Fluorescence quenching of 8-methyl quinolinium: An efficient halide indicator mechanism

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ABSTRACT

Fluorescence quenching of 8-methyl quinoline in acidified aqueous solution by various halides ($Cl-$, $Br-$, $I-$) is studied using steady state and time resolved fluorescence techniques. The quenching process is characterized by Stern–Volmer (S–V) plots. It is found that the mechanism of quenching is dynamic in nature and occurs through photo-induced electron transfer. Having considerably higher quenching constant, much longer fluorescence life-time (~42 ns), mono-exponential fluorescence decay and commercial availability project this molecule as a potential candidate for practical applications.

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1. Introduction

The study of quenching of luminescence has been an active area of research for the last few decades. Quenching can take place through various mechanisms and finds extensive applications in halide sensing [1] and biophysical systems [2]. Quenching measurements can reveal the accessibility of fluorophores to quenchers. If the solvent is very viscous i.e. diffusion is slow; quenching is inhibited in a diffusion controlled process. Hence the study of quenching can reveal the diffusion rates of quenchers. If a fluorophore is bound either to a protein or a membrane, which are impermeable to the quencher or if the fluorophore is located in the interior of the macromolecule, quenching of fluorescence cannot occur. On the other hand, the fluorophore bound to a membrane permeable to quencher would show change in fluorescence parameters in the presence of the quencher. Thus the quenching studies can be used to reveal the localization of fluorophores in protein and membranes and their permeability to quencher [1]. A variety of substances can act as quenchers. Some common examples are molecular oxygen [3–4], amines [5–9], metal ions [10,11] and halides [12–18].

Inorganic halides are abundant in nature as minerals or solvated halide ions from the dissolution of minerals or salts. The determination/recognition of halides in the environment is important both for monitoring excessive halide levels as well as halide deficiencies in natural resources [19–21]. Fluorescence quenching processes allow quantitative determination of halides [15,22–27]. 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 mechanism.

Further, quinoline moieties are considered as good candidates for sensing halides by fluorescence quenching and several studies have been devoted to it [11,15,23,25]. In quinoline, in the near ultraviolet the transversely polarized ^1L_a ($S_0 \rightarrow S_2$) absorption band is centered at about 278 nm, as it is in naphthalene and differs from naphthalene only in the sense that the vibrational structure is slightly less distinct [28]. The longitudinally polarized ^1L_b ($S_0 \rightarrow S_1$) absorption band lies at about 318 nm in naphthalene as well as in quinoline but is considerably more intense in quinoline [28]. The protonation of the non-bonded electron pair in quinoline causes the ^1L_a band to red-shift, as is to be expected for a perturbation in the α-position of a substituted naphthalene [28].

Although quinoline fluoresces only in hydroxylic solvents presumably due to the S_1 state being of n, π* character in aprotic solvents [29], its fluorescence is similar in terms of spectral position to that of naphthalene of origin in the ^1L_b state. Protonation of quinoline results in relatively intense fluorescence, which lies in the blue region of the spectrum. Quite possibly this blue emission originates from the ^1L_a state, which may drop below the ^1L_b state in the thermally equilibrated, photo-excited cation [29].

Yang and Schulman [30] noticed that 8-methyl quinoline is unique among the mono-methylquinolines in the sense that it shows red-shift in the absorption band derived from the short axis polarized (^1L_a) electronic transition relative to that in quinoline. The effect is even more pronounced in the 8-methylquinolinium cation, with the ^1L_a band clearly emerging on the long-wavelength side of the ^1L_b

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band, which is normally the longest wavelength absorption band in quinolines substituted with weakly interacting functional groups [30].

Recently, we investigated the spectral and temporal behavior of various methyl substituted quinoline cations [31] and found that 8-methylquinolinium ($8MQ^+$) differs from the parent quinoline as well as other methyl quinoline cations [31]. It was observed that the deactivation channel i.e., inter system crossing (ISC) is suppressed to a significant extent in case of $8MQ^+$ as compared to other methyl substituted quinolinium [31]. In the past there had been considerable amount of work on the quenching behavior of molecules of quinoline and quinine family [11,15,23,25]. However, the quest for the molecules having large quenching constant and simple dynamics is still there so that efficient probes for the recognition/sensing of halides can be designed. Therefore, we considered that it would be interesting to investigate the effect of the halide ions on the fluorescence behavior of $8MQ^+$ to discriminate the ISC and other quenching routes. Molecular structure of 8MQ is shown in Fig. 1.

To the best of our knowledge, fluorescence quenching of 8MQ by halides in acidified aqueous solution has not been studied yet. Hence, in the present work we have undertaken a detailed study of fluorescence quenching of $8MQ^+$ by halide (Cl^-, Br^- and I^-) ions and various quenching parameters have been estimated in order to understand the nature of the possible quenching mechanism. It is demonstrated that the dominant quenching route is photo-induced electron transfer (PET).

2. Experimental section

2.1. Materials

8-methylquinoline (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 grade or were checked for their fluorescence purity. Doubly distilled water was used in these experiments. The samples were prepared by dissolving appropriate concentration of 8MQ in 0.1 N H_2SO_4. NaCl, KBr and KI were used for the quenching study.

2.2. Instrumentation

At room temperature, steady state absorption spectra were recorded by dual beam JASCO V-550 spectrophotometer. The excitation and emission spectra were recorded by using JASCO FP – 777 spectrofluorometer and the data were analyzed with the available software. Samples were excited in frontal geometry to rule out inner filter effect. Fluorescence decay times were recorded with the help of Edinburgh –

199-time domain spectrometer and analyzed by TCC – 900software. The excitation source was a thyratron-gated hydrogen filled nanosecond flash lamp. Lamp profile was measured at the excitation wavelength using Ludox scatterer. The pulse width was about 1.5 ns with repetition rate of 30 kHz. Time correlated single photon counting (TCSPC) technique was used to collect the decay curves and the overall resolution of the system was about 200 p-seconds. 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; $I(\alpha, t) = \Sigma_i \alpha_i exp(-t/\tau_i)$, where, $I(t)$ is the fluorescence intensity at time t and α_i is the amplitude of the ith life time such that $\sum_i \alpha_i = 1$.

3. Result and discussion

In the present work we report the quenching behavior of 8-methylquinolinium ion ($8MQ^+$) in low acidic aqueous solution (0.1 N) by halide (Cl^-, Br^-, and I^-) ions. We present herein a brief summary of the results of our previous study [31]. At 298 K, in acidic aqueous solution, $8MQ^+$ shows absorption maximum at 315 nm (^1L_b) along with a broad shoulder with peak centered at ~337 nm (^1L_a) [30,31]. The corresponding emission peak was observed at 432 nm. It exhibits a mono-exponential long decay component with a decay time of ~41.6 ns [31]. The full width half-maximum (fwhm), the peak position of the emission band and the decay time are independent of the wavelength of excitation. Further, no change in excitation spectra was observed on monitoring the emission throughout the emission profile [31].

In the presence of the halide ions (Cl^-, Br^- and I^-), no change on the absorption maximum as well as on the shape of absorption spectrum is observed. Quenching of the fluorescence intensity is observed in the presence of halide ions. Fluorescence quenching by Cl^- ions is shown in Fig. 2. However, no other emission is developed. It is to be noted that the excitation spectra also do not show any change in the presence of the halides. Hence, formation of any exciplex/ground state complex can be discarded. We also did not notice any phosphorescence band emerging with the introduction of halides.

The Stern-Volmer relationship [32] shows the correlation of intensity changes with the quencher concentration [Q] as follows;

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

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 τ_0 corresponds to the
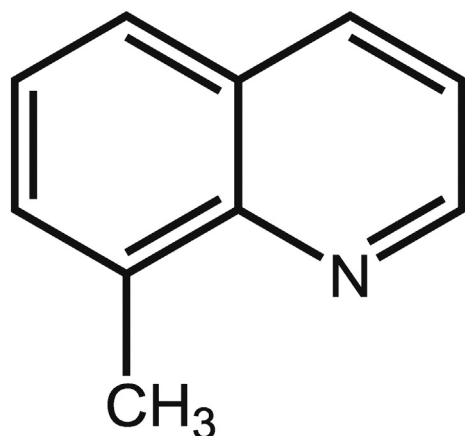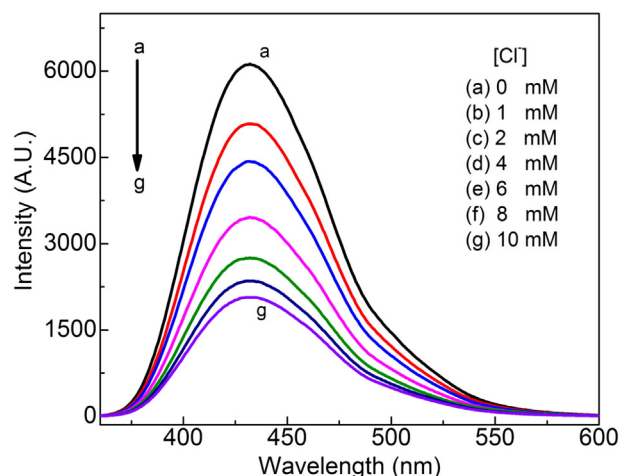

Fig. 1. Molecular structure of 8-methylquinoline.

Fig. 2. Emission spectra of $8MQ^+$ with the different concentrations of Cl^-.