvent was removed on a rotary evaporator. The residue was solubilized by adding a small amount of DMF (1 ml) and this solution was then diluted by adding water (40 ml). $NaClO_4$ (1 g) was added to this solution to deposit the crude metal complex **1** in the form of its ClO_4^- salt. Then, the obtained product was collected by filtration and recrystallized from chloroform-ethanol (5:1) to give a dark brown solid. Yield: 84%, m. p.> 270 ºC. ^1H NMR (DMSO-d_6, 400 MHz, ppm): δ 7.19 (d, 1H, J= 8.80 Hz), 7.37 (t, 2H, J = 6.40 Hz), 7.60 (t, 2H, J = 6.40 Hz), 7.64 (d, 2H, J= 5.20 Hz), 7.86 (m, 4H), 7.97 (m, 3H), 8.10 (m, 4H), 8.23 (t, 2H, J= 8.40 Hz), 8.45 (d, 2H, J= 9.20 Hz), 8.86 (d, 2H, J= 8.00 Hz), 8.90 (d, 2H, J= 8.00 Hz), 8.95 (d, 1H, J= 2.80 Hz), 9.10 (d, 2H, J= 8.00 Hz), 14.67 (br, 2H, NH+OH). IR (KBr, cm^{-1}); 3402, 3036, 1602, 1587 (phenol ring), 1516 (NO_2), 1489 (N=N), 1340 (NO_2), 1269, 1087 (ClO_4), 808, 765 and 623. Anal. Calcd. for $C_{45}H_{31}Cl_2N_{11}O_{11}Ru$: C, 50.33; N, 14.35; H, 2.91. Found: C, 50.14; N, 14.66; H, 3.18 %. λ_{max} (nm) (ε ($M^{-1}cm^{-1}$)): 289 (94300), 355 (46350) and 461 (28100) in DMSO. MALDI-TOF *m/z* 974.2 $[M\text{-}ClO_4]^+$ and 874.3 $[M\text{-}2ClO_4^-\text{-}H]^+$.

Acknowledgements

We are grateful to the Arak University for financial support of this work. We would also like to acknowledge Mr Peyman Zolgharnein for access to the MALDI-TOF mass facilities at the University of Sheffield.

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