Effect of solvents on photophysical properties and quenching of 2-[[3-(1H-benzimidazole-2-yl) phenyl] carbonimidoyl]phenol

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ABSTRACT: The effect of solvents of varying polarity on the absorption and fluorescence emission of the Schiff base, 2-[[3-(1H-benzimidazole-2-yl) phenyl]carbonimidoyl]phenol, was studied using Lippert-Mataga bulk polarity function, Reichardt's microscopic solvent polarity parameter and Kamlet's multiple linear regression approach. The spectral properties follow Reichardt's microscopic solvent polarity parameter better than Lippert-Mataga bulk polarity parameter, indicating the presence of both general solute-solvent interactions and specific interactions. Catalan's multiple linear regression approach indicates the major role of solvent polarizability/dipolarity influence compared with solvent acidity or basicity. The solvatochromic effect was utilized to calculate the dipole moments of ground and excited states of the Schiff base using different methods. Bathochromic shift in the emission spectrum and the increase in dipole moment in the excited state signifies the intramolecular charge transfer character in the emitting singlet state. Fluorescence quenching by aniline was also studied in 1,4-dioxane and n-butanol, and the results were analyzed using sphere of action static quenching and finite sink approximation models. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: fluorescence quenching; intramolecular charge transfer; Schiff base; solvent effect

Introduction

Schiff bases derived from aromatic amines and aldehydes are important compounds having potential applications in biological, catalytic to photo-luminescent systems (1–7). They are important ligands in coordination chemistry and also in the development of bio-mimetic chemistry of metal ions in particular, transition metal ions (8,9). They can also be used as highly sensitive fluorescent probes for many transition metal ions (10–12). Molecules containing a heterocyclic ring such as benzimidazole and part of the Schiff base may show enhanced biological activities (13,14). Spectroscopic investigations of 2-hydroxy Schiff bases are interesting because of their photochromic and thermochromic behaviour as a consequence of intramolecular charge transfer between phenolic oxygen and azomethine nitrogen sites.

Studies on the relationship between structure and optical behaviour in different media have interesting practical applications. Solvents affect the physical and chemical properties of solute (15). Solvent effect depends on the nature and extent of solute-solvent interactions developed in the solvation shell of the solute. Depending on the interaction of the solute with solvent in the ground state and first excited state of the solute, solvent will cause changes in electronic transitions (16,17). Solvatochromic effect can be used to determine the electro-optical parameters such as dipole moments of ground and excited states of the solute (18–20). The information on dipole moments can be utilized to elucidate geometrical and electronic structure of a molecule which is useful in designing non-linear optical materials (21). The dipole moment in the excited state of the fluorescent molecule also determines the energy

tunability range of emission as a function of the polarity of the medium. Solvatochromic studies on Schiff base molecules have shown alteration in photophysical properties such as electronic structure, dipole moments of ground and excited states, and intra and intermolecular interactions in solutions (22–24).

The molecular interactions such as excited-state reactions, molecular rearrangements, energy transfer, ground-state complex formation and collisional quenching result in reduction in the intensity of fluorescence emission, which is referred to as fluorescence quenching (25,26). Like solvatochromism, fluorescence quenching is a widely studied subject in terms of fundamental phenomenon as well as its applications for biochemical aspects. It can also be used to reveal the diffusion rates of the quenchers (27).

In the present investigation, we report the results on the effect of solvents of varying polarity on the photophysical

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Abbreviations: ICT, intramolecular charge transfer; RS, radii of solute; SA, solvent acidity; SB, solvent basicity; SP, solvent polarizability.

Structure 1.

properties of 2-[[3-(1H-benzimidazole-2-yl)phenyl] carbononimido] phenol (I, molecule composed of benzimidazole ring and Schiff base) (Structure 1). Results were analyzed using Lippert and Mataga bulk solvent polarity parameter (15,28), Reichardt's microscopic solvent polarity parameter (29) and solvatochromic parameters proposed by Catalan (30). Fluorescence quenching of I by aniline in 1,4-dioxane and n-butanol was studied. Ground-state complex formation model, sphere of action static quenching and finite sink approximation models were also used to analyze the results.

Experimental

Materials and methods

The Schiff base was prepared as reported elsewhere (31). Solvents used in the present study were of spectroscopic grade. Absorption and fluorescence spectral studies were carried out using 10^{-5} M solutions of I. The absorption and fluorescence spectra were recorded at room temperature on Hitachi U-3310 UV-VIS spectrophotometer and Hitachi F-7000 fluorescence spectrophotometer respectively. For fluorescence quenching analysis the solutions were prepared in 1,4-dioxane and n-butanol with a constant 10^{-5} M concentration of the solute (I) and varying concentrations (0.00, 0.02, 0.04, 0.06, 0.08 and 0.10 M) of the quencher (aniline). Fluorescence lifetime values were measured on ChronosBH fluorescence life time spectrometer-ISS.

The data regarding solvent polarity parameter (E_T^N), dielectric constant (ϵ) and refractive index (n) of each solvent were taken from the literature (29,32). The bulk solvent polarity parameter (Δf) was determined using equation (1) (15,33):

$$\Delta f = \left[\frac{\epsilon - 1}{2 + 1} - \frac{n^2 - 1}{2n^2 + 1} \right] \quad (1)$$

Calculation of dipole moments

The solvatochromic effects for a spherical molecule with isotropic polarizability were analyzed using equations (2) and (3) (34,35):

$$\bar{\nu}_a - \bar{\nu}_f = m_1 F_1(\epsilon, n) + \text{constant} \quad (2)$$

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -m_2 F_2(\epsilon, n) + \text{constant} \quad (3)$$

where $\bar{\nu}_a$ and $\bar{\nu}_f$ are wave numbers in cm^{-1} corresponding to absorption and fluorescence maxima, F_1 and F_2 are solvent polarity parameters as per equations (4) and (5) respectively:

$$F_1(\epsilon, n) = \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \frac{(2n^2 + 1)}{(n^2 + 2)} \quad (4)$$

$$F_2(\epsilon, n) = \frac{(2n^2 + 1)}{2(n^2 + 2)} \left[\frac{\epsilon - 1}{\epsilon + 1} - \frac{n^2 - 1}{n^2 + 1} \right] + \frac{3(n^4 - 1)}{2(n^2 + 2)^2} \quad (5)$$

The plots of $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(\epsilon, n)$ and $(\bar{\nu}_a + \bar{\nu}_f)/2$ versus $F_2(\epsilon, n)$ give slopes m_1 and m_2 respectively and are used in the calculation of dipole moments. m_1 and m_2 are related to dipole moments by equations (6) and (7) respectively:

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (6)$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (7)$$

where μ_g and μ_e are the dipole moments for ground state and excited state respectively of I, h is Planck's constant, c is the velocity of light and a is Onsager cavity radius of I.

The theoretical dipole moment (μ_g) for the solute (I) in the ground state was obtained from quantum chemical calculations. The calculations were carried out at the B3LYP levels of theory using the basis set 6-31G (d). Computations were carried out using Gaussian 09 program on a Pentium-4 PC (36).

If the dipole moments of ground and excited states are parallel, equations (6) and (7) are reorganized to obtain equations (8) and (9) (37):

$$\mu_g = \frac{m_2 - m_1}{2} \left(\frac{hca^3}{2m_1} \right)^{1/2} \quad (8)$$

$$\mu_e = \frac{m_2 + m_1}{2} \left(\frac{hca^3}{2m_1} \right)^{1/2} \quad (9)$$

If the dipole moments μ_g and μ_e are not parallel to each other, an angle ϕ between the two can be determined from expression 10 (37)

$$\cos \phi = \frac{1}{2\mu_g\mu_e} \left[(\mu_g^2 + \mu_e^2) - \frac{m_2}{m_1} (\mu_g^2 - \mu_e^2) \right] \quad (10)$$

The dipole moment of I in the excited state was also estimated using another method based on empirical solvent polarity parameter (E_T^N). This method correlates the spectral shift better than the traditionally used bulk solvent polarity functions and the problem associated with the estimation of Onsager cavity radius is also minimized. This polarity scale includes intermolecular solute/solvent hydrogen bond donor/acceptor interactions along with solvent polarity. The theoretical basis for the correlation of the spectral band shift with E_T^N is according to equation (11) (38):

$$\bar{\nu}_a - \bar{\nu}_f = 11307.6 \left[\left(\frac{\Delta\mu}{\Delta\mu_B} \right)^2 \left(\frac{a_B}{a} \right)^3 \right] E_T^N + \text{constant} \quad (11)$$

where $\Delta\mu_B$ and a_B are the changes in dipole moment and Onsager cavity radius respectively of the Betaine dye, $\Delta\mu$ and a are the changes in dipole moment and Onsager cavity radius of I. The change in dipole moment $\Delta\mu$ can be extracted from the slope of the plot of $(\bar{\nu}_a - \bar{\nu}_f)$ versus E_T^N from the reported values of $\Delta\mu_B$ and a_B which are 9D and 6.2 Å respectively for the Betaine dye (39).

Fluorescence quenching analysis

Fluorescence quenching of the solute has been analyzed using steady-state Stern-Volmer (S-V) relationship given in equation (12) (15):

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \quad (12)$$

where I and I_0 are the fluorescence intensities with and without quencher respectively, $K_{SV} = k_q\tau_0$ is the S-V constant, k_q is quenching rate parameter, $[Q]$ is the quencher concentration and τ_0 is the fluorescence lifetime without quencher. The above eqn can be effective only when the S-V plots are linear. Non-linearity with positive deviation can also be expected from these plots indicating the presence of other mechanisms such as formation of ground-state complex, combined static and dynamic quenching etc.

Ground-state complex formation model

In order to obtain information about ground-state complex formation, equation (12) is modified to equation (13) (15):

$$[(I_0/I) - 1]/[Q] = (K_{SV} + k_g) + (K_{SV}k_g)[Q] \quad (13)$$

where k_g is the ground-state association constant. K_{SV} and k_g can be obtained by least-squares fit method. Ground-state complex formation can also be examined by observing change in absorption spectrum at higher concentrations.

Sphere of action static quenching model

Static quenching plays a significant role in quenching the fluorescence intensity. It has been analyzed by adopting sphere of action static quenching model. Several models were proposed to explain the static quenching in which all lead to the S-V equation (14) (15):

$$[1 - (I/I_0)]/[Q] = K_{SV}(I/I_0) + (1 - W)/[Q] \quad (14)$$

where $(1 - W)$ is the fraction of molecules which are deactivated immediately after being formed, $W = \exp\left(-\frac{V}{[Q]}\right)$ or $\ln(1/W) = V/[Q]$, where V is the static quenching constant and it represents an active volume element surrounding the solute molecule in the excited state. K_{SV} can be obtained by least-squares fit method and hence $k_q = K_{SV}/\tau_0$. A plot of $[1 - I/I_0]/[Q]$ versus I/I_0 gives the intercept $(1 - W)/[Q]$. By using the value of W , static quenching constant ' V ' and radius of sphere of action ' r ' are determined.

Static quenching occurs when the distance between the solute molecule in the excited state and the quencher molecule lies between the interactive distance R ($R = R_S + R_Q$) and the kinetic distance ' r ' provided the interactions are diffusion limited. Here R_S and R_Q denote the radii of solute and quencher molecule respectively (40,41).

Finite sink approximation model

In order to obtain information regarding the diffusion limitations of the interactions, finite sink approximation model is used. S-V equation (12) is modified to equation (15):

$$K_{SV}^{-1} = (K_{SV}^0)^{-1} - \frac{(2\pi N)^{1/3}}{4\pi ND\tau} [Q]^{1/3} \quad (15)$$

where K_{SV}^0 is the S-V constant without quencher, N is the Avogadro number, D is the mutual diffusion coefficient obtained from the slope of the plot of K_{SV}^{-1} versus $[Q]^{1/3}$, and others have their usual meanings. From the intercept $((K_{SV}^0)^{-1})$, the distance parameter R' is calculated using eqn $K_{SV}^0 = 4\pi DR'\tau$. Bimolecular interactions are said to be diffusion limited only when the value of k_q obtained from equation (14) is greater than $4\pi NDR'$ (42).

Results and discussion

Absorption and fluorescence spectral studies

Absorption and fluorescence spectra of **1** in 1,4-dioxane and methanol solvents are shown in Fig. 1. The results of maximum absorption wavelengths, fluorescence wavelengths and Stokes shifts are listed in Table 1. From Table 1, it is observed that Stokes shift increases with solvent polarity. This suggests that the dipole moment of **1** in the excited state is greater than that of the ground state (43). The bathochromic shift observed in the emission spectra with the increase in solvent polarity can be attributed to π - π^* transition.

In order to get further information about solvatochromic behaviour of **1**, spectroscopic properties were correlated with different solvent polarity scales. Energies of absorption ($\bar{\nu}_a$), fluorescence emission ($\bar{\nu}_f$) and Stokes shift ($\Delta\bar{\nu}$) versus bulk solvent polarity parameter (Δf) were plotted (Fig. 2). A poor correlation was obtained in the case of absorption ($r = 0.15$, $n = 8$) (Fig. 2a) and fluorescence ($r = 0.43$, $n = 8$) (Fig. 2b). However, a plot of $\Delta\bar{\nu}$ versus Δf has shown better linearity for aprotic solvents ($r = 0.97$, $n = 4$) (Fig. 2c) compared with protic solvents ($r = 0.48$, $n = 4$). This suggests that there is specific solvent effect along with the general solvent effects.

The poor correlation of fluorescence and absorption with Δf could be explained as follows. The specific interactions between the solvent and the solute molecules, viz. hydrogen bonding, the tendency of polar solvent molecules to form aggregates of two or more molecules etc., which are observed as deviations

Figure 1. (a) Absorption spectra; and (b) fluorescence emission spectra of **1**.

Table 1. Variation in Stokes shift with solvent polarity parameter of I

Solvent	E_N^T	Absorption maximum $\lambda_{a, \text{ nm } (\bar{\nu}_a, \text{ cm}^{-1})}$	Emission maximum $\lambda_{f, \text{ nm } (\bar{\nu}_f, \text{ cm}^{-1})}$	Stokes shift (cm^{-1})	$(\bar{\nu}_a + \bar{\nu}_f)/2$ (cm^{-1})
1,4-Dioxane	0.164	311 (32154)	391 (25575)	6579	28864
THF	0.207	298 (33557)	386 (25906)	7651	29731
EA	0.228	298 (33557)	384 (26041)	7516	29799
DMF	0.386	301 (33222)	400 (25000)	8222	29111
2-Propanol	0.546	292 (34246)	406 (24630)	9616	29438
n-Butanol	0.586	293 (34129)	405 (24691)	9438	29410
Ethanol	0.654	310 (32258)	407 (24570)	7688	28414
Methanol	0.762	293 (34130)	408 (24510)	9620	29320

DMF, dimethyl formamide; EA, ethyl acetate; THF, tetrahydrofuran.

Figure 2. Plots of (a) Energy of absorption versus bulk solvent polarity parameter $\Delta f(\epsilon, n)$; (b) Energy of fluorescence emission versus bulk solvent polarity parameter $\Delta f(\epsilon, n)$; and (c) Stokes shift versus bulk solvent polarity parameter $\Delta f(\epsilon, n)$.

from the solvent polarity parameter Δf , are not considered in Lippert–Mataga theory. However, the empirical polarity parameter proposed by Reichardt correlates better than the traditionally used solvent polarity parameter Δf (29). The $\bar{\nu}_a$, $\bar{\nu}_f$ and $\Delta\bar{\nu}$ were correlated with E_N^T . The least-squares correlation analysis gave a better correlation for $\bar{\nu}_f$ ($r = 0.83$, $n = 8$) compared to $\bar{\nu}_a$ ($r = 0.02$, $n = 8$) and $\Delta\bar{\nu}$ ($r = 0.52$, $n = 8$). This confirms the presence of general solute–solvent interactions as well as H-bonding interactions.

In order to understand the general solvent effect and specific solvent effects like solvent dipolarity and polarizability on the spectroscopic characteristics of I, $\bar{\nu}_a$, $\bar{\nu}_f$ and $\Delta\bar{\nu}$ were correlated with the solvatochromic parameters such as solvent polarizability (SP), solvent dipolarity (SdP), solvent acidity (SA) and solvent basicity (SB), using multiple regressions according to Catalan (30). Better correlation was obtained for $\bar{\nu}_f$ ($r = 0.74$, $n = 8$) than

$\bar{\nu}_a$ ($r = 0.46$, $n = 8$) and $\Delta\bar{\nu}$ ($r = 0.41$, $n = 8$). The result has been analyzed using equation (16) for better correlated $\bar{\nu}_f$,

$$\bar{\nu}_f = 32786 - 2975SP + 7815SdP - 2128SA - 713SB \quad (16)$$

$$r = 0.74, n = 8$$

From the above equation, it is clear that among non-specific dielectric interactions, the influence of SP is more compared to SdP and the influence of SA is more compared with SB.

Determination of dipole moments

Studies on variation in Stokes shift values with solvent polarity parameters gave further insight into the above discussion. Variation in Stokes shift and the arithmetic mean of Stokes shift

with solvent polarity parameters F_1 and F_2 respectively are shown in Figs. 3a and 3b which show good correlations ($r = 0.83, 0.96$ respectively) for selected number of data points. Figure 3c shows the linear correlation of $\bar{\nu}_a - \bar{\nu}_f$ with E_T^N having correlation $r = 0.91$.

The value of the dipole moment of I in the ground state was obtained using quantum chemical calculation and is equal to 5.72D. The optimized geometry and direction of dipole moment is shown in Fig. 4. The dipole moment of I in the excited state calculated using Bakshiev (μ_e^D), Kawski-Chamma-Viallet (μ_e^E) and Reichardt's empirical solvent polarity parameter (μ_e^F) are in fair agreement (Table 2).

The dipole moment of I in the ground state (μ_g^B) and that in the excited state (μ_e^C) calculated by assuming that they are parallel are found to be different from those calculated from other methods ($\mu_g^A, \mu_e^D, \mu_e^E, \mu_e^F$ in Table 2). This suggests that the two dipole moments are not parallel. The angle between μ_g^B and μ_e^C is found to be 29° . From Table 2, it is clear that the dipole moment of I in the excited state is higher than that in the ground state. This could be due to the intramolecular charge transfer (ICT) as shown in Fig. 5.

Figure 3. Plots of (a) Stokes shift versus $F_1(\epsilon, n)$ using Bakshiev's method; (b) arithmetic mean of Stokes shift versus $F_2(\epsilon, n)$ using Kawski-Chamma-Viallet method; and (c) Stokes shift versus solvent polarity parameter using Reichardt's method.

Figure 4. Optimized molecular geometry of I in the ground state.

Table 2. Values of Onsager radius ' a ' (Å) and the dipole moments (D)

Parameter	Value
a	4.11
μ_g^A	5.72
μ_g^B	1.70
μ_e^C	5.00
μ_e^D	9.08
μ_e^E	10.48
μ_e^F	9.32

a , Onsager cavity radius of the molecule; A, dipole moment of the Ground state of I calculated using quantum chemical method; B, ground state dipole moment calculated using equation (8); C, excited state dipole moment obtained using equation (9); D, Excited state dipole moment obtained using Bakshiev method; E, excited state dipole moment according to Kawski-Chamma-Viallet method; F, excited state dipole moment determined using Reichardt's empirical solvent polarity parameter.

Figure 5. Resonance structures of I.

Figure 6. Fluorescence emission spectra of I in (a) 1,4-dioxane; and (b) n-butanol in presence of aniline with 0 to 0.1 M concentration.

Figure 7. Stern-Volmer plot of the solute (I) in presence of (a) 1,4-dioxane; (b) n-butanol and aniline of varying concentrations.

Figure 8. Modified Stern-Volmer plots according to sphere of action static quenching model.

Fluorescence quenching studies

Analysis by Stern-Volmer equation. Fluorescence emission spectra for a fixed value of solute (I) concentration (10^{-5} M) in 1,4- dioxane and n-butanol with varying concentrations of aniline are shown in Fig. 6. The steady-state S-V plots according to equation (12) are shown in Fig. 7. This shows non-linearity with positive deviation indicating the presence of other quenching mechanisms such as ground state complex formation, static quenching etc. along with dynamic quenching.

Analysis using ground state complex formation model. The possibility of formation of ground state complex was analyzed using equation (13). K_{SV} values obtained in both the solvents from the plot of $[I_0/I - 1]/[Q]$ versus $[Q]$ were found to be imaginary and not useful in analyzing the data further. Therefore the observed fluorescence quenching is not due to ground state complex formation. The fluorescence quenching was further analyzed by sphere of action static quenching model.

Analysis by sphere of action static quenching model. Plot of $[1 - I/I_0]/[Q]$ versus I/I_0 is shown in Fig. 8 and was found to be linear. The dynamic quenching constant (K_{SV}) was calculated from equation (14) and the corresponding value of bimolecular quenching parameter k_q was calculated by using experimentally

Figure 9. Variation of K_{SV}^1 versus $[Q]^{1/3}$.

Table 3. Parameters analyzed using static action quenching model

Solvent	K_{SV} (M^{-1})	τ_0 (ns)	$k_q \times 10^9$ ($M^{-1}s^{-1}$)	Range of W	V (M^{-1})	r ($\text{\AA}$)
1,4- Dioxane	14.38	4.23	3.39	0.037–0.81	33.10	23.59
n-Butanol	55.55	5.39	10.30	0.013–0.80	43.12	25.76

K_{SV} , k_q , dynamic and bimolecular quenching constants respectively calculated from sphere of action static quenching model; τ_0 , fluorescence lifetime value without quencher; $R = R_S + R_Q = 4.11 + 2.84 = 6.95 \text{ \AA}$

Table 4. Values of different parameters obtained from finite sink approximation model

Solvent	K_{SV}^0 (M^{-1})	$D \times 10^5$ ($cm^2 s^{-1}$)	R' (Å)	$k_q \times 10^9$ ($M^{-1} s^{-1}$)	$4\pi NR'D \times 10^9$ ($M^{-1} s^{-1}$)
1,4-Dioxane	9.50	0.22	13.61	3.39	2.24
n-Butanol	33.55	0.61	13.36	10.30	6.21

K_{SV}^0 , dynamic quenching constant calculated from finite sink approximation model; k_q , bimolecular quenching rate parameter calculated from sphere of action static quenching model.

determined values of fluorescence lifetime value without quencher (τ_0 , Table 3). Fluorescence lifetime values for solutions of I without quencher in 1,4-dioxane and n-butanol are found to be 5.39 ns and 4.23 ns respectively. In order to find out the static and dynamic quenching effects, the values of static quenching constant 'V' and radius of sphere of action 'r' have been calculated (Table 3). It was found that the radius of sphere of action was greater than the encounter distance (R), the sum of the radii of solute (R_S) and quencher molecule (R_Q), calculated according to the literature (44). Hence it is clear that the bimolecular interaction is due to static and dynamic quenching, provided the interactions are diffusion limited. To find out whether interactions are diffusion limited, a finite sink approximation model was used.

Analysis using finite sink approximation model. In order to study the diffusion limitation of the interaction the finite sink approximation model has been invoked, according to which the plot of K_{SV}^{-1} versus $[Q]^{1/3}$ is as shown in Fig. 9. The value of mutual diffusion coefficient 'D' and distance parameter R' (Table 4) are calculated (equation (15)) from the plots. From Table 4, it is clear that the value of k_q calculated from equation (14) is greater than that obtained using $4\pi NR'D$. Hence, the interaction is diffusion limited (40,45).

Conclusions

Fluorescence and the quenching studies are important for the fundamental understanding of the phenomena in the molecule as well as for giving information about the molecular interactions and the chemical environment. Solvatochromic studies on photophysical properties of Schiff base I were carried out in different solvents. In the fluorescence spectra red shifts were observed with increase in solvent polarity indicating $\pi-\pi^*$ transition. The higher value of dipole moment of I in excited state than in the ground state suggests that its polarity is more in the excited state compared to that in the ground state. This could be due to ICT in the excited singlet states. The fluorescence quenching studies of I in 1,4-dioxane and n-butanol by aniline show that quenching is due to both dynamic and static phenomena and it is diffusion limited. Further work is in progress to study the usefulness of I as a fluorescent probe for providing information about biochemical systems.

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