

Photophysical properties of 5-hydroxyindole (5HI): Laser flash photolysis study

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Abstract. Steady state fluorescence emission and transient absorption spectra of 9-fluorenone (9FL) were measured in the presence of 5-hydroxyindole (5HI) in highly polar acetonitrile (ACN) environment at ambient temperature. Cyclic voltammetry measurements demonstrate that ground state 5HI as a donor could take part in highly exothermic electron transfer (ET) reactions with excited 9FL, which should serve as electron acceptor. From the transient absorption measurements it is inferred that in geminate ion-pair (GIP) (or contact ion pair), formed initially due to photoinduced ET, the decay of this contact ion-pair occurs not only through ion recombination (back electron transfer to ground state of reactants), but through the other processes also such as proton-transfer (hydrogen abstraction) from radical cation to anion and separation of ion-pair producing the free ions. From the computed reorganisation energy parameter (λ) and experimentally observed $-\Delta G_{ET}^0$ values it is hinted that there is a possibility that highly exothermic forward electron transfer reactions in the singlet state S_1 occur, within present reacting systems, in Marcus inverted region. Back transfer seems to follow the same path. Investigations with similar other reacting systems are underway.

Keywords. Photoinduced electron transfer; H-abstraction; neutral radical; transient absorption; first order and second order decay kinetics.

1. Introduction

Investigations on the photophysical properties of indole and its derivatives are gaining increasing interest and the photophysics of indole still remains a very useful subject to reveal the mechanism of long range electron transfer in proteins. Lately our research group is involved in studying the photoinduced electron transfer (PET) reaction using various indoles as electron donors.¹ These indoles were found to undergo highly exothermic electron transfer (ET) reactions in Marcus inverted region. Thus it is expected that artificial photosynthetic devices could be developed using the indoles as donors. Though several investigations have been carried out on various indoles,^{2–8} almost no attention was given to study the electron donating properties of hydroxyindole. Electrochemical measurements demonstrate that half-wave oxidation potential ($E_{1/2}^{OX}$) of 5-hydroxyindole (5HI) is relatively lower (+0.34 V) than the corresponding value for 5-methylindole (5MI) (+1.50 V). Thus the 5HI seems to be much potential electron donor than 5MI. The half-wave reduction potential ($E_{1/2}^{RED}$) of 9FL was found to be –1.28 V. Both steady state and time resolved measurements were made on 5HI using the well-

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Electrochemical measurements (using standard calomel electrode as the reference electrode and tetraethylammoniumperchlorate (TEAP) as the supporting electrolyte) were performed with a PAR model 370-4 electrochemistry system.^{10,11}

3. Results and discussion

3.1 Singlet quenching in fluid solution at the ambient temperature

The steady state fluorescence of 9FL (excitation wavelength ~ 377 nm) in highly polar ACN is found to be efficiently quenched (figure 2), without any change in shape and

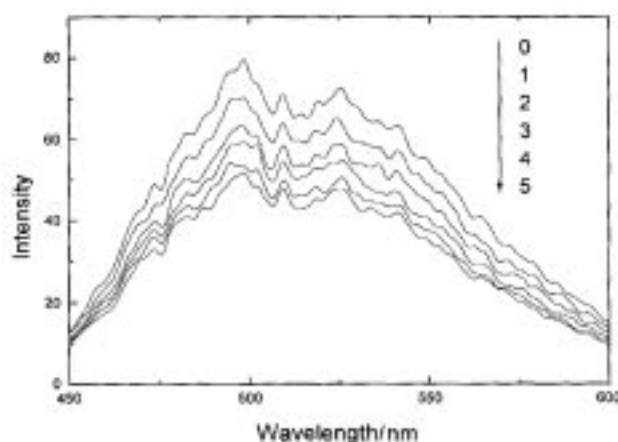


Figure 2. Fluorescence emission spectra of 9FL ($\lambda_{\text{ex}} = 377$ nm) ($C = 7.0 \times 10^{-4}$ mol dm $^{-3}$) in ACN fluid solution at 296 K in presence of 5HI. Concentration of 5HI (mol dm $^{-3}$) in (0) 0; (1) 5.5×10^{-4} ; (2) 1.1×10^{-3} ; (3) 1.6×10^{-3} ; (4) 2.2×10^{-3} ; (5) 3.3×10^{-3} .

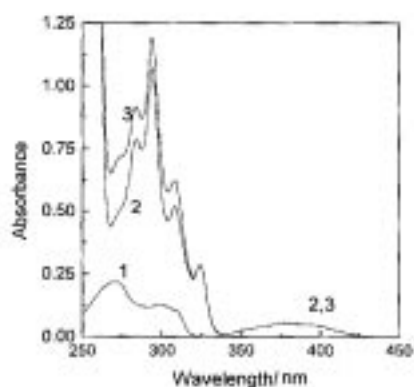


Figure 3. Steady state electronic absorption spectra of 5HI ($C = 1.9 \times 10^{-5}$ mol dm $^{-3}$, curve 1), 9FL ($C = 3.2 \times 10^{-4}$ mol dm $^{-3}$, curve 2) and mixture (curve 3) of 5HI ($C = 1.9 \times 10^{-5}$ mol dm $^{-3}$) and 9FL ($C = 3.2 \times 10^{-4}$ mol dm $^{-3}$) in ACN fluid solution at 296 K. $l = 1$ cm.

Table 1. Fluorescence quenching data for the present D–A systems at ambient temperature in ACN solvent, τ_0 is the acceptor fluorescence lifetime in absence of the donor (quencher).

System	λ_{em}/nm	$\tau_0/ns (\pm 6 \text{ ps})$	${}^a k_q/dm^3 \text{ mol}^{-1} \text{ s}^{-1} \times 10^{10}$
5HI + 9FL*	500	14.6	1.32 (1.58)

^aObtained from steady state fluorescence emission intensity measurements. In this column the values in parentheses are obtained from time resolved measurements

*Excited singlet state

energy positions, in the presence of 5HI (quencher). The same observation was made even in the higher concentration of the quencher ($\sim 4 \times 10^{-3} \text{ mol dm}^{-3}$). At the wavelength used for excitation of the fluorescence emission of the acceptor (9FL), the donor molecule is transparent (figure 3). Thus the possibility of occurrence of competitive absorption by the donor as well as its filtering effect on the emission intensity of the acceptor is very slim. In polar ACN fluid solution at the ambient temperature the absorption spectra of the mixture of the donor (5HI) and the acceptor 9FL appear to be just a superposition of the corresponding spectra of the individual donor and acceptor species. This observation supports in favour of the lack of formation of the ground state charge transfer (CT) complex between the donor and the acceptor molecules used.

The bimolecular quenching rate constants, k_q , determined from both the linear Stern-Volmer (SV) plots^{12,13} of (1) fluorescence intensity reduction and (2) fluorescence lifetime quenching of 9FL as a function of 5HI concentrations are found to be same within the experimental error (table 1). This observation demonstrates the dynamic behaviour of the observed quenching. It is important to point out here that as the fluorescence quenching of 9FL occurs in the region of 5HI concentrations (figure 2) where the 9FL absorption spectrum is not at all affected, the simple Stern Volmer (SV) equation was used to analyse the quenching phenomena.

The redox potential values in ACN of both 5HI ($E_{1/2}^{OX} \approx +0.34 \text{ V}$) and 9FL ($E_{1/2}^{RED} \approx -1.28 \text{ V}$), are obtained from the electrochemical measurements by cyclic voltammetry technique. From the observed values it is apparent that 5HI should act as an electron donor in presence of 9FL which would serve as an acceptor in photoinduced ET reactions where the acceptor moiety is excited (the lowest singlet-singlet (0, 0) transition energy of the excited chromophore nearly equals to 3.29 eV). The Gibbs free energy of forward ET reactions (ΔG_{ET}^0) from well known Rehm-Weller relation^{12,14,15} can be computed for our present reacting systems in highly polar ACN solutions. From the negative value of ΔG_{ET}^0 ($\approx -1.67 \text{ eV}$) it is apparent that the ET reactions in ACN are highly exothermic ($\Delta G_{ET}^0 < 0$) and hence energetically favourable from the thermodynamic point of view. When both the interacting partners are in the ground states, chances of the occurrence of ET reactions seem to be remote, because of the observed positive value of ΔG_{ET}^0 ($\sim +1.62 \text{ eV}$).

The k_q values (table 1) are found to be very close to diffusion-controlled limit (k_{diff} for ACN $\sim 2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) which indicates that the photoinduced electron transfer (PET) reactions possess a major role in quenching mechanism of the steady state fluorescence emission spectra of 9FL in presence of the electron donor 5HI. Nevertheless for the direct evidence of occurrence of PET, transient absorption measurements were made by using laser flash photolysis technique. The results are described below.

3.2 Transient absorption spectroscopy

In laser flash photolysis experiments pulsed laser excitation at 355 nm, using Nd : YAG laser, was used to excite specifically the acceptor 9FL molecules from the mixture of this acceptor and the donor 5HI.

The transient absorption band of the acceptor 9FL at 420 nm was observed with 23 μ s lifetime in ACN solvent. Following observations made by earlier authors^{16,17} this band of 9FL could be assigned to triplet-triplet absorption spectra. Interestingly with addition of the donor (5HI), in the mixture of 9FL and ACN, a more complex transient spectra were observed with new bands around 460, 500 and 550 nm in addition to the triplet band at 420 nm (figure 4). In the same figure the variation of intensity of the transient absorption spectra with changes of delay times between exciting and analysing pulses is shown.

Following the observations made by the earlier authors¹⁸⁻²⁰ the new band system at around 460 nm region has been assigned to the band of 9FL radical anion of contact ion-pair (CIP) of the D-A system as the decay at 460 nm is found to be monoexponential decay from the fitting analysis (figure 5). It is known that radical anions and cations in contact ion-pair recombine by this type of decay kinetics. So in this contact ion-pair, recombination occurs through first order decay. This anionic band is formed due to the photoinduced ET reaction between the excited acceptor 9FL and the present donor in the ground state. The other new absorption band near 550 nm (figure 4) with half life of $\sim 2 \mu$ s could be assigned to free radical ions (anion) of 9FL²¹⁻²³ as the decay at 550 nm obeys second order kinetics (figure 5) where charge recombination between this anion and the donor cation occurs by second order slow diffusion process. These results clearly indicate that the formation of both contact ion-pair and free ions occur by the photoinduced electron transfer mechanism.

In support of the transient absorption spectra where acceptor anion of the contact ion-pair (at 460 nm) and free or solvent separated anion at 550 nm regions were observed, we

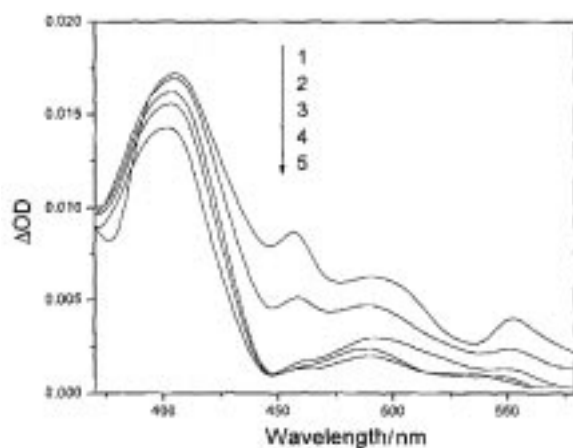


Figure 4. Transient absorption spectra of 9FL (ex. wavelength ~ 355 nm using the third harmonic of Nd : YAG, laser fluence ~ 150 mJ/pulse), in ACN (conc. $\sim 5.5 \times 10^{-4}$ mol dm⁻³) at the ambient temperature in presence of the donor 5HI (conc. $\sim 7.8 \times 10^{-4}$ mol dm⁻³) at delay times: 1: 0.5 μ s; 2: 2.0 μ s; 3: 5.0 μ s; 4: 8.0 μ s; 5: 10 μ s.

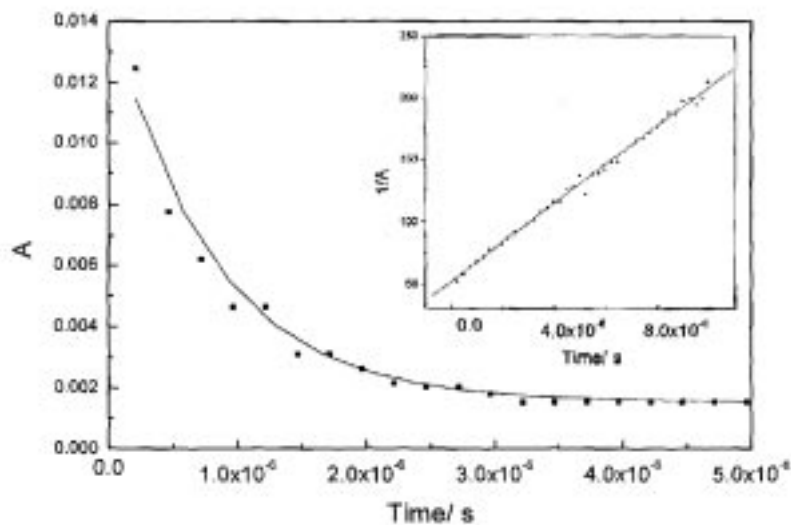
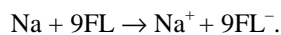


Figure 5. The time profile of the absorbance (A) of the contact ion-pair of 9FL anion radical in presence of 5HI at 460 nm. The solid line represents the fitting equation: $Y = A_0 + A \exp(-t/\tau)$. Inset: plot of $1/A$ as a function of delay times of free anion of acceptor 9FL at 550 nm of same system above. The solid line is the second order fitting ($r^2 \sim 0.99$).

measured the steady state electronic absorption spectra of the acceptor 9FL in the presence of metallic sodium in ACN solvent in an attempt to produce artificially 9FL anion according to the reaction mechanism below:



Expectedly in the presence of metallic Na, the absorption bands were found both in the 460 and 550 nm regions, which gradually disappear in the presence of molecular oxygen. This demonstrates the bands should be due to the formation of anions and the longer wavelength band should be due to the free ion and the shorter one should be responsible for the ion present in the contact ion-pair. It may be pointed out that both for $5\text{HI}^+/9\text{FL}^-$ and $\text{Na}^+/9\text{FL}^-$ ion-pairs, absorption bands at the similar energy positions were found. This observation is due to the fact that in the regions of 460 and 550 nm only the radical anions (9FL^-) are accessible experimentally as the absorption of the radical cation of the donor 5HI lies at a much lower wavelength region (~ 390 nm) (vide infra).

The decay kinetics at 420 nm of the transient absorption spectra of 9FL exhibits mono-exponential behaviour in the presence of donor (5HI) in polar ACN environment. The decay rate (or the lifetime of the species, $\tau \sim 23 \mu\text{s}$) of the 420 nm band of 9FL remains unchanged even in the presence of the donor 5HI. However, triplet quenching of 9FL by the donor could not be disregarded in this case as the charge recombination lifetime within the present reacting systems, which has been discussed below, was observed to be in the microsecond range. Thus, it may be inferred from the present stage of investigation that electron transfer occurs in this system from ground state donor to both excited singlet

and triplet of the acceptor but the ET reactions from the triplet is delayed due to its long lifetime.

The time profile of the absorbance of the acceptor 9FL anion (contact ion-pair) in ACN near 460 nm (figure 5) shows that with further increase of delay beyond 4 μs , the value of absorbance of the anion remains the same. The lifetime τ_{ip} is the ion-pair lifetime defined as in (1, 1a).²⁴

$$\tau_{ip} = (k_{CR} + k_{dis})^{-1}, \quad (1)$$

$$\phi_R = k_{dis} \tau_{ip}, \quad (1a)$$

where k_{CR} and k_{dis} represent the rates associated with geminate recombination and charge dissociation processes respectively.

The yield (ϕ_R) of dissociated ion radical formation is given by (1a) and is obtained experimentally by taking the ratio of the absorbance due to the dissociated ions at longer delay time and the initial value estimated by extrapolating the absorbance at $t = 0$.²⁴ Low yield of dissociated ion-radical ($\phi_R \sim 0.1$) was obtained. The rates due to ion-pair recombination (k_{CR}) and solvent separated ion-pair formation (k_{dis}) are computed using (1) and (1a) which are found to be nearly $1.15 \times 10^6 \text{ s}^{-1}$ and $1.27 \times 10^5 \text{ s}^{-1}$ respectively for the present D–A systems. Greater value of recombination rate constant indicates in favour of the formation of the contact ion-pair of tight nature.

Monitoring the decay of free anion of 9FL at 550 nm, the ratio of the rate constant of back electron transfer (k_b) to the molar extinction coefficient (ϵ) is obtained from the slope of second order plot.^{19,20} The calculated value of k_b is equal to $2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is nearly equal to the diffusion controlled limit as expected. This indicates that the decay at 550 nm results from the slow recombination, by diffusion-assisted process, of the free cationic and anionic species.

The free anion of 9FL is produced by ionic dissociation of contact ion-pair (CIP, scheme 1). The yield, ϕ_R (discussed above) is actually similar to the ϕ_{sep} (efficiency of free anions formation²⁵) which can be defined as $\phi_{sep} \equiv [\text{no. of free ions produced}]/[\text{no. of contact ion-pair formed}]$. The rate of charge recombination between contact ions, k_b , is also computed from (2). This value ($1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) is very similar to the value obtained from the analysis of the second order fitting (discussed above).

$$\phi_{sep} = (k_{diff} - k_b)/(k_{diff}), \quad (2)$$

k_{diff} is the second order diffusion-controlled rate constant.

The absorption of the counter ion (radical cation of 5HI), appears as a small shoulder near 390 nm²⁶ which is practically hidden over the broad transient absorption band envelope of 9FL (figure 4).

Following the earlier report²⁰ the new absorption band found near 490 nm (figure 4) could be assigned as the neutral radical of 9FL. As from the present study the decay at 490 nm was found to obey first order kinetics (lifetime $\sim 6.2 \mu\text{s}$) it shows this band corresponds to contact neutral radical of 9FL.

The shoulder near 510 nm, which looks somewhat prominent at low delay times used and gradually disappears with increase of delay (figure 4) between the exciting and analysing pulses, could be assigned to the neutral radical of 5HI (scheme 1) following the observations made earlier by Zhang *et al*²⁷ in case of dihydroxy indole molecule.

These neutral radicals are formed due to cleavage of either N–H or O–H bond in GIP followed by H-abstraction (scheme 1). This reaction mechanism involves sequential electron-proton transfer, which is an dominant quenching process. From the structural point of view, 5HI have phenolic O–H and indolic N–H bonds, any one of which can act as hydrogen (proton) donor due to cleavage.²⁷ It was observed by earlier workers that if H of O–H were involved, transient absorption band at around 490 nm region²⁷ and if H-atom liberates due to cleavage of N–H bond, a 510 nm absorption band appears.²⁷ Nevertheless, the broad transient absorption band observed in the present study (figure 4) in this region makes the situation difficult to assign unambiguously the origin of the overlapping bands individually. So at the present stage of investigation no definite conclusions could be reached about the nature of H-atom, whether it belongs to O–H or N–H group, which undergoes abstraction. Nevertheless, further investigations using the similar donor acceptor systems are now underway to look better insight into the mechanism.

Thus the photoinduced electron transfer seems to be responsible for both the singlet and the triplet quenching reactions. On the basis of the experimental results observed in the present study the reaction mechanisms, as depicted in scheme 1, have been proposed.

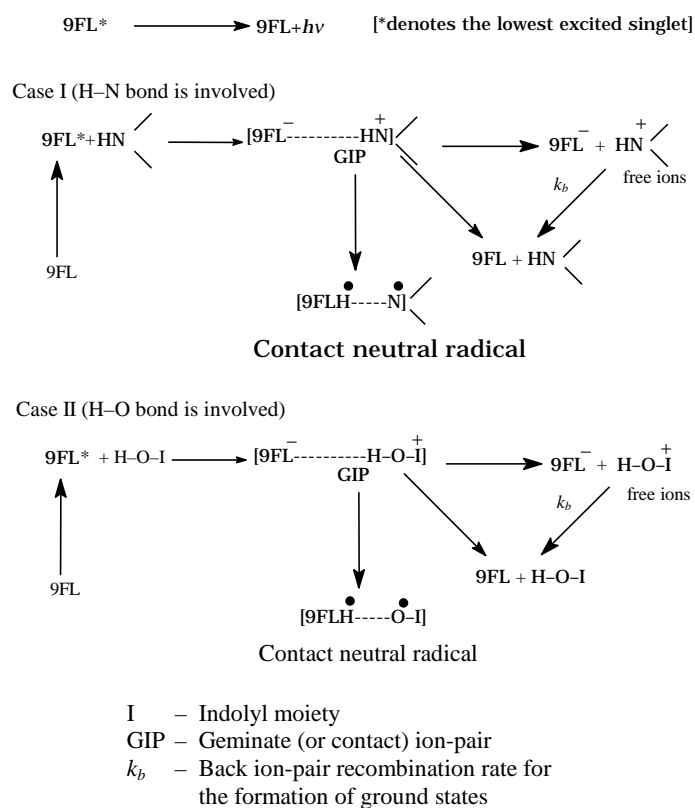
The Gibbs free energy changes for back electron transfer reactions by ion pair recombination to form ground state, $\Delta G_b(G)$, and excited triplet, $\Delta G_b(T)$ of the fluorescer (acceptor) are computed from (3) and (4).^{28,29}

$$\Delta G_b(G) = -E_{1/2}^{OX}(D/D^+) + E_{1/2}^{RED}(A^-/A), \quad (3)$$

$$\Delta G_b(T) = E_{1/2}^{RED}(A^-/A) - E_{1/2}^{OX}(D/D^+) + E_T^*, \quad (4)$$

where E_T^* is the triplet energy level ($T_1 \leftarrow S_0$).

In the case of 9FL, Turro *et al*³⁰ reported the singlet (S_0)-triplet (T_1) energy gap is of about ~ 2.3 eV. Here $\Delta G_b(G)$ possess large negative value (≈ -1.62 eV), whereas $\Delta G_b(T)$ possess positive value ($\approx +0.68$ eV) in ACN solvent. Thus from thermodynamical point of view the possibility of formation of ground state by ion recombination is quite high whereas formation of triplet of 9FL by this process could be excluded. But in GIP (or contact ion pair) as depicted in scheme 1, the decay of contact ion-pair occurs not only through ion recombination (back electron transfer to ground state of reactants), but through the other processes also such as proton-transfer (hydrogen abstraction) from radical cation to anion (see above) and separation of ion-pair producing the free ions. Considering the dielectric continuum model,³⁰ the total reorganization energy (λ) for contact distance (r_D , donor radius ~ 3.7 Å, and r_A (acceptor) ~ 4.15 Å) has been computed (≈ 1.26 eV). This value is less than $-\Delta G_{ET}^0$ for forward electron transfer (ET) (≈ 1.67 eV) in the excited singlet state and $-\Delta G_b(G)$, for back transfer (≈ 1.62 eV) reactions. These observations are indicative of occurrences of the highly exothermic forward and backward singlet ET reactions in Marcus inverted region. In the lowest excited triplet state of 9FL, lower magnitude of $-\Delta G_{ET}$ (~ 0.68 eV) relative to λ indicate in favour of occurrence of such reactions in normal region.



Scheme 1.

4. Conclusions

From both electrochemical and time resolved measurements it reveals that the highly exothermic electron transfer reactions occur between the ground state 5HI and excited 9FL (S_1/T_1) followed by H-atom abstraction. Long charge recombination lifetime, of the order of microseconds, demonstrates the possibilities of involvements of both the lowest excited singlet and triplet states in quenching reactions through Photoinduced electron transfer processes. These observations indicate that 5HI is not only a potential electron donor but due to its excellent H-bonding ability, it may use as an antioxidant.

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