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# Photophysical behavior and fluorescence quenching by halides of quinidine dication: Steady state and time resolved study

Neeraj Kumar Joshi<sup>a</sup>, Neeraj Tewari<sup>a,1</sup>, Priyanka Arora<sup>a</sup>, Ranjana Rautela<sup>a</sup>, Sanjay Pant<sup>a</sup>, Hem Chandra Joshi<sup>b,\*</sup><sup>a</sup> *Photophysics Laboratory, Department of Physics, DSB Campus, Kumaun University, Nainital 263002, Uttarakhand, India*<sup>b</sup> *Institute for Plasma Research, Laser Diagnostics Division, Bhat, Near Indira Bridge, Gandhinagar 382428, Gujarat, India*

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## ABSTRACT

The fluorescence quenching of quinidine in acidified aqueous solution by various halides ( $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ ) was studied using steady state and time resolved fluorescence techniques. The quenching process was characterized by Stern–Volmer (S–V) plots. Possibility of conformers (one is not quenched by halide and the other is quenched) is invoked to explain the observed results.

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## 1. Introduction

Inorganic halides are abundant in nature as minerals or as solvated halide ions by the dissolution of minerals or salts. The determination of halide concentration in the environment is important for both monitoring excessive halide levels as well as monitoring halide deficiencies in natural resources [1–3].

Fluorescence quenching processes allow quantitative determination of halides [4–10]. The determination of halide using fluorescence quenching is a popular technique because of the high sensitivity that it can offer and the simplicity of quenching reactions (where only a small volume of sample is required, the reactions are usually non-destructive). Besides, the phenomenon of fluorescence quenching has found applicability in various studies [11–15,16–18].

A typical bimolecular quenching involves close contact between the fluorescent species and the quencher and can be due to heavy atom effect, energy or electron transfer process. On the other hand some trivial processes such as attenuation of the emitted light by the fluorophore itself (self-absorption) or absorption from other species may lead to decrease in the fluorescence intensity, which are not considered as quenching processes.

\* Corresponding author. Tel.: +91 7923962056.

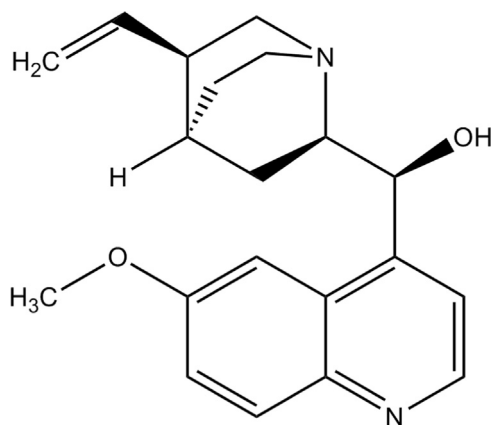
E-mail address: [hem\\_sup@yahoo.co.uk](mailto:hem_sup@yahoo.co.uk) (H.C. Joshi).

<sup>1</sup> Present address: Lajpat Rai (P.G.) College, Sahibabad, India.

In earlier works excited state dynamical behavior of quinine, quinidine and related compounds has been reported in acidified aqueous solution at different pH values and at different temperatures as well as in polymers [9,10,19–26]. Quinidine has two protonable groups with  $\text{p}K_a$  values of 4.2 and 7.9–8.8 [8]. However, in 1N  $\text{H}_2\text{SO}_4$  we can only expect  $\text{Qd}^{++}$  [8].

Moreover, because of projected applications of such molecules in sensors for halide ions and to understand various quenching processes, a systematic study of fluorescence quenching is needed. In the past quenching by chloride ions in some cinchona alkaloids e.g. quinine sulfate and cinchonine was reported [9,10,19] but the detailed mechanism regarding quenching was not traced out. Again due to the difference in stereo-structure, quenching study of individual alkaloids becomes interesting. As quinine and quinidine are enantiomers, it would be interesting to investigate whether their structures have some role in affecting the quenching behavior.

To the best of our knowledge, fluorescence quenching of quinidine by halides in acidified aqueous solution has not been studied yet. Hence in the present work we have undertaken a detailed study of its quenching by halides and various quenching parameters have been estimated in order to understand the nature of the possible quenching mechanism. Possibility of conformers (one is not quenched by halide and the other is quenched) is invoked to explain the observed results. The molecular structure of quinidine is shown in Scheme 1.



Scheme 1. Molecular structure of quinidine.

## 2. Experimental section

### 2.1. Materials

Quinidine (obtained from Aldrich) of 98% purity was tested for its fluorescence purity by matching with reported fluorescence spectrum (to ensure that there is no contamination) and used as such. All the solvents used were either of spectroscopic grades or were checked for their fluorescence purity. Doubly distilled water was used in these experiments. The samples were prepared by dissolving appropriate concentration of quinidine in 1N H<sub>2</sub>SO<sub>4</sub>. NaCl, KBr and KI were used for the quenching study. Concentration of H<sub>2</sub>SO<sub>4</sub> has been kept the same in all the samples to rule out the effect of the presence of SO<sub>4</sub><sup>2-</sup> ion.

### 2.2. Instrumentation

Steady state absorption spectra, at room temperature, were recorded by a dual beam JASCO V-550 spectrophotometer. The excitation and emission spectra were recorded by using a JASCO FP-777 spectrofluorometer and the data were analyzed by related software. The samples were excited in frontal geometry to rule out any inner filter effect. Fluorescence decay times were recorded with the help of a Edinburgh-199-time domain spectrometer and analyzed by TCC-900 software. The excitation source was a thyatron-gated hydrogen filled nanosecond flash lamp. Lamp profile was measured at the excitation wavelength using a Ludox scatterer. The pulse width was about 1.5 ns with repetition rate of 30 kHz. A time correlated single photon counting (TCSPC) technique was used to collect the decay curves and the resolution of the system was about 200 ps. The number of counts in the peak channel was at least 10,000. Time-resolved fluorescence decay curves were analyzed by deconvoluting the observed decay with the instrument response function (IRF) to obtain the intensity decay function represented as a sum of discrete exponentials;  $I(\alpha, t) = \sum_i \alpha_i \exp(-t/\tau_i)$ , where  $I(t)$  is the fluorescence intensity at time  $t$  and  $\alpha_i$  is the amplitude of the  $i$ th life time such that  $\sum_i \alpha_i = 1$ . The mean lifetime,  $\tau_m = \sum_i \alpha_i \tau_i$ , gives the information on the average fluorescence yield of the system.

## 3. Results and discussion

Steady state absorption, fluorescence and decay curves of Qd<sup>++</sup> were recorded at 298 K in the absence and in the presence of halide ions (Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>). Qd<sup>++</sup> exhibits absorption maximum at ~355 nm. The emission spectra (Fig. 1) for Qd<sup>++</sup> show red-shift in

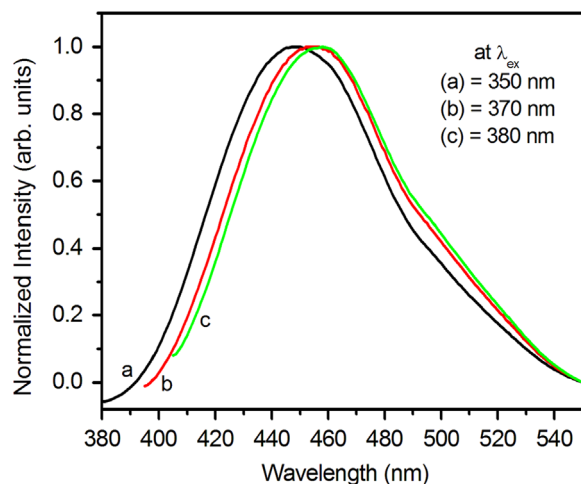


Fig. 1. Emission spectra (showing EERS) of Qd<sup>++</sup> for different excitation wavelengths: (a) 350 nm, (b) 370 nm and (c) 380 nm.

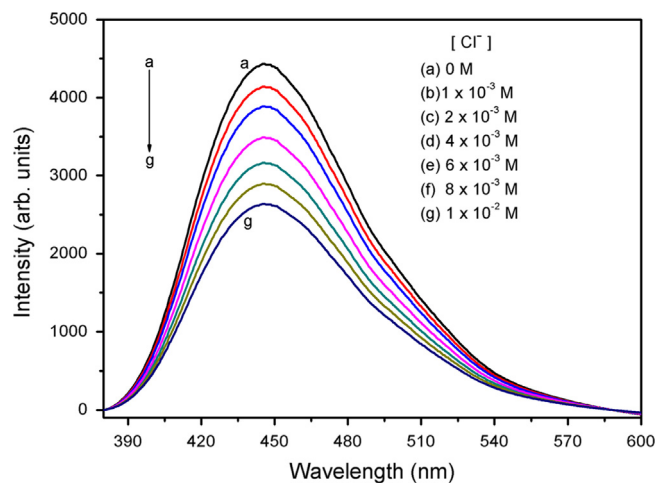


Fig. 2. Emission spectra of Qd<sup>++</sup> in the presence of various concentrations of Cl<sup>-</sup>.

emission maximum upon excitation on the red edge of the absorption spectrum, i.e., edge excitation red shift (EERS). Similar trend is observed in the presence of the halides.

In the presence of halide ions no change on the absorption maximum as well as on the shape of absorption spectrum is present. Quenching in the fluorescence intensity is observed in the presence of halide ions. Fluorescence quenching by Cl<sup>-</sup> ions is shown in Fig. 2. Further, no other emission is developed. These observations suggest that the fluorophore-quencher interaction does not change the shape of the fluorescence spectra. Hence, formation of any emissive exciplex can also be discarded. It is to be noted that the excitation spectra show successive red-shifts while monitored towards the red side of the emission even in the absence of the halides and hence cannot be attributed to exciplex formation.

The Stern-Volmer relationship [27] establishes the correlation of intensity changes with the quencher concentration  $[Q]$  as follows:

$$I_0/I = 1 + (K_{SV} + K_g)[Q] + K_{SV}K_g[Q]^2 \quad \text{or}$$

$$[I_0/I - 1]/[Q] = (K_{SV} + K_g) + K_{SV}K_g[Q] \quad (1)$$

where  $K_{SV}$  ( $=k_q\tau_0$ ) and  $K_g$  are the dynamic/(S-V) quenching constant and ground state association constant of the complex, respectively.  $k_q$  is the bimolecular quenching constant and  $\tau_0$

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