



## Development of an ion-sensor using fluorescence resonance energy transfer



Dibyendu Dey, Jaba Saha, Arpan Datta Roy, D. Bhattacharjee, Syed Arshad Hussain\*

Department of Physics, Tripura University, Suryamaninagar, 799022, Tripura, India

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### ABSTRACT

A method is presented for the sensing of ions by determining the concentration of corresponding salts (KCl, NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, FeCl<sub>3</sub>, FeSO<sub>4</sub>, AlCl<sub>3</sub>) in water, based on fluorescence resonance energy transfer (FRET) process. The principle of the proposed sensor is based on the change of FRET efficiency between two laser dyes Acriflavine and Rhodamine B in presence of different ions (K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>). Nanodimensional clay platelet laponite was used to enhance the efficiency of the sensor.

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### 1. Introduction

The development of ion sensor technology has emerged as a dynamic approach for identifying and quantitating specific analytes of environment. Now a days the growing need for multicomponent analyses and shorter sample preparation methods, new sensing techniques with decreasing costs are very important. There are several sensing techniques which include ion selective or gas sensitive electrodes, thermistors, chemically and biologically modified metal or semiconductors [1–3]. Chalcogenide glass sensors are used for the detection of millimole levels of copper, iron, chromium, lead, cadmium and mercury in natural waste waters [4]. The method is also used for the detection of heavy metal ions in solutions [4]. But the sensing of ions present in micromole amount could be much interesting and useful. It will be very much interesting to sense K<sup>+</sup> and Na<sup>+</sup> ions in blood samples. In blood the K<sup>+</sup> and Na<sup>+</sup> concentrations are 4.5 and 120 mM respectively [5]. Increase in concentration of these ions in blood can cause serious health problems. Another type of sensor is fluorescent ion sensors. There are few reports where the detection of heavy metal ions such as Hg<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> have been done by fluorescent ion sensors with high sensitivity and simplicity [6–9]. But in this method the change in fluorescent intensity could be perturbed by environmental factors [10,11]. It is interesting to mention in this context that the introduction of ratiometric sensors can minimize this environmen-

tal perturbation, because it measures the ratio of two emissions in different environment. The design of ratiometric sensors can be done by two method (i) ICT (intermolecular charge transfer) and (ii) FRET (fluorescence resonance energy transfer). For many ICT based ion sensors it is difficult to determine the ratio between two relatively broad signal emissions. Recently FRET based sensing has become most effective method for the detection of ions in environment. FRET based sensors have been widely used in metal ion detection [12,13], sensing of the fluorophores [14–18], Silica [19,20], and polymer particles [21–23]. In one of our recent paper we have used FRET for the sensing of permanent hard water components in water for a concentration range of 0.03–0.2 mg/ml [24].

Here in the process of designing ion sensor based on FRET process, we have used two dyes Acriflavine (Acf) and Rhodamine B (RhB) as energy donor and acceptor respectively. In principle both the dyes are suitable for fluorescence resonance energy transfer. Both the dyes are highly fluorescent and the fluorescence spectrum of Acf sufficiently overlaps with the absorption spectrum of RhB. P.D. Sahare et al. [25] reported the fluorescence resonance energy transfer in binary solution mixture of these two dyes. Recently we have demonstrated a pH sensor [26], DNA sensor [35] and hard water sensor [24] based on the FRET between Acf and RhB.

In the present communication we tried to investigate the effect of K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup> on the FRET efficiency between two fluorophores, Acf and RhB in presence and absence of nanoclay sheet laponite. The energy transfer efficiency has been affected if the distance between the donor–acceptor pair has been altered due to the presence of any external agency or change of

\* Corresponding author. Tel.: +91381 2375317; fax: +913812374802.

E-mail addresses: [sa.h153@hotmail.com](mailto:sa.h153@hotmail.com), [sah.phy@tripurauniv.in](mailto:sah.phy@tripurauniv.in) (S.A. Hussain).

the microenvironment. It has been observed that when distance between fluorophores (dyes) is decreased due to adsorption of the dyes on to nanoclay sheet, the FRET efficiency increases [26,27]. Here we have used nanoclay sheet laponite to enhance the sensitivity of sensing. Our investigation showed that FRET efficiency decreases with increasing salt concentration. It has also been demonstrated that with proper calibration, FRET between Acf and RhB can be used to sense different ions on the basis of their size and charge up to micromole level.

## 2. Materials and methods

### 2.1. Material

Both the dyes Acf and RhB were purchased from Sigma Chemical Co., USA and used as received. Ultrapure Milli-Q water (resistivity 18.2 MΩ cm) was used as solvent. The dyes used in our studies are cationic in nature. The clay mineral used in the present work was Laponite, obtained from Laponite Inorganic, UK and used as received. The size of the clay platelet is less than 0.05 μm and CEC is 0.739 meq/g determined with CsCl [28]. All the salts KCl, NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, FeCl<sub>3</sub>, FeSO<sub>4</sub>, and AlCl<sub>3</sub> were purchased from Thermo Fisher Scientific India Pvt. Ltd. and used as received. Dye and salt solutions were prepared in Milli-Q water. For spectroscopic measurement the dye solution concentration was optimized at 10<sup>-6</sup> M. The clay dispersion was prepared by using Milli-Q water and stirred for 24 h with a magnetic stirrer followed by 30 min ultrasonication before use. The concentration of clay was kept fixed at 2 ppm throughout the experiment. To check the effect of clay on the spectral characteristics, the dye solutions (Acf and RhB) were prepared in the clay suspensions (2 ppm). In order to check the effect of salt on spectral characteristics in presence of clay, first of all the salts were added in the clay dispersion individually at different concentration. Then the dyes were added in the salt mixed clay dispersions. In all cases the clay concentration was 2 ppm and the dye concentration for both Acf and RhB was 10<sup>-6</sup> M. The pH of the (Acf + RhB) mixed aqueous solution was measured as 5.8 in this present experiment.

### 2.2. UV-vis absorption and fluorescence spectra measurement

UV-vis absorption and fluorescence spectra of the solutions were recorded by a Perkin Elmer Lambda-25 Spectrophotometer and Perkin Elmer LS-55 Fluorescence Spectrophotometer respectively. For fluorescence measurement the excitation wavelength was 420 nm (close to the absorption maxima of Acf).

## 3. Results and discussions

### 3.1. FRET between Acf and RhB in aqueous solution and clay dispersion

The absorption and emission maxima of Acf are centered at 449 and 502 nm respectively which is assigned due to the Acf monomers [25]. On the other hand RhB absorption spectrum possess prominent intense 0–0 band at 553 nm along with a weak hump at 520 nm which is assigned due to the 0–1 vibronic transition [29]. The RhB fluorescence spectrum shows prominent band at 571 nm which is assigned due to the RhB monomeric emission [29]. The corresponding absorption and emission spectra of the above results are shown in Fig. 1 of the supporting information.

Fig. 1a shows the fluorescence spectra of pure Acf, RhB and their mixture in water solution in presence and absence of salt (KCl, MgCl<sub>2</sub>, and FeCl<sub>3</sub>). All the spectra were measured with excitation wavelength 420 nm (close to absorption maximum of Acf).

**Table 1**

Values of energy transfer efficiency (*E*%) for Acf and RhB mixture (1:1 volume ratio) with different salts (KCl, MgCl<sub>2</sub>, FeCl<sub>3</sub>) in absence and presence of clay. Dye concentration was 10<sup>-6</sup> M, salt concentration was 10 μM and clay concentration was 2 ppm. The values are calculated from the spectra of Fig. 1.

Salt	FRET efficiency ( <i>E</i> %) without clay	FRET efficiency ( <i>E</i> %) with clay
KCl	9.7	56.8
MgCl <sub>2</sub>	7.4	47.4
FeCl <sub>3</sub>	5.2	38.5

This excitation wavelength was chosen in order to excite the Acf molecule directly and to avoid the direct excitation of RhB molecule. From the figure it has been observed that the fluorescence intensity of pure Acf (curve 1 of Fig. 1a) is much higher, on the other hand the fluorescence intensity of pure RhB (curve 2 of Fig. 1a) is almost negligible. However, the Acf–RhB mixture fluorescence spectrum is (curve 3 of Fig. 1a) very interesting. Here the Acf emission decreases with respect to pure Acf and on the other hand RhB emission increases with respect to pure RhB (curve 3 of Fig. 1a). This is mainly due to the transfer of energy from Acf molecule to RhB molecule via fluorescence resonance energy transfer. In order to confirm this, excitation spectra was recorded with monitoring emission wavelength 500 nm (Acf emission maximum) and 571 nm (RhB emission maximum) and observed that both the excitation spectra are very similar to the absorption spectrum of Acf monomer (Fig. 2 of supporting information). This confirms that the RhB fluorescence is mainly due to the light absorption by Acf and corresponding transfer to RhB monomer. Thus FRET between Acf and RhB has been confirmed. FRET efficiencies have been calculated using the following equation [30]

$$E = 1 - \frac{F_{DA}}{F_D}$$

where *F*<sub>DA</sub> is the fluorescence intensity of the donor in the presence of acceptor and *F*<sub>D</sub> is the fluorescence intensity of the donor in the absence of the acceptor.

In order to sense different ions we have introduced different salts in the Acf–RhB mixed aqueous solution and the FRET between Acf and RhB has been measured. The change in FRET efficiency due to the presence of ions/salts has been examined in order to sense the presence of corresponding ions. Fluorescence spectra of Acf–RhB mixture in presence of KCl (curve 4), MgCl<sub>2</sub> (curve 5), FeCl<sub>3</sub> (curve 6) have also been shown in Fig. 1a. It has been observed that in all the cases the FRET efficiency decreased. However, the change in FRET efficiency is very small. The FRET efficiency changes from 11.37% (in absence of salt) to 9.2% (in presence of KCl) or 7.4% (in presence of MgCl<sub>2</sub>) or 5.2% (in presence of FeCl<sub>3</sub>). The corresponding efficiencies are listed in Table 1.

In order to increase the FRET efficiency between Acf and RhB we have introduced nanoclay platelet laponite in the Acf–RhB mixture. Fluorescence spectra of pure Acf (curve 1), RhB (curve 2) and Acf–RhB mixture (curve 3) in presence of laponite are shown in Fig. 1b. The corresponding FRET efficiencies are also listed in Table 1. It has been observed that FRET efficiency increases to 78.17% in presence of clay for Acf–RhB mixture which was 11.37% in absence of clay platelet. Now salts are introduced in the Acf–RhB mixture in presence of clay laponite. Corresponding fluorescence spectra (KCl (curve 4), MgCl<sub>2</sub> (curve 5), FeCl<sub>3</sub> (curve 6), are also shown in Fig. 1b. The FRET efficiencies are also listed in Table 1.

It is worthwhile to mention in this context that clay particles are negatively charged and have layered structure with a cation exchange capacity [31,32]. Both the dyes Acf and RhB under investigation are positively charged. Accordingly they are adsorbed onto the clay layers. On the other hand FRET process is very sensitive to distances between the energy donor and acceptor and

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