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Optical Recognition of Anions by Ruthenium (II)-Bipyridine-Calix[4]Arene System

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Abstract The two *t*-butylcalix[4]arene attached ruthenium(II)-bipyridine complexes (Rubc2 and Rubc3) has been synthesized and the anion recognition studies have been carried out using emission techniques. The binding of anions, which are sensed by the complexes, are studied by UV-visible and emission techniques. The complex Rubc2 recognizes the Cl^-, $H_2PO_4^-$ and AcO^- anions. The complex Rubc3 recognizes the Br^- and AcO^- anions. The AcO^- quenches the emission intensity of both two complexes but the other anion increases the emission intensity of the complexes. The excited state lifetime and transient absorption studies were carried out the AcO^- facilitates non radiative pathway. The other anions stabilize the excited state and facilitate the radiative pathway.

Keywords Ru(II)-bipyridine-calixarene system · Anion · Luminescent sensor · Transient absorption spectrum · Excited state lifetime

Introduction

Anions are ubiquitous throughout biological systems and playing important role [1–3]. Chloride ion (Cl^-) has prominent role in ion channels [4–6]. The imbalance of Cl^- is responsible for many diseases like, cystic fibrosis, inherited kidney stone disease, and myotonia [7]. Fluoride (F^-) ion plays an important role in dental care and osteoporosis [8–10]. Phosphate ion also is an essential component in teeth and bone [11–17]. The potassium bromide was used as sedative in early days [18, 19]. Over dosage of bromide

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leads to bormism, a chronic toxicity of neural disorder [20]. The sodium iodide symporter is an important plasma membrane glycoprotein that mediates active I^- transport in the thyroid gland, which is the first step in thyroid hormone biogenesis [21]. Because of these reasons enumerated above recognition of anions receives importance in the fields of pharmaceutical and forensic sciences.

The design of anion sensors is a fast emerging research field due to the importance of detecting anions in medicine, chemical industry, and the environment [22–25]. Molecules containing amide group are mostly used for the recognition of anions due to their tendency to make hydrogen bond with anions [26]. Various type of molecules having amide, pyrrole and urea moiety have been used for anion recognition so far [27–29]. Through arrangement of these groups, by means of a proper supramolecular templates, the selective recognition of anions is achieved [30]. Calixarenes form the suitable supramolecular template owing to their facile synthetic tuning for the recognition of different types of molecules (small molecules like H_2, NO, cations, proteins) including anions [31–35]. The neutral group like pyrrole has been incorporated in the calixarene (calixpyrrole) to use them as sensors for anions [36–38]. From the change in the ^{1}H-NMR positions the recognition of anions has been achieved using calixpyrrole system [39]. Substitution at the lower rim has considerable effect on anion binding [40]. Lower rim thiourea substituted calixarene platforms are used for detection of AcO^-, HSO_4^- [41]. The imidazonium group can also bind with the anions as established previously [42].

The metal complexes having redox characteristics are used for electrochemical sensing of anion [43]. Incorporation of a metal center in calixarene leads to the design of several strategies like electrochemical, photochemical techniques to use them as sensors [44, 45]. The simple ruthenium(II) complexes carrying alkynyl groups have been used for anion sensing [46, 47]. Proper introduction of amide receptors on the bipyridine ligands leads to efficient anion sensing

using the photo and electrochemical properties of ruthenium(II)-bypiridine complexes [48–50]. Amide and amine groups attached ruthenium(II)-bipyridine complexes exhibit change in the emission properties upon binding with anions [51, 52].

In the molecular recognition studies using luminescence as the analytical tool, the well-established procedure is the attachment of organic fluorophore at the lower rim of calixarene [53]. The ruthenium(II)-bipyridyl complexes attached with calixarenes at its lower rim of the calixarene are good redox couples and they have been used for anion recognition by electrochemical means [54]. Even though, the luminescent properties of these complexes are well known there is no thorough study of anion recognition using optical techniques like steady state and time resolved absorption and emission techniques. We have previously demonstrated the photoinduced electron transfer reactions of ruthenium(II)-bipyridine complexes with organic sulfides [55] and phenols [56]. The intra molecular electron transfer of ruthenium(II)-bipyridine complexes carrying amino acids in ligand bipyridine has also been studied by our group [57]. The supramolecular compound cyclodextrin attached ruthenium(II)-bipyridine and osmium(II)-bipyridine have been used by Haider et al. [58] Harriman et al. [59] studied the ruthenium(II)-bipyridine-calixarene containing quinone moiety and their interaction with cationic complexes using steady state and time resolved optical spectral techniques. But there is no report of the ruthenium(II)-bipyridine-calixarene system using time resolved optical spectral techniques and there is no report for these techniques used for anion recognition.

Materials and Methods

The complexes, Rub2 and Rub3 are synthesized from the literature methods and characterized using FT-IR, ^{1}H NMR and HR-MS techniques (Figs S1 and S2). The observed δ and mass values are close to the reported values [54]. HPLC grade acetonitrile purchased from Merck is used as solvent throughout the studies. The *tert*-butylammonium fluoride, *tert*-butylammonium chloride, *tert*-butylammonium bromide, *tert*-butylammonium iodide, *tert*-butylammonium phosphate, *tert*-butylammonium acetate, *tert*-butylammonium perchlorate and *tert*-butylammonium cyanide are purchased from Sigma-Aldrich Pvt Ltd.

Determination of Binding Constants Using UV-Visible Absorption Spectral Titrations

The appropriate concentration of guest is fixed and the concentration of host [H] is varied from 1:10 to higher ratio. The binding constant (K) for the binding anion with

Rub2/Rub3 is evaluated with the aid of Benesi-Hildebrand method using Eq. (1) [60].

$$1\big/\Delta A = 1\big/K\Delta\varepsilon[H] + 1\big/\Delta\varepsilon[Anion] \qquad (1)$$

Here, ΔA—the change in the absorbance of the [Anion] on the addition of [H]. $\Delta\varepsilon$—the difference in the molar extinction coefficient between the free [Anion] and [H]-[Anion] complex. [H]—the total concentration of host. [Anion]—the total concentration of anions. For all the anions examined, plots of $1/\Delta A$ as a function of 1/ [Anion] give good straight line, supporting the 1:1 complex formation.

Determination of Binding Constants Using Luminescent Spectral Titrations

We have observed either luminescence enhancement or quenching depending on the nature of binding of anion with the calixarene system in our work. Therefore we have used different methods for the determination of binding constant depending on the behavior of the system. When we observed luminescence enhancement modified Benesi-Hildebrand method is used (Eq. (2)) [61]

$$I_0\big/(I-I_0) = b\big/(a-b) \times \left[1\big/K_a[H] + 1\right] \qquad (2)$$

where, I_0 is the luminescence intensity of the host in the absence of guest, I is the luminescence intensity of the host in the presence of guest (anion), [H] is the concentration of the host, and K_a is the binding constant for the binding of the host with guest. In the Eq. (2), a and b are constants. The values of I_0 and I are available from
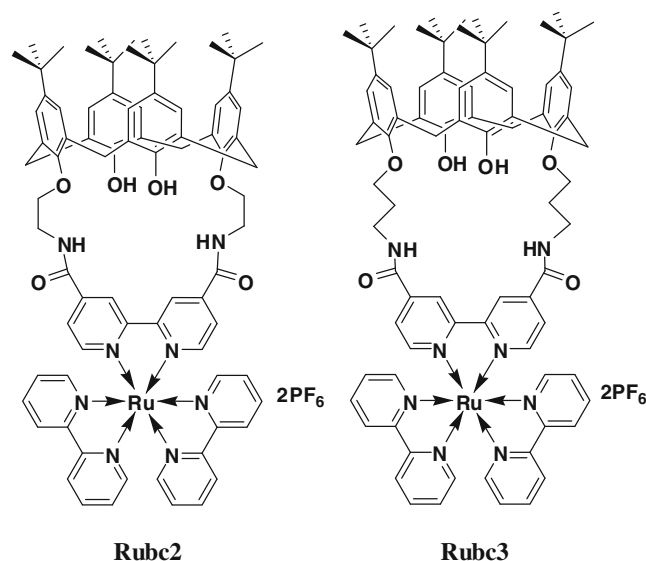

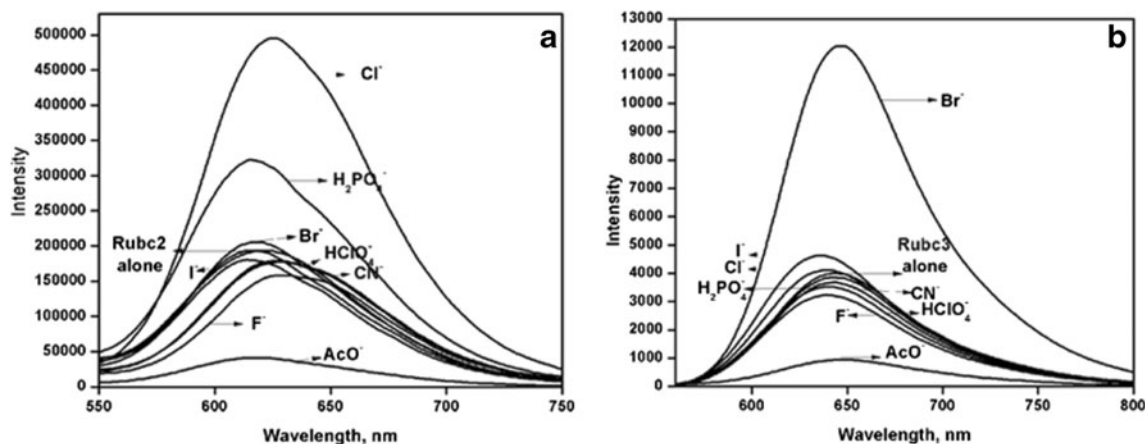**Chart 1** Structure of the ruthenium(II)-bipyridyl-calixarene complexes used in this study

Fig. 1 Comparision of emission intensity of complexes (**a**) Rubc2 (1×10^{-5} M) in presence of various anions (1×10^{-5} M) (**b**) Rubc3 (1×10^{-6} M) in presence of various anions (1×10^{-6} M) in acetonitrile

luminescence measurements. The value of K_a can be determined by plotting I_0/I—I_0 against the inverse of the concentration, (M^{-1}).

We have calculated the binding constant for the system which quenches the luminescence intensity by using the following modified Stern-Volmer equation, Eq. (3) [18]

$$\log\left[(I_0{-}I)\big/I\right] = n\log[H] + \log K_a \qquad (3)$$

[H]—concentration of host, K_a—binding constant, n is the stoichiometric ratio.

We have calculated the quenching constant, k_q by using the Stern-Volmer equation, Eq. (4) [40]

$$I_0\big/I = 1 + k_q\tau[H] \qquad (4)$$

I_0—Luminescence intensity in the absence of guest molecule. I—Luminescence intensity in the presence of various concentration of host molecule. [H]—Concentration of host molecules. τ—Excited state lifetime in the absence of quencher.

Transient Absorption Spectra and Excited State Lifetime [55]

Transient absorption measurements were made with a laser flash photolysis technique using an Applied Photophysics SP-Quanta Ray GCR-2(10) Nd:YAG laser as the excitation source. The time dependence of the luminescence decay is observed using a Czerny-Turner monochromator with a stepper motor control and a Hamamatsu R-928 photomultiplier tube. The production of the excited state on exposure to light of wavelength 355 nm was measured by monitoring (pulsed xenon lamp of 250 W) absorbance change. The change in the absorbance of the sample on laser irradiation is used to calculate the rate constant as well as to record the time-resolved absorption transient spectrum. The change in the absorbance on flash photolysis is calculated using the expression

$$\Delta A = \log I_0\big/(I_0{-}\Delta I) \qquad (5)$$
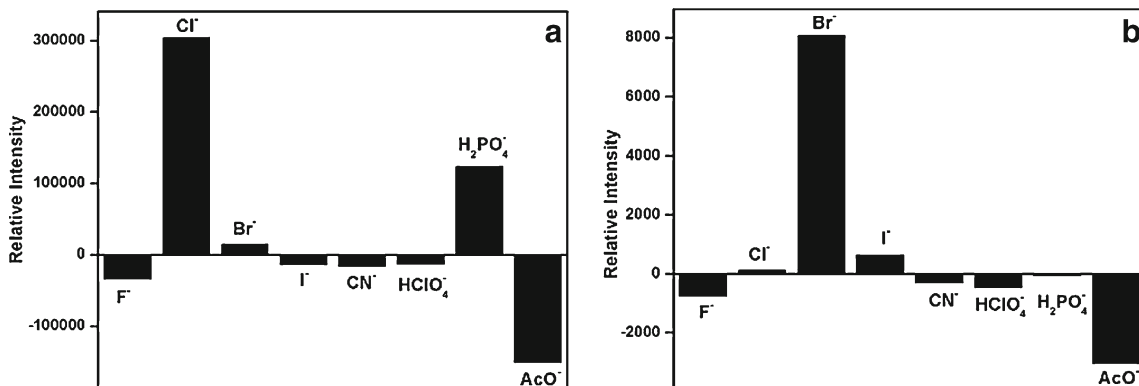
$$\Delta I = (I{-}I_t) \qquad (6)$$

Fig. 2 Relative emission intensity changes of Ru(II)complexes (**a**) Rubc2 (1×10^{-5} M) in presence of various anions (1×10^{-5} M) (**b**) Rubc3 (1×10^{-6} M) in presence of various anions (1×10^{-6} M) in acetonitrile
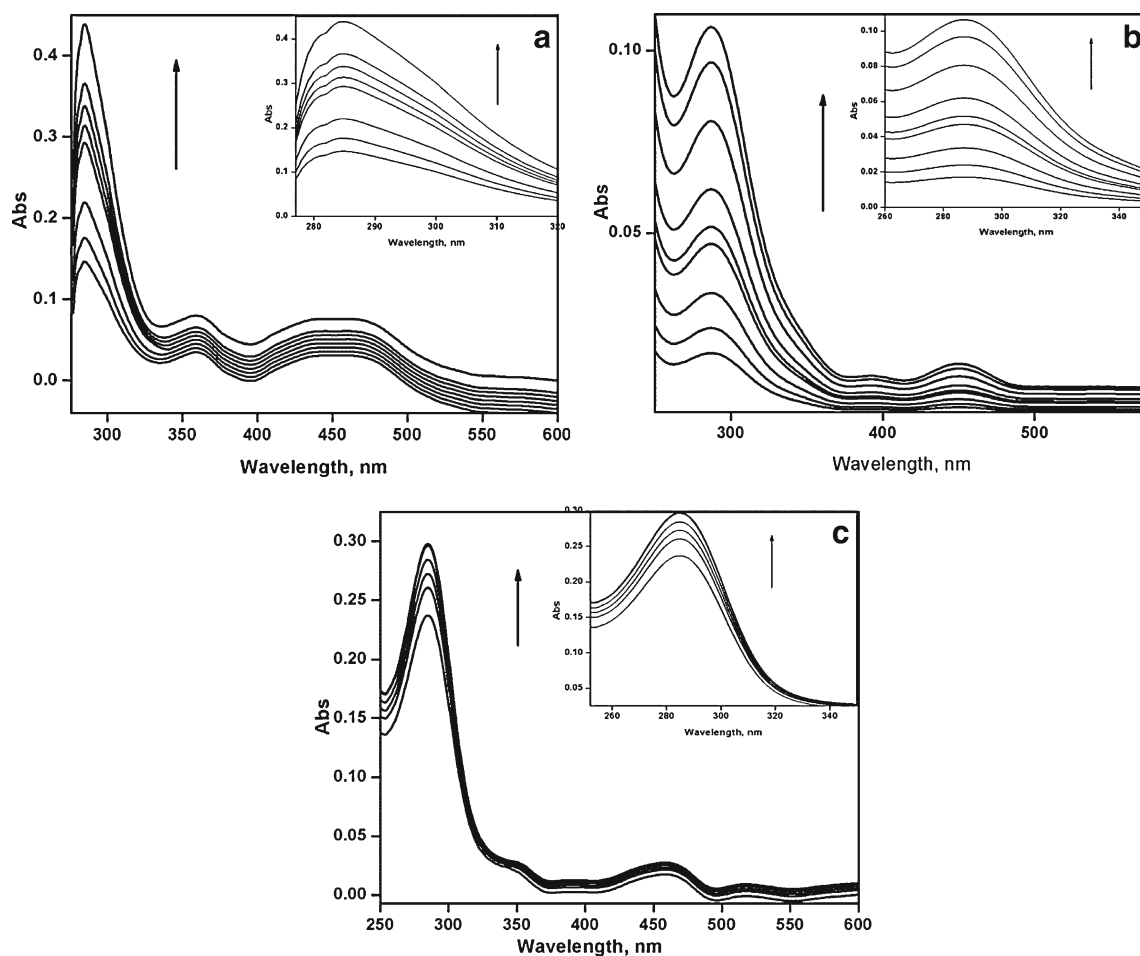
Fig. 3 Absorption changes of Rubc2 (1×10^{-5} M) in presence of increasing concentration of (**a**) Cl⁻, (**b**) $H_2PO_4^-$, (**c**) AcO⁻ ($1\times 10^{-4} - 9\times 10^{-4}$ M) in acetonitrile

where ΔA is the change in the absorbance at time t, I_0, I and I_t are the voltage after flash, the pretrigger voltage and the voltage at particular time respectively. A plot of $\ln(\Delta A_t - \Delta A_\infty)$ *vs* time gives a straight line. The slope of the straight line gave the rate

constant for the decay and the reciprocal of rate constant gave the lifetime of the triplet. The time-resolved transient absorption spectrum was recorded by plotting the change in absorbance at a particular time *vs* wavelength.
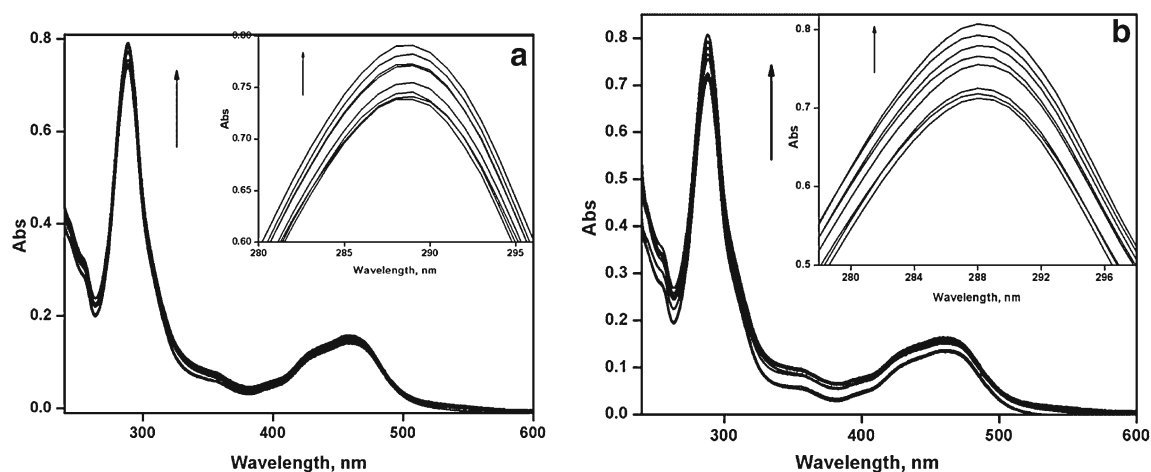

Fig. 4 Absorption changes of Rubc3 (1×10^{-6} M) in presence of increasing concentration of (**a**) Br⁻, (**b**) AcO⁻ ($1\times 10^{-5} - 9\times 10^{-5}$ M) in acetonitrile

Table 1 Binding constant values (K_a) of Rubc2 and Rubc3 with anions using absorption spectral technique in acetonitrile

Anion	Rubc2 (M^{-1})	Rubc3 (M^{-1})
AcO⁻	$4.3\pm0.5\times10^3$	$2.9\pm0.6\times10^2$
Cl⁻	$1.7\pm1.2\times10^4$	–
Br⁻	–	$1.3\pm1.7\times10^3$
H$_2$PO$_4$⁻	$1.4\pm0.8\times10^3$	–

The excited state lifetime decay using flash photolysis is measured by the same instrument in the emission mode. Here the wavelength is fixed at the λ_{max} of emission in steady state method and the decay is measured.

Results and Discussion

Recognition of Anions by Emission Spectral Technique

The structure of complexes is shown in chart 1. The concentration of Rubc2 is fixed at 1×10^{-5} M and that of Rubc3 is fixed at 1×10^{-6} M in acetonitrile. Since molar extinction coefficient is higher for Rubc3 compared to Rubc2 we have used different concentrations for Rubc2 and Rubc3. The emission intensity is measured for the two complexes in the presence of various anions (F⁻, Cl⁻, Br⁻, I⁻, HClO$_4$⁻, H$_2$PO$_4$⁻, AcO⁻ and CN⁻) in acetonitrile at room temperature. The emission intensity change at wavelength 642 nm for Rubc2 and that of 650 nm for Rubc3 is followed and the changes in the emission intensity are depicted in Fig. 1. There is a substantial increase of the emission intensity of Rubc2 in the presence of Cl⁻ and H$_2$PO$_4$⁻ and of Rubc3 in the presence of Br⁻. The emission intensity of both Rubc2 and Rubc3 decreases in the presence of AcO⁻. Other anions show neither consistent nor substantial emission intensity changes. The relative change in the emission intensity is depicted in Fig. 2.

Binding Efficiency of Anions by Steady State Absorption Spectral Techniques

We have carried out binding studies of anions which were recognized by two Ru(II)-complexes Rubc2 and Rubc3. We have calculated the binding constant values using UV-vis
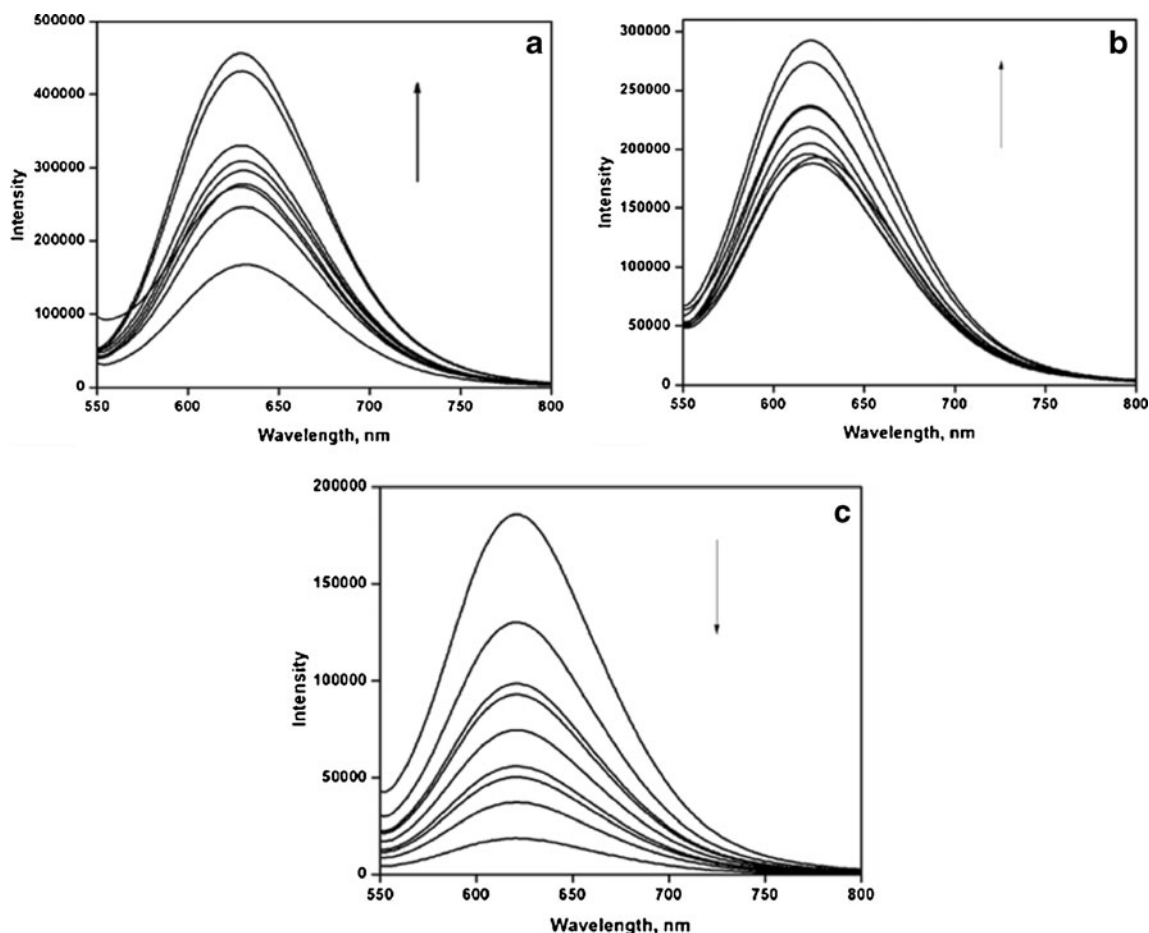

Fig. 5 Luminescence changes of Rubc2 (1×10^{-5} M) in presence of increasing concentration of (**a**) Cl⁻, (**b**) H$_2$PO$_4$⁻, (**c**) AcO⁻ ($1\times10^{-5}-9\times10^{-5}$ M) in acetonitrile
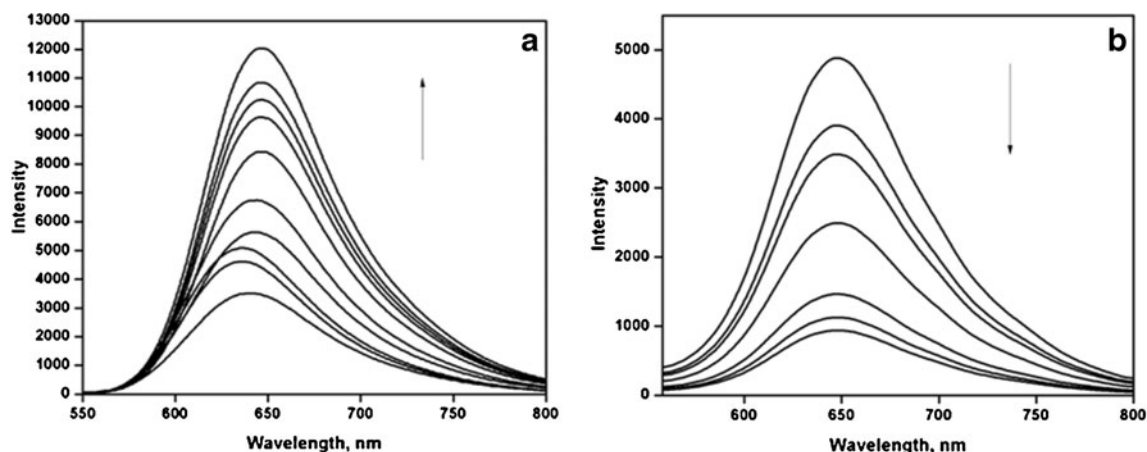
Fig. 6 Luminescence changes of Rubc3 (1×10^{-6} M) in presence of increasing concentration of (**a**) Br$^-$, (**b**) AcO$^-$ ($1\times 10^{-6} - 9\times 10^{-6}$ M) in acetonitrile

spectral technique. The change in the absorbance of Ru(II)-calixarene complexes upon addition of anions is shown in Figs. 3 and 4. On the addition of anions with the complexes there is no observable change in the MLCT band around at 450 nm. But there is an increase in the absorbance at 280 nm which shows that the binding of anion is with the ligand. We have calculated the binding constant values using Benesi-Hildebrand equation [60] (Eq. (1)) and the values are collected in the Table 1. The Benesi-Hildebrand plots are shown in Figs S3 and S4. The binding of anions with both complexes are moderate and Cl$^-$ has efficient binding with Rubc2 than H$_2$PO$_4^-$ and AcO$^-$. The Br$^-$ ion binds efficiently with Rubc3 than AcO$^-$. On comparing the binding with AcO$^-$ ion Rubc2 shows more efficiency than Rubc3.

Binding Efficiency of Anions by Steady State Emission Spectral Techniques

Since the luminescence is more sensitive technique than absorption technique, we carried out binding studies using luminescence spectral technique. Rubc2 shows increase in the emission intensity in the presence of Cl$^-$ and H$_2$PO$_4^-$ at 642 nm and Rubc3 shows increase in the emission intensity in the presence of Br$^-$ at 650 nm. Both complexes show quenching in the presence of AcO$^-$ (Figs. 5 and 6) at respective wavelengths.

We have used modified Benesi-Hildibrand equation (Eq. (2)) for calculating binding constant values for the system

which enhances the emission intensity [61, 62]. The Benesi-Hildebrand plots are shown in Figs S5 and S6. Modified Stern-Volmer equation (Eq. (2)) [30] is used for calculating binding constant values for the AcO$^-$ which shows quenching of emission intensity. The modified Stern-Volmer plots are shown in Fig S7. The binding constant values are collected in Table 2. With Rubc2 the Cl$^-$ ion shows the highest binding constant value, whereas H$_2$PO$_4^-$ and AcO$^-$ possess moderate binding constant values. With Rubc3, both Br$^-$, AcO$^-$ possesses moderate binding constant values. These binding constant values are comparable with reported values by Beer et al. using NMR techniques [54]. These values are comparable with the values of binding constants observed using absorption techniques. Since there is quenching of emission intensity for AcO$^-$ with both Rubc2 and Rubc3, we have calculated the quenching constant values which are collected in Table 3. The Stern-Volmer plots are depicted in Fig S8. Since these values are in the range of 10^{10} it is clear that the quenching is more efficient than diffusion controlled rate. Thus static quenching plays significant role due to ground state complex formation between the host and guest, AcO$^-$ ion.

Recognition of Anions by Excited State Lifetime Studies

Since, there is emission intensity enhancement of Ru(II)-calixarene complexes in the presence of Cl$^-$, Br$^-$ and H$_2$PO$_4^-$ but quenching in the presence of AcO$^-$, it may be

Table 2 Binding constant values (K_a) of complexes with anions using emission technique in acetonitrile

Anions	Rubc2 (M^{-1})	Rubc3 (M^{-1})
AcO$^-$	$5.9\pm1.4\times10^3$	$3.7\pm0.7\times10^2$
Cl$^-$	$9.9\pm0.3\times10^3$	–
Br$^-$	–	$4.9\pm1.2\times10^3$
H$_2$PO$_4^-$	$2.7\pm1.1\times10^2$	–

Table 3 Quenching constants (k_q) of Rubc2 and Rubc3 in the presence of AcO$^-$ in acetonitrile

Complex	Quenching Constant (M^{-1} s^{-1})
Rubc2	8.7×10^{10}
Rubc3	1.2×10^{10}

Table 4 Excited state lifetimes of complexes in the presence of anions by time resolved emission spectroscopy in acetonitrile

Anion	Rubc2 τ (ns)	Rubc3 τ (ns)
–	390	561
AcO$^-$		
1×10^{-5} M	372	498
3×10^{-5} M	303	400
Cl$^-$		
1×10^{-5} M	432	–
3×10^{-5} M	468	–
Br$^-$		
1×10^{-5} M	–	583
3×10^{-5} M	–	610
HPO$_4^-$		
1×10^{-5} M	417	–
3×10^{-5} M	466	–

flash photolysis technique. The excitation wavelength is fixed at 355 nm using laser source and the decay of the excited molecule has been measured at 642 nm for Rubc2 and 650 nm for Rubc3 by emission mode. The linear fitting of this decay gives the rate of decay. From the rate of decay, excited state lifetime is obtained. The excited state lifetimes of both complexes are collected in Table 4. The excited state lifetime of Rubc2 is 390 ns. The presence of Cl$^-$ and H$_2$PO$_4^-$ increases the excited state lifetime of Rubc2. These changes are shown in Fig. 7. Similarly the excited state lifetime of Rubc3 is 561 ns. The presence of Br$^-$ increases the excited state lifetime. These changes are shown in the Fig. 8. The presence of AcO$^-$ decreases the excited state lifetime of both Rubc2 and Rubc3.

Recognition of Anions by Transient Absorption Spectral Studies

The transient absorption spectra of Rubc2 and Rubc3 in the absence and presence of anions are shown in Fig. 9. In these spectra, the peak around 360 nm represents the triplet state,
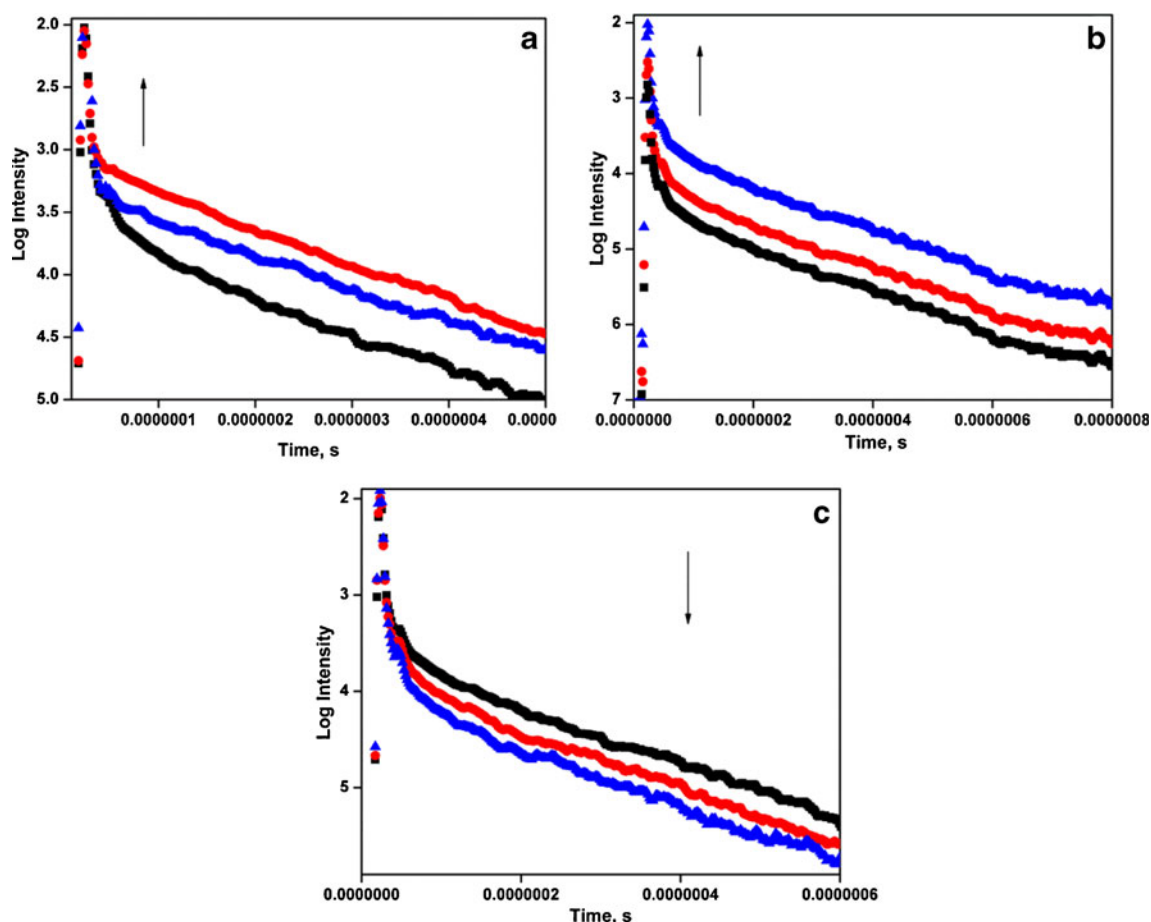
interesting to examine the lifetime of Rubc2 and Rubc3 in the excited state in the presence of anions. The excited state lifetime has been measured using emission mode of laser

Fig. 7 Excited state lifetime changes of Rubc2 (1×10^{-6} M) in presence of increasing concentration of (**a**) Br$^-$ (1×10^{-6}, 3×10^{-6} M), (**b**) AcO$^-$ (1×10^{-6}, 3×10^{-6} M) in acetonitrile
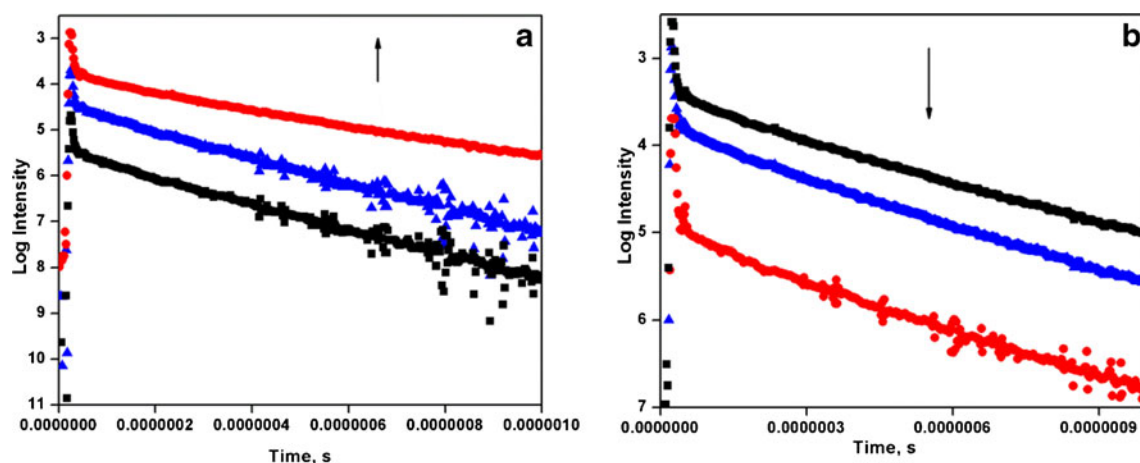
Fig. 8 Excited state lifetime changes of Rubc3 (1×10^{-6} M) in presence of increasing concentration of (a) Br$^-$ (1×10^{-6}, 3×10^{-6} M), (b) AcO$^-$ (1×10^{-6}, 3×10^{-6} M) in acetonitrile

the bleaching around 450 nm shows recovery of ground state, peak around 550 nm shows the formation of Ru (bpy)$_3^+$, and bleaching around 650 nm represents the relaxation of the emission [63]. The transient absorption spectra for both complexes are similar therefore their excited state behavior is also similar. The decay and formation rate constants and lifetime of decay and recovery are collected in Table S1. The kinetic traces are depicted in Figs S10 and S11. In the presence of Cl$^-$, Br$^-$ and H$_2$PO$_4^-$ the peak around the 350 nm increases. This shows that the presence of anions stabilizes the triplet state species. If, the rate of decay decreases, the lifetime of this species increases. This has been shown in Table S1. Similarly the difference in absorption increases around 450 nm and 650 nm for both two complexes substantiating the increase in the emission intensity and absorbance in steady state techniques.

In the presence of AcO$^-$, the difference in absorption around 350 nm decreases, which shows that, it, destabilizes the triplet state of the complex. The difference in absorption around 450 nm and 650 nm also decreases. This substantiates

the quenching of steady state methods by AcO$^-$. The decay rate is slightly higher for these species in the presence of AcO$^-$. The difference in absorption is weak around 540 nm which represents the Ru(bpy)$_3^+$ species for complexes alone. The presence of other anions has not changed the peak around 540 nm. But the presence of AcO$^-$ increases the difference in absorbance around 540 nm. The traces in the Figs S10 and S11 show the formation of this state substantially. The rate of decay of these species decreased and lifetime of the species increased. This shows the AcO$^-$ facilitates the non radiative pathways by producing Ru(bpy)$_3^+$, therefore quenching occurs in the steady state emission techniques.

Conclusion

The two ruthenium(II)-bipyridine-calixarene complexes (Rubc2 and Rubc3) can be used as anion sensors up to 10^{-6} M concentrations. The binding of the anions which are recognized by complexes has been calculated. This shows
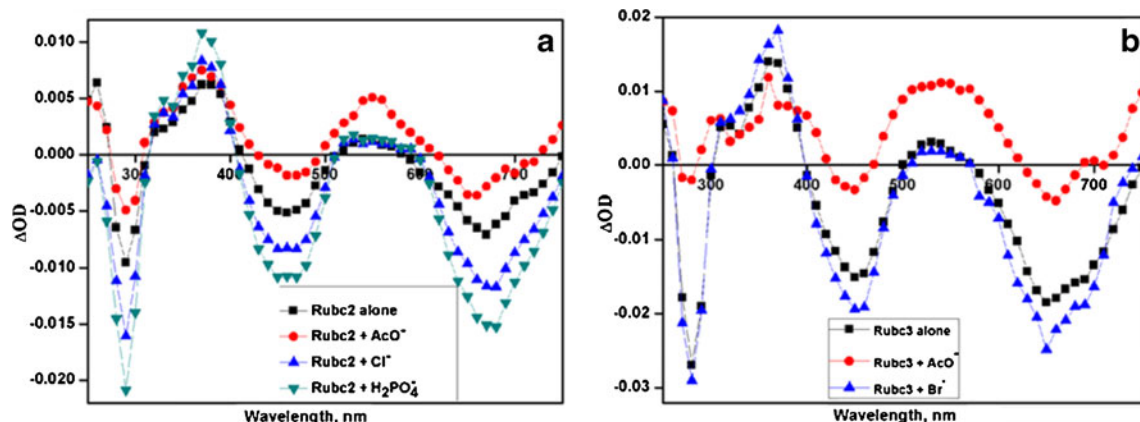

Fig. 9 Transient absorption spectra of (a) Rubc2 (■) (1×10^{-5} M) in presence of Cl$^-$ (1×10^{-5} M) (▲), H$_2$PO$_4^-$ (1×10^{-5} M) (▼), AcO$^-$ (1×10^{-5} M) (●) and (b) Rubc3 (1×10^{-6} M) (■) in presence of Br$^-$ (1×10^{-6} M) (▲), AcO$^-$ (1×10^{-6} M) (●) in acetonitrile

substantial binding of these anions with the complexes. The behavior of the anions towards the complexes is different. The excited state lifetime and transient absorption spectral studies show that their interaction with excited state complexes is different. AcO^- facilitates the nonradiative pathway but the other anions stabilize the excited state thus enhances the emission intensity in the steady state method.

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