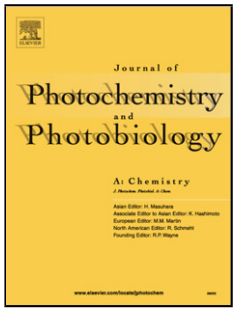

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New Luminescent probe for the selective detection of Dopamine based on *in situ* prepared Ru(II) complex-Sodium Dodecyl Benzyl Sulfonate assembly

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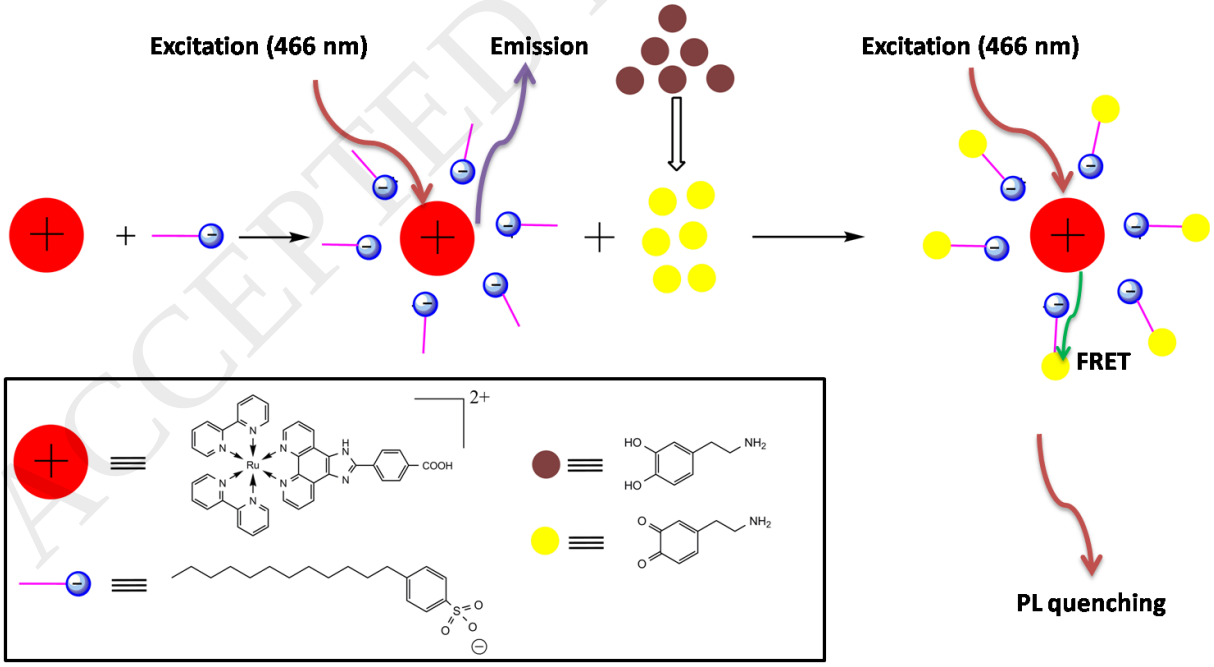
Graphical abstract:



Highlights

- First approach to develop Ru(II) complex with surfactant SDBS as a luminescent sensor
- The high selectivity and sensitivity are resulted due to presence of SDBS
- The quenching mechanism follows FRET among luminescent assembly and dopamine
- Present work will pave way for initiation of new kind of coordination complex based luminescent sensors upon tuning with surfactants

Abstract:

Due to clinical importance, detection of dopamine by using easy and rapid method is still ongoing challenge. Here we present a simple and quite efficient method for dopamine (DA) detection in alkalescent medium using *in situ* prepared Ru(II) complex and sodium dodecyl benzyl sulfonate (SDBS) as highly luminescent luminophore. The luminescence enhancement in the Ru(II) complex (Ru-CIP) has been observed in the miceller medium formed by SDBS. The capability to successively quench the luminescence intensity has been tested for variety of molecules and only dopamine as analyte found to be able to quench luminescence effectively. Hence selective quenching of luminescence by dopamine was used as a tool to detect dopamine and two linear concentration ranges has been established from 0.1 µM to 1µM and from 2 µM to 10 µM with limit of detection (LOD) is 6.6 nM (S/N = 3). Spectral evidence showed that luminescence quenching mechanism arose via Forster resonance energy transfer (FRET) among oxidized DA (i.e. DA quinone) and *in situ* generated Ru-CIP and

SDBS assembly. Due to ultra sensitivity and high selectivity of the prescribed (Ru-CIP-SDBS) luminescent probe has a strong potential for practical analytical application in clinical diagnosis.

Keywords:

Luminescence; Ru(II) complex; SDBS; Surfactant; Dopamine; Sensor

1. Introduction:

Dopamine (4-(2-aminoethyl)-benzen-1,2-diol, DA) as a neurotransmitter plays pivotal roles in several brain functions operated by central nervous system.[1, 2] The main functions of dopamine in human body include control of motor activity, behavioral emotions, autonomic and endocrine functions related to secretions of hormones.[3, 4] Abnormality in the dopamine levels in the body fluids leads to several serious maladies like Parkinson's disease, schizophrenia due to its deficiency while Huntington's disease, condition similar to euphoria due to its over secretion.[5] Sympathoadrenal system activity can be monitored by the concentration of DA in urine which resulted into serious diseases like pheochromocytoma.[6] Therefore, the dopamine content in blood or urine is paramount importance as a biomarker in medical diagnostics concerning these diseases.[7] By taking these things into consideration stringent method for the detection of dopamine is necessary to avoid serious health complications.

So far lots of methods have been developed for the detection of DA[8, 9], which mainly includes electrochemical[10, 11] including electrochemiluminescence[12, 13],

chromatographic,[14] colorimetric methods.[15, 16] Electrochemical method's resultant potential of DA is overlay or quite close to interfering species like uric acid (UA), ascorbic acid (AA) making analysis of DA a tedious procedure. While chromatographic analysis,[14] flow injection analysis,[17] requires sophisticated high end instrumentation facility. Thus spectroscopic method, among which, fluorescence spectroscopy which bears several advantages like low cost of analysis, ease of operation and handling, good reproducibility and high selectivity and sensitivity, making it most suitable method for DA detection.[18-21] Additionally, tedious sample preparation is not required for unlike other available methods. Quantum dots or nanoparticles are described as material for the detection of DA by variation in fluorescence as sensing parameter.

Ma and co-workers demonstrated DA photoluminescence (PL) sensor using CdSe nanocrystals with citrate as capping agent, which work by tapping excitons.[22]

Zhong and co workers described the use of adenosine capped CdSe/ZnS quantum dots for the detection of dopamine in human urine samples where LOD upto 29.3 nM was reached.[18]

Zhao et al synthesized (3-aminopropyl) trimethoxysilane (APTMS)-capped ZnO quantum dots for determination of DA quantitatively in aqueous solutions. The linear concentration range of 0.05 to 10.0 µM with LOD of 12 nM was obtained.[20]

Rui Ban et al developed luminescence DA sensor employing host guest chemistry of β-cyclodextrin capped gold nanoclusters. The limit of detection reached as low as 2 nM.[23]

Chen and coworkers reported highly photoluminescent silica nanoparticles with APTMS capping agent to detect DA in aqueous solution. Linear proportionality with DA concentration of 0.005µM to 10 µM were obtained with detection limit as low as 0.3 nM.[21]

Recently MoS_2 nanohybrid as fluorescence sensor for detection of DA was illustrated by Cyriac and co-workers and demonstrated two linear ranges from 2.5 nM to 5.0 µM and from 5.0 µM to 10.4 µM with limit of detection of 0.9 nM.[19]

Among all these, Ru complex based luminescent probe for DA detection was rarely explored. Ru complexes among which $[Ru(bpy)_3]^{2+}$ is well known for possessing vibrant luminescence properties by taking advantage of these properties many luminescent chemosensors are developed and explored for their analytical properties in clinical diagnosis.[24]

Shielding of particular functional groups on ligand, more specifically nitrogen containing groups on the fluorophore by the addition of surfactant could lead to the modulation of the fluorescence signal.[25, 26] Additionally *in situ* created miceller environment can modulate the emission properties of the fluorophore.[27] Thus modulation of signal on the fluorophore could be used as a tool to detect response from the analyte. Using surfactant assemblies fluorescence emission have been modulated to develop discriminative sensors.[28] (Liping Ding and co-workers have recently developed SDS modulated fluorophore containing pyrene based ligands which shows multiple emission bands for detections of ions simultaneously in a given solution.[27]

Ru complexes and their properties in the surfactant media are widely studied and severely reported in the literature[29-31] but the application of such Ru complexes and surfactant are still unknown and rare to be observed. Surfactants like SDS, SDBS, Triton X 100 are known to create alteration in the luminescent properties of Ru-complexes.[32, 33] In that complexes get weakly bound to the surfactant assemblies and strength of the binding highly relied upon the nature of ligands on the metal complex.

In the present work, using emission intensity as a probe we have selectively and sensitively detected DA by *in situ* dispersing $[Ru(bpy)_2(CIPH_2)]^{2+}$ in SDBS miceller aqueous media, a

highly luminescent assembly. The absorption spectrum of DA in basic media overlap with the PL spectra of $[Ru(bpy)_2(CIPH_2)]^{2+}$ in SDBS medium which attributes for good selectivity via Forster resonance energy transfer (FRET) among them. The mechanism of quenching is well illustrated in Scheme 1. To the best of our knowledge this is first ever approach to *in situ* prepared Ru(II) complex-SDBS highly luminescent assembly for the detection of DA upto nanomolar level.

Firstly, the luminescence of $[Ru(bpy)_2(CIPH_2)]^{2+}$ was triggered in the presence of optimum concentration of SDBS, later on it was successively quenched by increasing concentration of DA. *In situ* developed novel luminescence probe for the detection of DA has several advantages over existing methods for DA detection, alongside high sensitivity and selectivity this method could be operated in wide linear range, easy to operate, safe with less operational cost, quite simple and fast responsive method.

2. Experimental

2.1 Chemicals and materials

All purchased reagents were analytical grade and used in experiments as received without further purification. The main chemical reagents (and their sources) were: 1,10 phenanthroline-5,6-dione, 4-carboxybenzaldehyde and $RuCl_3.3H_2O$ from Ark Pharma Scientific Ltd., China. 2,2'-bipyridine from J & K Scientific Ltd., China. Dopamine hydrochloride (DA) purchased from Aladdin Industrial Co., Shanghai, China. Sodium dodecyl benzene sulfonate (SDBS) was purchased from Shanghai chemical company, Shanghai, China. Common inorganic salts, KCl, $MnSO_4$, $AlCl_3$, $CuCl_2$, NH_4Cl, and $NaNO_3$ were purchased from Shanghai Chemical Company, Shanghai, China and their solutions were

prepared by dissolving in deionized water. Ascorbic acid (AA), Uric acid (UA), Glucose and Sucrose were obtained from Shanghai Chemical Company, Shanghai, China.

Bovine Serum Albumin (BSA), amino acids (L-glycine (Gly), L-alanine (Ala), L-proline (Pro), L-phenylalanine (Phe), L-serine (Ser), L-cysteine (Cys), L-glutamic acid (Glu), L-tyrosine (Tyr), L-glutamine (Gln), L-leucine (Leu), L-aspartic acid (Asp), L-lysine (Lys), L-histidine (His),L-valine (val), L-isoleucine (ile) , L-arginine (Arg), LD-tryptophan (Try), glutathione (GSH), were purchased from Shanghai Chemical Company, Shanghai, China.

Phosphate buffer solution (0.1 M) calibrated by using a pH meter was used as a buffer to maintain the pH in all testing sample solutions. Deionized water (18.2 MΩ cm), used in all experiments was generated by passing the natural water through a reverse osmosis process equipped with a Milli-Q water purification system.

2.2 Apparatus and measurements:

^{1}H-NMR spectra were measured with a Bruker Avance 400 MHz spectrometer using TMS as an internal standard.

Luminescence spectra and intensities were recorded on Edinburgh Instruments' FS5 spectrofluorimeter equipped with a xenon discharge lamp using 1 cm quartz cells.

Luminescence lifetime measurements were performed with Steady State and Transient State Fluorescence Spectrometer (FluoroLog 3-22-TCSPC, Horiba).

All pH measurements were carried out using Mettler Toledo, FE 28 pH meter.

UV–vis absorption spectral measurements were carried out on Shimadzu UV-2700 spectrophotometer.

All the experiments were carried out at room temperature. Typically, all glasswares and magnetic stirrer bars used during analysis were soaked in aqua regia (HNO_3/HCl = 1:3, *v*/v) about 5 h, then thoroughly cleaned in water and dried in oven prior to use.

2.3 Synthesis of $[Ru(bpy)_2(CIPH_2)]^{2+}$ complex:

Synthetic procedure steps and NMR spectra of $[Ru(bpy)_2(CIPH_2)]^{2+}$ complex for convenience referred as Ru-CIP complex are described in Electronic supporting information. The complex Ru-CIP has been synthesized by following slightly modified reported literature method.[34, 35] Briefly, 1,10 phenanthroline-5,6-dione via Steck and Dey[36] coupling with 4-carboxybenzaldehyde formed 4-carboxyl-imidado[4,5-f][1,10]-phenanthroline (CIP) ligand. In a typical reaction $Ru(bpy)_2Cl_2$ (146 mg, 0.30 mmol, 1.0 eq) was treated with silver nitrate (102 mg, 0.60 mmol, 2.0 eq) in methanol for 3 hours at room temperature. The solution was filtered in order to remove silver salts and the filtrate was added to a round bottom flask containing CIP ligand (98 mg, 0.30 mmol, 1.0 eq). The solution was refluxed for 3 hours in dark under an argon atmosphere. At this time the reaction mixture was allowed to go to room temperature and the solvent was evaporated under reduced pressure. The obtained solid was washed repeatedly with copious quantity of diethyl ether; the obtained product was dried under vacuum (243 mg).Yield: 78%.

2.4 Calculation of quantum yield:

Luminescence quantum yield (Φ) at room temperature was measured by comparison with aerated aqueous solution of standard $[Ru(bpy)_3]Cl_2$ (Φ std= 0.042)[37] by the optically dilute method.[38]

The QY of the synthesized complex (Φ sample) was calculated from Eq. (1):

$$\Phi_{sample} = (OD_{std} \times A_{sample}) / OD_{sample} \times A_{std}) \times \Phi_{std} \quad (1)$$

Where A_{sample} and A_{std} are the integrated area under the luminescence curve for the sample and standard respectively. The OD_{std} and OD_{sample} are the absorbance of standard and sample at excitation wavelength, respectively.

2.5 Preparation of highly luminescent Ru-CIP-SDBS assembly

The behavior of the Ru complexes can be altered significantly in the miceller media, in literature this phenomenon has been discussed in detail.[26, 30] *In situ* formed micelle can trigger the luminescence of virtually non luminescent complex.[26] Adherent with this phenomenon we have added 0.16 mM SDBS to the Ru-CIP aqueous solution which leads to *in situ* formation of highly luminescent Ru-CIP-SDBS assembly. As generated Ru-CIP-SDBS was used for the detection of DA in aqueous solutions.

2.6 Procedure for the detection of DA:

All DA detection measurements were performed under alkalescent environment and pH was controlled by PBS buffer solutions.

Detection of DA by *in situ* generated Ru-CIP-SDBS was performed as described below: 10 µM of Ru-CIP aqueous solution was reacted with 0.16 mM SDBS, to this solution different concentration of DA solution was added. This mixture was incubated for 1 hr at room temperature with constant stirring. Later on, luminescence measurements were performed by exciting sample at wavelength 466 nm.

3. Results and Discussion

UV-visible absorption and luminescence of Ru-CIP in aqueous solution:

The basic photophysical properties of Ru-CIP were measured in the aqueous solution by UV-visible and steady state emission spectroscopy.

As seen in the Figure 1a, the UV-vis absorption spectra of the Ru-CIP inherit typical absorption peaks similar to $[Ru(bpy)_3]^{2+}$. One intense band in 250 nm to 300 nm region corresponds to π-π* transition localized on the bpy and band observed at 458 nm corresponds to metal to ligand charge transfer transition (MLCT). Studies with similar complexes showed that appeared band at 330 nm and MLCT band tailing upto 570 nm are attributed to the intra ligand (ligand- ligand) transition occurring on the CIP ligand.[34] This essentially means that any changes in the surrounding medium around CIP could lead to observable changes in the absorption feature.[39, 40]

Upon excitation at MLCT band of Ru-CIP, gives an emission spectrum with the peak centered at 621 nm (Figure 1b) with the quantum yields and lifetimes comparable to those for $[Ru(bpy)_3]^{2+}$, (~900 ns) when measured at anaerobic conditions.[41] The Stokes shift was more than 50 nm so the background interference could be eliminated.

Determination of concentration of SDBS:

Modulation of luminophore emission by addition of surfactant is a key point for some ligand for the development of selective sensors.[28] As evidenced by literature, surfactant upon aggregation can modulate the fluorescence emission of the Ru complex containing pyrene[27] dipyro[26] based fluorophores. In that case, a pyrene-based fluorophore (PB) containing a metal ion receptor group was specially designed and synthesized and later on anionic surfactant sodium dodecyl sulfate (SDS) was added to generate assemblies which can effectively adjust its fluorescence behavior.

While in the present case, upon addition of SDBS to Ru-CIP solution the luminescence is enhanced due to the formation of anionic surfactant, SDBS adsorption on the Ru-CIP (Scheme 1) and counter ion stabilization/exchange effect by anionic surfactant.[42, 43] Titration involving Ru-CIP with varying concentration of SDBS has been performed in PBS pH 8 solutions (Figure 2) and as shown SDBS assemblies can significantly adjust the emission of the present probe. Remarkable change in the emission profile is observed along varying SDBS concentration. It showed continuous increase of luminescence along SDBS concentration until 0.16 mM is reached. Afterwards it had showed steady decrease in the luminescence (Figure 2).

Therefore we have chosen optimum concentration, 0.16 mM of SDBS giving high luminescence value to construct a binary fluorescent ensemble for the detection of DA in the aqueous solutions. Such *in situ* formed Ru-CIP-SDBS assembly is stable over the period of 24 hours.

Effect of pH on measurement:

Since the characteristics of solution change with the pH, it is significant to monitor the performance of the sensor at different pH values. Therefore, the effect of pH on the luminescence properties has extensively studied in order to elucidate optimal pH value to carry out detection of DA (Figure 3). It is severely discussed that basic pH is the best choice for the DA measurements as the pK_a of the DA is 8.87.[44]

The observed pH effect in figure 4 can be explained by taking into consideration of pK_a of individual oxidizable unit. The pK_a of Ru-CIP has been previously determined by Pellegrin et al.[40, 45]

Accordingly the pK_a scheme is as described below,

$[Ru(bpy)_2(CIP\mathbf{H_3})]^{3+} \rightarrow [Ru(bpy)_2(CIP\mathbf{H_2})]^{2+} + H^+$ ($pK_a = 5.0$) (2)

$[Ru(bpy)_2(CIP\mathbf{H_2})]^{2+} \rightarrow [Ru(bpy)_2(CIP\mathbf{H})]^{+} + H^+$ ($pK_a = 8.9$) (3)

$[Ru(bpy)_2(CIP\mathbf{H})]^{+} \rightarrow [Ru(bpy)_2(CIP)]^{0} + H^+$ ($pK_a = 9.5$) (4)

These pK_a values are best support our experimental observations, at pH 4 to 6 complex is at its tri-cationic form (3+) while in neutral condition we could expect the formation of (2+) state of the complex. As expected strong mutual interaction between moderately charged cationic, 2+ and 3+ complex and *in situ* generated anionic SDBS micelles were observed which results into intense emission.(Figure 3) Upon further increase of pH to 8, when it's getting closer to the monocationic (+1) state of the complex resulted into weaker emission as compared to lower pH values. At pH 9, complex almost reaches to its neutral state thus virtually no interaction and no effect on emission upon addition of SDBS

Figure 3 illustrates comprehensively the quenching of Ru-CIP in the presence of SDBS by DA at different pH. Therefore in order to make a balance between efficient quenching by DA and to increase detection limit of DA as maximum as possible under our present experimental conditions, we have chosen pH 8 for this study.

The control experiments had performed in order to make sure the presence of SDBS in solution plays a vital role in order to quench the luminescence of Ru-CIP by DA and in the absence of it quenching is not favored. Figure 4 shows quenching of Ru-CIP luminescence by DA in the presence or absence of SDBS. DA only quenches luminescence due to SDBS thus question of Ru-CIP complex alone could act as a luminescent probe is completely eliminated.

Sensitivity of Ru-CIP-SDBS for DA detection:

The luminescence quenching of Ru-CIP in SDBS miceller media by varying concentration of DA is depicted by luminescence spectra in Figure 5a. The pH of the sensing solution was maintained at 8 by PBS buffer solution.

In the absence of DA, the Ru-CIP-SDBS assembly exhibit strong emission centered at 621 nm when excited at 466 nm. With increasing concentration of DA monotonic decrease in luminescence intensity of Ru-CIP-SDBS assembly is observed. It is apparent by looking at the Figure 5 that the Ru-CIP-SDBS system can respond to the presence of DA concentration as low as a 20 nM and two linear concentration ranges are observed one from 0.1 µM to 1µM and another from 2 µM to 10 µM (figure 5b) which is quite similar when MoS_2 nanohybrid used for the detection of DA.[19]

Figure 5b shows the plot of luminescence quenching of Ru-CIP-SDBS against the concentration of DA. The observed luminescent quenching is inline with the amount of DA added to the solution of luminophore, thus it can be directly use for quantitative determination of DA analyte.

The quenching of the Ru-CIP-SDBS by different concentration of DA can be well described by Stern-Volmer type equation,

$I_0/I = 1 + K_{sv}[A]$

Where I_0 and I are the PL intensity of Ru-CIP-SDBS in the absence and presence of DA, respectively, and K_{sv} is the Stern-Volmer quenching constant.

The K_{sv} value calculated for the first linear range from 0.1 µM to 1µM was 2.89 X 10^6 M^{-1} and for the second linear range from 2 µM to 10 µM it was 1.60 X 10^6 M^{-1}.

The limit of detection (LOD) was obtained from S/N =3 is as low as 6.66 nM which is comparable to lowest obtained value for DA reported in the literature so far.[19, 21]

Possible quenching Mechanism by DA:

In literature some reports are available for the detection of DA using different fluorescence probes and proven to be followed various mechanisms such as electron transfer (ET), florescence resonance energy transfer (FRET), inner filter effect (IFE), etc. In order to elucidate the mechanism involved in our newly designed luminescent probe Ru-CIP-SDBS which contains Ru linked to bpy, phenanthroline and imidazole moieties and in SDBS miceller media acting as a luminescence "switch off" sensor for DA we have taken the aid of photophysical characterization. Changes in charge on the complex, surrounding environments near functionality are known to be produce alteration in the overall optical properties. Hence, absorption features can show the possible interaction of Ru-CIP-SDBS with DA in PBS at pH 8.

Electron transfer from Ru-CIP to DA as DA in oxidized form is well known as an electron acceptor[20] is not evident in our observation as there is no bleaching / or decrease of absorption is observed at the MLCT band (458 nm) corresponding to Ru(II) to Ru(III) state upon quenching of luminescence intensity by DA.

Thus, the quenching effect presumably results from the effective energy transfer that occurred between Ru-CIP-SDBS and DA. Because of the redox activity of dopamine, we attributed these findings to non covalent interactions between Ru-CIP-SDBS and mainly two forms of dopamine: the reduced dopamine (electron donors) and the oxidized dopamine-quinone (electron acceptors). As we all know, dopamine in its hydroquinone form is known to undergo oxidation to its quinone analogue under basic pH conditions in the presence of ambient oxygen or in the presence of some oxidizing agents.

Since the pH of our sensor was 8, the oxidation of DA is an inevitable possibility. As reported by Zhang et al and Mani et al the oxidation of DA leads to additional absorption peak around

450 nm and tail of absorption upto 600 nm.[19, 21] For that we have measured absorption spectra of each entity to ensure possible quenching mechanism. For absorption spectra of oxidized DA refer to Figure S8 in the supporting information.

As described earlier, Ru-CIP has absorption of MLCT with maximum at 458 nm and absorption tails upto 570 nm. Upon addition of SDBS upto 0.16 mM in Ru-CIP solution the entire absorption spectrum get red shifted by 8 nm with maxima peaking up at 466 nm. Further addition of DA to the solution leads to the extension of absorption tail upto 760 nm (Figure 6a).

Thus absorption spectrum of Ru-CIP-SDBS with DA overlaps with emission spectrum of Ru-CIP in SDBS media (Figure 6b). Thus, due to FRET effect from the donor (Ru-CIP- SDBS) to the acceptor (DA quinone) leads to efficient luminescence quenching.

The quenching mechanism of our luminescent probe was presented in Scheme 1. While testing DA solution along with probe, the DA molecules get oxidized in the solution upon aeration and adsorbed on the Ru-CIP-SDBS via non-covalent interactions such as strong electrostatic interaction and non-covalent interaction like hydrogen bonding between SDBS molecule H- atom and strongly electronegative O- atom of DA quinone.

Dopamine as a neurotransmitter get synthesized using amino acid as precursors like phenylalanine, tyrosine.[46] Therefore, structural resemblances exist between DA and tyrosine. As proposed by Sharma et al. interaction between surfactant and amino acid could result into the formation of surfactant-amino acid assembly.[47] This assembly between surfactant and amino acid formed via resulting electrostatic and hydrophobic interactions among them. [47, 48] Therefore, in an overall luminescent probe of Ru-CIP-SDBS the Ru-CIP is rather freely available to activate DA molecules by FRET.

The short distance between the donor (Ru-CIP-SDBS) and the acceptor (DA quinone) together with the overlap of the emission spectrum of Ru-CIP-SDBS and absorption spectrum of DA quinone fulfill the requirement of FRET process. During the FRET process, the energy transferred from the photoexcited Ru-CIP-SDBS to the oxidized DA quinone molecules, resulting in the effective luminescence quenching of the Ru-CIP-SDBS. The ultra sensitivity arises due to larger spectral overlap (Figure 6b) which paves way for efficient energy transfer (FRET).

The observed two linear components in the Stern-Volmer plot (Figure 5b) are resulted due to the multiple quenching pathways arise between Ru-CIP and oxidized DA molecule which are similar to those observed in some cases.[19, 49] Initially at lower concentration of DA, the resulting absorption of oxidized DA around excitation wavelength (466 nm) is at minimal. Therefore, when the concentration of DA is lower in sample solution, FRET predominates. While at higher concentration of DA there is significant contribution of oxidized DA absorption around 466 nm (Figure S8). In that case, inner filter effect (IFE) which mainly arises due to absorption of quencher at an excitation wavelength also contributes towards quenching in addition to the FRET.

Selectivity of Ru-CIP-SDBS for DA detection (Interference study):

Our newly developed Ru-CIP-SDBS probe is intended to be used for the selective detection of DA. Therefore it is worthwhile to check the luminescence response of chemosensor for other common occurring molecules of biological importance. As shown in Figure 7, along with DA quenching effect of other common biomolecules and ions were investigated. In Figure 7, the ratio of intensities I_0/I has been derived experimentally, where I_0 and I are correspond to values of luminescence intensity at an excitation wavelength of 466 nm for "Ru-CIP SDBS" and "Ru-CIP SDBS with analyte" respectively.

Alongwith DA, Amino acids and biomolecules including serine (Ser), lysine (Lys), leucine (Leu), glutamic acid (Glu), alanine (Ala), cysteine (Cys), phenylalanine (Phe), threonine (Thr), histidine (His), valine (Val), glycine (Gly), aspartic acid (Asp), arginine (Arg), proline (Pro), tyrosine (Tyr), tryptophan (Trp), glutathione (GSH), Bovine Serum Albumin (BSA), glucose, sucrose, ascorbic acid (AA), uric acid (UA) and ions such as K^+, Mn^{2+}, Al^{3+}, Cu^{2+}, NH_4^+, Na^+ were investigated .

None of them had significant quenching effect on luminescence intensity of Ru-CIP-SDBS except DA. It is worth to note that probe is highly selective over two major interfering molecules AA and UA signifies efficacy among other reported sensors.

In all, this implies the greater selectivity of our newly developed Ru-CIP-SDBS luminescent probe towards detection of DA. The attractive selectivity of Ru-CIP SDBS luminescent assembly towards DA molecules in the PBS buffer solution at pH 8 arises due to spectral overlap of absorption spectrum of DA in Ru-CIP-SDBS with that of PL spectrum of Ru-CIP in SDBS medium which pave FRET among them. In other words, only absorption spectrum of Ru-CIP-SDBS and DA together overlaps with emission spectrum of Ru-CIP-SDBS in aqueous solution, thus making resulting FRET possible, while other interfering molecules do not exhibit such a property. Therefore, it makes Ru-CIP SDBS probe selective for detection of DA in presence of other interfering substances. Thus our proposed probe can use for the detection of DA in biological samples without separating the analyte from interfering substances.

Conclusions :

In summary, *in situ* developed facile new luminescent binary ensemble (Ru-CIP SDBS) turn off sensor which could sensitively and selectively detect dopamine in an aqueous solution for first time. Our obtained results showed that luminescence of Ru-CIP enhanced in SDBS

miceller environment and upon addition of DA molecules absorption got extended upto 760 nm which leads to overlap with emission spectrum of Ru-CIP-SDBS paving FRET among them, thus luminescence quenching. This developed sensor operates with high selectivity and comparable satisfactory sensitivity in basic aqueous solution (Table 1). Limit of detection (LOD) of the present probe was calculated to be 6.6 nM (S/N =3), with two linear ranges ranging from 0.1 µM to 1µM and from 2 µM to 10 µM. Till date, sensing of DA in the surfactant media is has never been reported. Therefore present probe is a first example of its own kind opening a new avenue in sensing area. Present study demonstrated that use of SDBS could greatly enhance sensitivity, selectivity of the luminescent Ru- complexes. Further work in the direction of structural ligand control in order to increase selectivity, specificity for particular biological target with use of various surfactants is currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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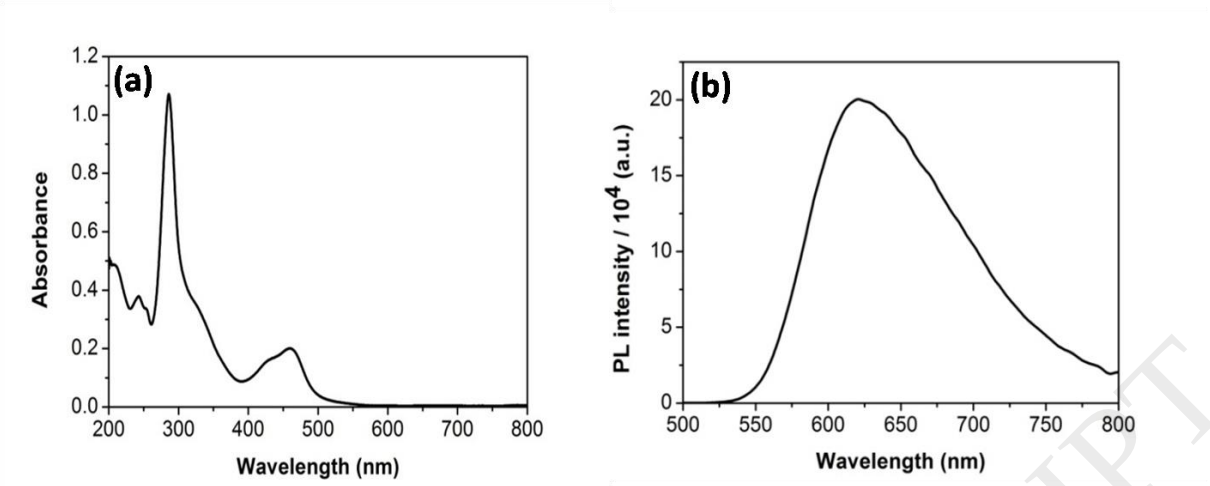


Fig. 1 (a) UV-visible absorption spectrum of Ru-CIP and (b) Steady state emission spectrum of Ru-CIP in PBS (pH 8) solution, λex = 458 nm.

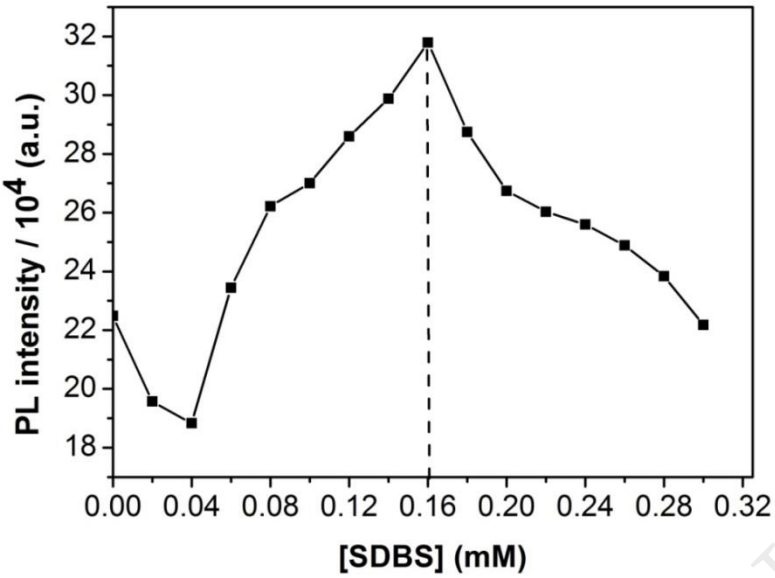


Fig. 2 Emission intensity ratio, I_0/I of Ru-CIP as a function of SDBS concentration in PBS solution at pH 8 (λ_{ex} = 466 nm), concentration of Ru-CIP was 10 µM.

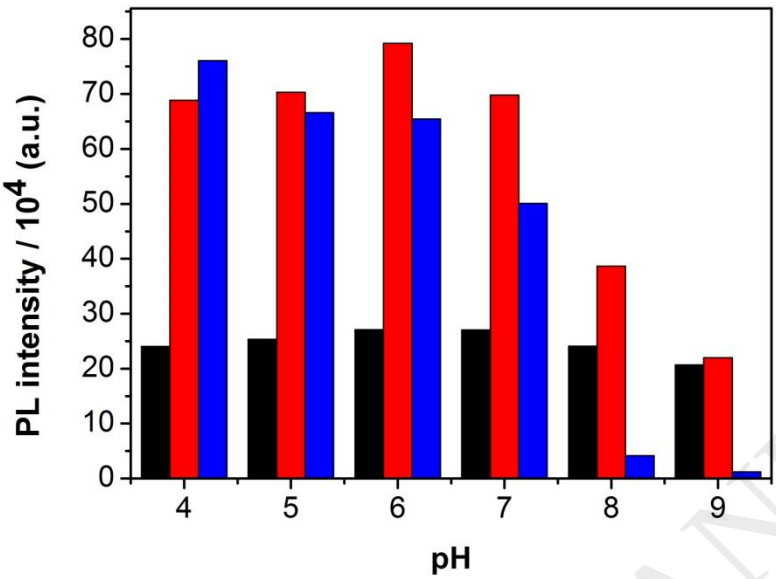


Fig. 3 Luminescence response of Ru-CIP, Ru-CIP-SDBS, Ru-CIP-SDBS + DA at different pH values in PBS solution. Concentrations of Ru-CIP, SDBS, and DA were 10 µM, 160 µM and 10 µM respectively.

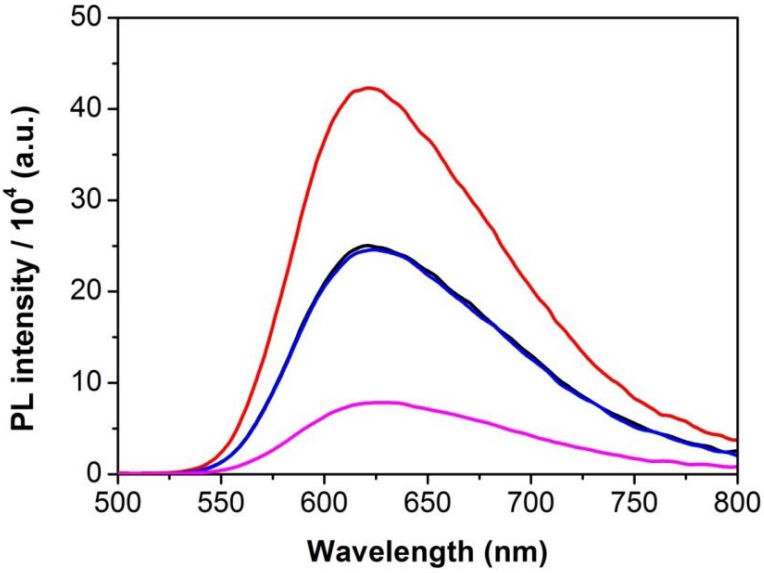


Fig. 4 Luminescence spectra of 10 μM Ru-CIP (black), Ru-CIP-SDBS (red) with 160 μM SDBS, Ru-CIP + DA (blue) with 10 μM DA and Ru-CIP-SDBS + DA (violet) with 10 μM DA for comparison.

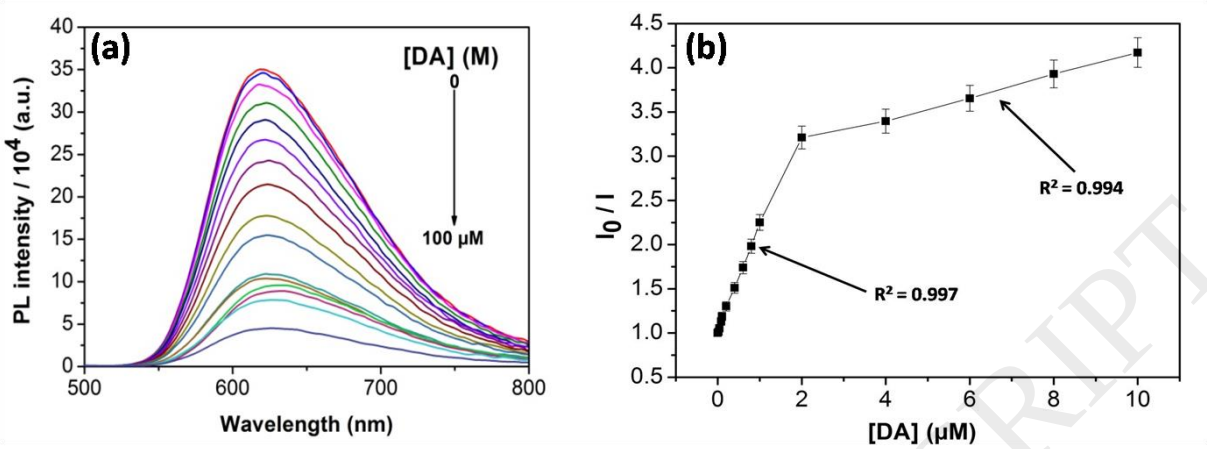


Fig. 5 a) Luminescence response of 10 µM Ru-CIP with 160 µM SDBS after incubation with different concentrations of DA (20 nM to 10 mM) for 1 h (λex = 466 nm). **b)** Operational range of the sensor. Plot of changes in I_0/I at 621 nm against varying concentration of DA. Where I_0 and I are the luminescence intensities before and after addition of the DA, respectively. (For linear fit refer to SI figure S6 and S7).

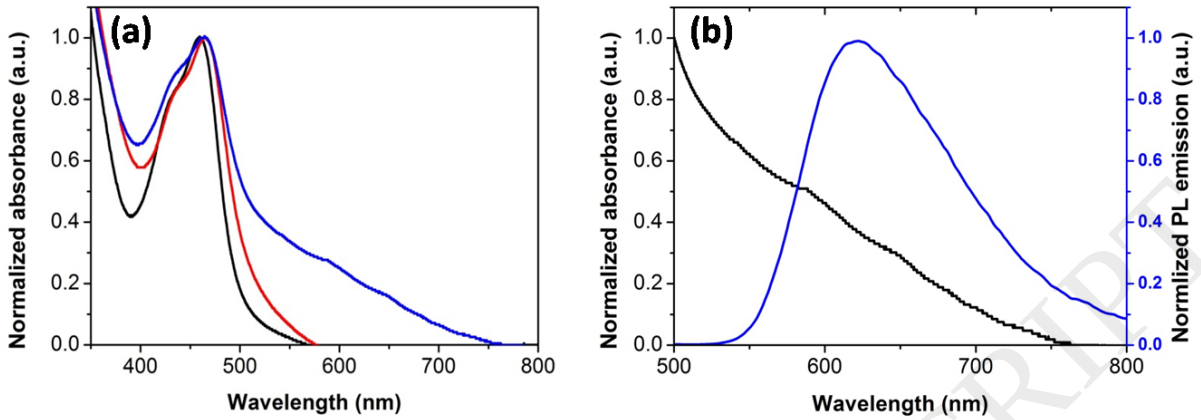


Fig. 6 a) Plot showing comparison of absorption spectra in PBS solution with pH 8 at different conditions i) Ru-CIP (black), ii) Ru-CIP in SDBS miceller medium (red) and iii) Ru-CIP-SDBS after DA addition. Concentrations of Ru-CIP, SDBS and DA were 10 µM, 160 µM, 10 µM respectively. b) Plot showing spectral overlap between absorption spectrum of Ru-CIP-SDBS + DA (10 µM Ru-CIP + 160 µM SDBS + 100 µM DA), black trace and emission spectrum of Ru-CIP-SDBS, blue trace at pH 8.

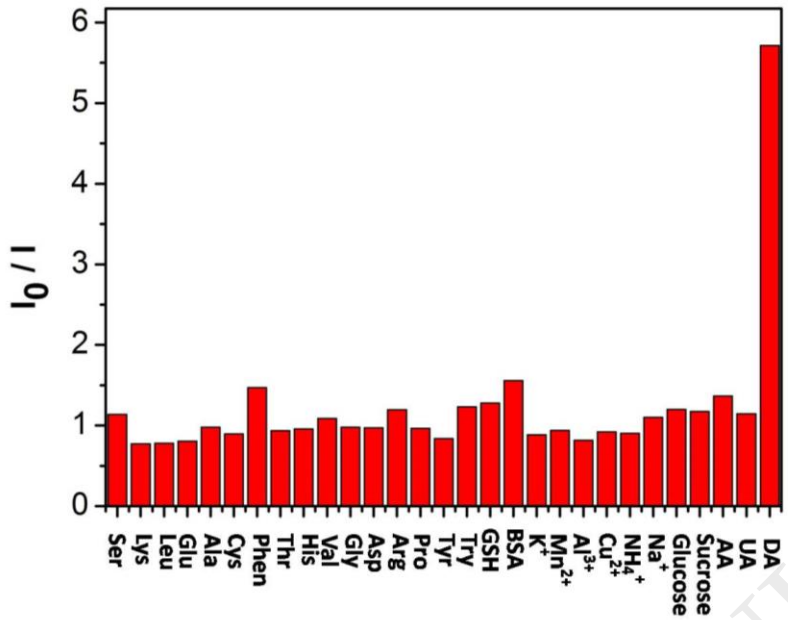
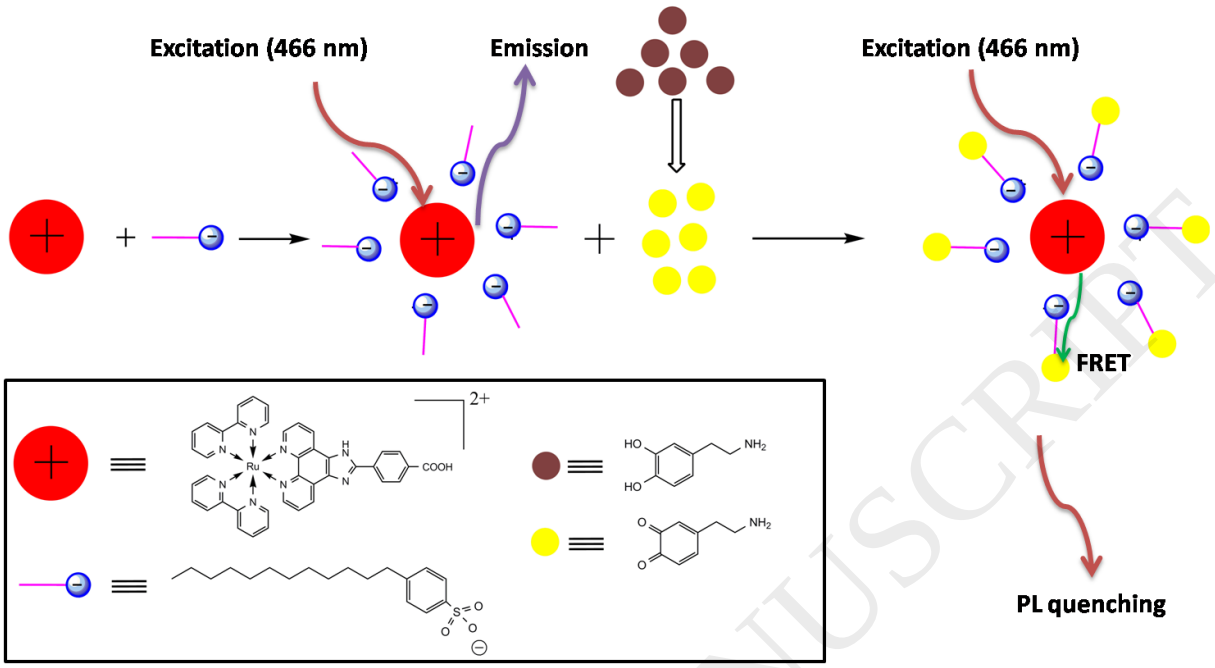


Fig. 7 Luminescence response of Ru-CIP-SDBS with different guest molecules. The concentration of all analytes were 100 μM in PBS solution at pH 8.



Scheme 1: Schematic illustration of the constructed $[Ru(bpy)_2(CIPH_2)]^{2+}$ with SDBS luminescent probe for detection of DA.

Table 1. Comparison with reported analytical method for DA detection

Methods	**Linear range**	**Limit of detection (LOD)**	**References**
Colorimetry	0.5 µM -10 µM	200 nM	[50]
Electrochemistry	0.40 µM – 374 µM	0.13 µM	[51]
Turn-off Fluorescence assay	2.5 nM - 5.0 µM and from 5.0 µM -10.4 µM	0.9 nM	[19]
Turn-off Fluorescence assay	0.005 µM – 10 µM	0.3 nM	[21]
Turn-off Fluorescence assay	0.05 µM – 10 µM	12 nM	[20]
Turn-off Luminescence assay	0.1 µM -1µM and from 2 µM -10 µM	6.66 nM	Present work