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Fencing of Photoinduced Electron Transfer in Nonconjugated Bichromophoric System by β-cyclodextrin Nanocavity

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Abstract

Fencing of photoinduced electron transfer (PET) between the donor and acceptor in nonconjugated bichromophoric system by inclusion of donor group in the hydrophobic β-cyclodextrin nanocavity has been observed using steady state and time resolved fluorescence technique. The molecular modelling calculations further confirm the inclusion of donor group in the β-cyclodextrin nanocavity.

Introduction

Electron transfer is the most elementary and ubiquitous of all chemical reactions and plays a crucial role in many essential biological processes [1]. Photoinduced electron transfer (PET) between donor–acceptor systems have been widely studied, because of their potential applicability in molecular photonic switching devices, molecular AND/OR gates and molecular sensors [2–5]. The spacial organisation imparted to electron donor and acceptor in solution allows one to exert some control over the efficiency of PET reactions. Chemistry in organised media differs markedly from that in any homogeneous fluid medium and mimics the extremely efficient chemical processes in the biological systems [6–8]. The ultimate goal of the photophysical studies in such organised assemblies is to understand the biological processes that occur in the hydrophobic pockets of various protein or the membrane surfaces. Among all the confined systems, exciting achievements have been witnessed with cyclodextrin as artificial hosts in many of the most actively pursued research field such as drug delivery systems, molecular sensing technologies, biomimetic recognition and catalysis [9–11]. We have recently focussed our research towards the development of bichromophoric fluorescent chemosensors where the ion recognition takes place at the receptor sites with concomitant change in the photophysical behaviour of acridinedione (ADD) fluorophore by modulation of PET and intramolecular charge transfer (ICT) processes [12, 13]. ADD dyes have been shown to mimic the NADH analogues to a greater extent because of their tricyclic structure, which is capable of protecting the enamine moiety [14, 15].

We present here the first nonconjugated but covalently linked bichromophoric system (ADD-1) that shows fluorescence enhancement in the presence of β-cyclodextrin (β-CD) by fencing of PET between the donor and the ADD acceptor. The inclusion behaviour of bichromophoric ADD dyes were evaluated by monitoring their respective UV–vis, steady state and time resolved emission studies as a function of β-CD concentration. In ADD-1, the anisole group and the ADD fluorophore act as electron donor and acceptor respectively (Scheme 1).

Experimental

Acridinedione dyes were synthesised by procedures reported in the literature [16]. Methanol HPLC was obtained from Qualigens India Ltd. The water used was triply distilled over alkaline permanganate in an all glass apparatus. β-CD (Fluka) were used as received. Absorption spectra were recorded in an Agilent 8453 diode array spectrophotometer. Fluorescence spectra were recorded using a Perkin-Elmer LS5B luminescence spectrophotometer. Fluorescence quantum yields were obtained from the corrected fluorescence spectra using the expression

$$\phi_f = (A_s/A_r)(a_r/a_s)(n_s/n_r)^2 \times 0.546$$

where, A_s and A_r are the area under the corrected fluorescence spectrum, a_s and a_r are the absorbances at the wavelength of excitation (366 nm), n_s and n_r are the refractive indices of the solvent for the sample and

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ADD-1 **ADD-2**

Scheme 1.

reference respectively using dilute solutions with absorbance less than 0.02. The area under the spectra was obtained by numerically integrating the area by Simpson's method. Quinine sulphate in 0.1 N sulphuric acid was used as the reference for quantum yield determination. (ϕ_f of quinine sulphate = 0.546).

Fluorescence decays were recorded using TCSPC method using the following setup. A diode pumped millenia CW laser (Spectra Physics) 532 nm was used to pump the Ti:sapphire rod in Tsunami picosecond mode locked laser system (Spectra Physics). The 750 nm (80 MHz) was taken from the Ti:sapphire laser and passed through pulse picker (Spectra Physics, 3980 2S) to generate 4MHz pulses. The second harmonic output (375 nm) was generated by a flexible harmonic generator (Spectra Physics, GWU 23PS). The horizontally polarised 375 nm laser was used to excite the sample. The fluorescence emission at magic angle (54.7°) was dispersed in a monochromator ($f/3$ aperture), counted by a MCP PMT(Hamamatsu R 3809) and processed through CFD, TAC and MCA. The instrument response function for this system is ~52 ps, the fluorescence decay was analysed by using the software provided by IBH (DAS-6) analysis and PTI global analysis software.

Results and discussion

The absorption and emission spectra of ADD dyes show a maximum around 385 and 440 nm respectively in 4% methanol solution and this band has been assigned to the intramolecular charge transfer from the ring nitrogen to the ring carbonyl oxygen centre within the ADD fluorophore [17]. In our earlier investigation, we found that the inclusion of ADD fluorophore in β-CD nanocavity results in the blue shift of the absorption spectrum along with decrease in absorbance due to the low polar environment of the hydrophobic nanocavity [18, 19].

No significant change was observed in the absorption spectrum of ADD-1 on increasing the concentration of β-CD in 4% methanol solution. This suggests that there is no inclusion of the acridinedione moiety in the β-CD nanocavity. In contrast to the absorption, the fluorescence intensity of ADD-1 increases with increase in β-CD concentration without change in the emission maximum. The fluorescence emission spectra of ADD-1 at different β-CD concentration are depicted in Figure 1. We have also carried out blank experiments with ADD-2 (methoxy group is absent) by increasing the concentration of β-CD in 4% methanol. In this system we do not observe any characteristic change in the absorption and emission spectra. It is interesting to compare the present results with those reported earlier for the ADD class of dyes. The ADD dyes having methyl group at the 10th postion (ADD ring amino group) and hydrogen at the 9th position showed a remarkable quenching of fluorescence. ADD forms 1:1 complexes with one of the sides included into the β-CD cavity [19]. The fluorescence quenching has been attributed for the hydrogen bond in the excited state between the carbonyl group and the secondary hydroxyl group of β-CD. In contrast to the fluorescence quenching of ADD dyes, fluorescence enhancement of ADR dyes in the β-CD cavity was observed [18]. The modes of inclusion for the two series of dyes (ADD & ADR) were different. In the ADR dyes, the phenyl substitution in the ring nitrogen was included inside the cavity, which results in blue shift

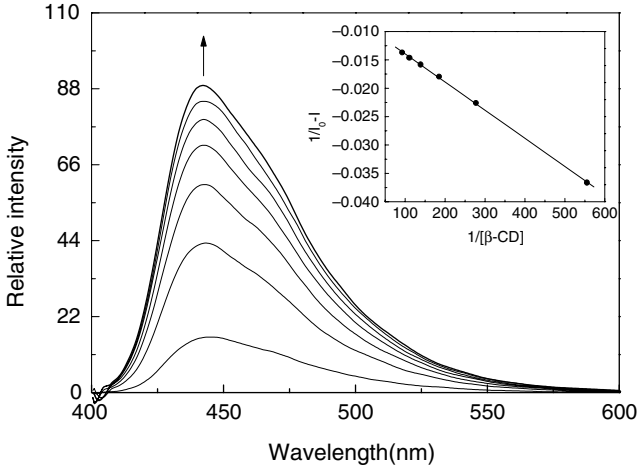
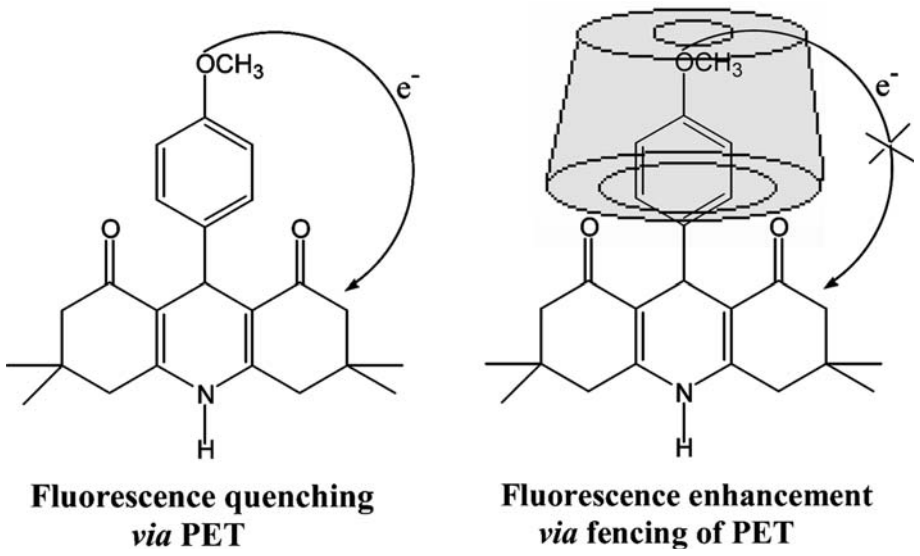


Figure 1. Fluorescence enhancement of ADD-1 in 4% methanol by β-CD. The concentration of β-CD is (from bottom to top) 0; 1.80; 3.60; 5.40; 7.20; 9.00 and 10.80 mM. Inset shows the Benesi–Hildebrand plot for the 1:1 inclusion complex between ADD-1 and β-CD.



Scheme 2.

in the absorption spectrum along with decrease in absorbance on increase in the β-CD concentration. From the above observations, it is clear that in ADD-1 the mode of inclusion is different to that reported earlier [18, 19].

ADD-1 is weakly fluorescent ($\phi_f = 0.08 \pm 0.05$) compared to the homologous fluorophore (ADD-2) without the electron donor group ($\phi_f = 0.61 \pm 0.05$). This observation reveals that there is an intramolecular fluorescence quenching via PET from the electron rich methoxy moiety to the relatively electron deficient excited state of the ADD fluorophore in ADD-1 system. The fluorescence decay behaviour of ADD-1 further confirms PET induced fluorescence quenching. Fluorescence decay of ADD-1 and ADD-2 are single exponential with a lifetime of 0.71 ± 0.03 ns and 8.0 ± 0.02 ns in 4% methanol respectively. The shorter lifetime of ADD-1 in comparison with the ADD-2, represents PET quenched lifetime of acridinedione fluorophore. The inclusion of the donor group of ADD-1 in β-CD nanocavity fences the PET between the nonconjugated donor and acceptor that result in the fluorescence enhancement (Scheme 2). Interaction of the dye molecule with a saccharide unit in cyclodextrin may also alter the spectral properties. In order to confirm that the spectral change observed for ADD-1 is due to the inclusion or hydrogen bonding interaction with the hydroxyl group present in the β-CD, the same set of experiments were carried out with varying concentration of a acyclic saccharide D(+)-Glucose (0.001–0.01 M) instead of β-CD. There is no change in the absorption and emission spectrum of ADD-1 on increasing the concentration of D(+)-Glucose which rules out the enhancement in the fluorescence intensity due to the hydrogen bonding interaction with a saccharide unit and further confirms the inclusion of hydrophobic donor group in the β-CD nanocavity.

The fluorescence enhancement of ADD-1 by β-CD was analysed using the Benesi-Hildebrand plot [20] as given in Equation (1).

$$\frac{1}{I_0 - I} = \frac{1}{I_0 - I'} + \frac{1}{K(I_0 - I')[\beta - CD]} \qquad (1)$$

where, K, I_0, I and I' are the equilibrium constant, the observed fluorescence intensity in the absence of β-CD, the observed fluorescence intensity in the presence of β-CD and the fluorescence intensity of the ADD-1/β-CD inclusion complex respectively. Figure 1 inset shows the linear dependences between $1/I_0$–I vs $1/[\beta\text{-CD}]$. This reflects the consecutive process for the formation of 1:1 inclusion complex between ADD-1 and β-CD. From the slope and the intercept, the binding constant of 1:1 complex (K) was determined to be $193 \pm 2\ M^{-1}$.

The complexation between β-CD and ADD-1 has also been investigated by the time-resolved fluorescence

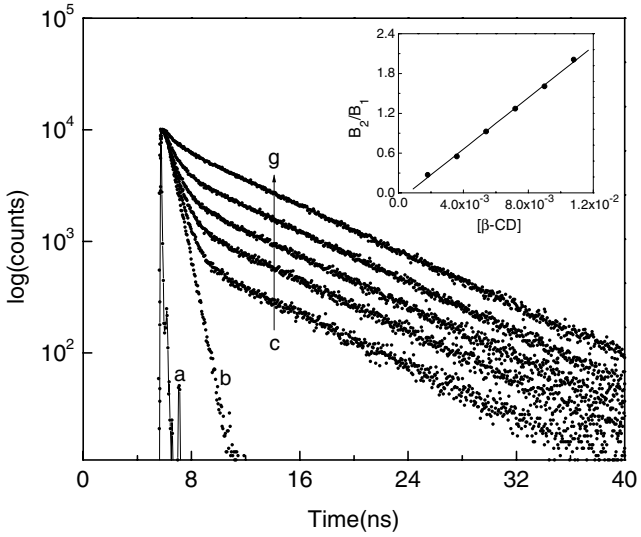


Figure 2. Fluorescence decay profiles of ADD-1 at different concentration of β-CD. (a) Laser profile; (b) dye alone; (c) 0.45 mM; (d) 0.90 mM; (e) 1.80 mM; (f) 3.60 mM; and (g) 10.80 mM. Inset shows the plot of B_2/B_1 vs $[\beta\text{-CD}]$.

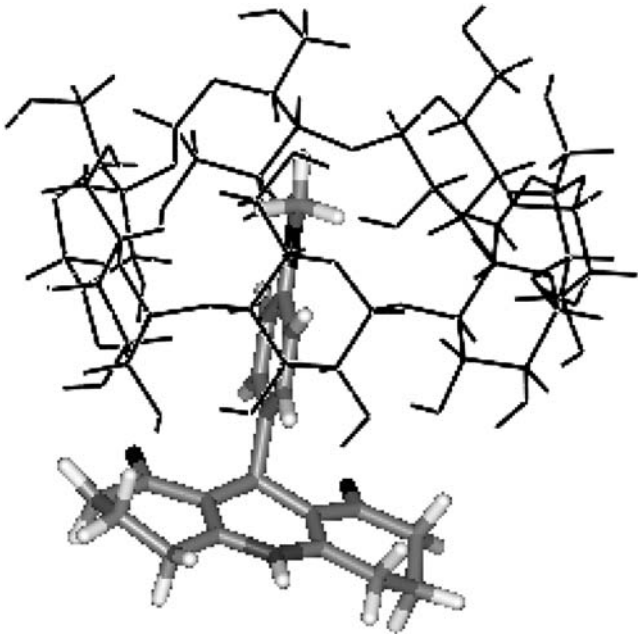


Figure 3. Optimised plausible binding mode for 1:1 host-to-guest complexation of ADD-1 with β-CD.

technique. Figure 2 presents the fluorescence decay of ADD-1 at different concentrations of β-CD in 4% methanol. Prior to the β-CD addition, ADD-1 exhibits a single exponential lifetime ($\tau = 0.71 \pm 0.03$ ns) in 4% methanol solution. Whereas in the presence of β-CD, the fluorescence decay of ADD-1 is biexponential. The biexponential decay data suggests the presence of two distinct species, consisting of free (lifetime of PET quenched fluorophore, 0.71 ± 0.03 ns) and complexed form (lifetime of PET fenced fluorophore, 7.58 ± 0.03 ns). The shorter component pre-exponential factor (free ADD-1) decreases gradually on increasing the concentration of β-CD, and the new longer component (ADD-1/β-CD complex) pre-exponential factor increases. The time resolved fluorescence technique provides a sensitive and systematic means of resolving the exact contribution of each component. The ratio of the pre-exponential factors(B_2/B_1) is related to the concentration of the two components by the Equation 2.

$$\frac{B_2}{B_1} = C_2 K_{r2} \varepsilon_2 / C_1 K_{r1} \varepsilon_1 \qquad (2)$$

where C, k_r and ε are the concentration of ADD-1, the radiative rate constant and the molar absorption coefficient at the excitation wavelength respectively. The subscripts 1 and 2 refer the free and bound ADD-1 respectively. Since k_r is a constant and $\varepsilon_1 = \varepsilon_2$, Equation (2) is simplified as $B_2/B_1 \cong C_2/C_1$. In excess of [β-CD] with respect to the dye, B_2/B_1 can be written as Equation (3).

$$B_2/B_1 = K[\beta - \mathrm{CD}] \qquad (3)$$

The data indeed result in a linear plot, which is shown in the inset of Figure 2. The binding constant (K) calculated for the ADD-1/β-CD complex through such a plot is $193 \pm 2\ \mathrm{M}^{-1}$. This is in good agreement with the binding constant calculated by steady-state measurement.

Molecular modelling calculations were done to study the inclusion of ADD dyes with β-cyclodextrin in vacuum with the aim of constructing the actual models of the ADD/β-CD complex using the molecule simulation & modelling package from Accelrys Inc. San Diego(A) in a Silicon Graphics 02 work station. Several starting geometries for ADD/β-CD complex were modelled and the guest molecule was then pushed through the cavity of β-CD in 1 Å steps. The energy minimisation of the whole complex was verified until convergence criteria of 0.001 kcal/mol per Å has reached. The experimental results, when combined with the molecular modelling, suggest the pattern of a favourable mode of inclusion. This shows that the phenyl moiety would penetrate into the β-CD cavity, while the acridine moiety would stay outside the cavity rim. The formation of 1:1 host guest complexes are anticipated from the molecular mechanics optimised structure. The interaction energy of the complex was constructed by calculating the differences between the total energies of the complex and the sum of the lowest energies found for the structure optimised for ADD dyes and β-CD. The negative of interaction energy is the binding energy. Therefore, the binding energy represents the gain of potential energy due to ADD/β-CD complex formation. We see that the binding energy is 51 kcal/mol when the head region of ADD-1 is docked through the primary hydroxyl group of β-CD as shown in the Figure 3. The energy value is lower when the anisole group is replaced with the phenyl group (ADD-2) indicating that the ADD-1/β-CD complex formation is energetically more favourable and the proposed model is feasible.

In conclusion, the donor–acceptor coupled nonconjugated bichromophoric system (ADD-1) shows fluorescence enhancement in the presence of β-CD. This fluorescence enhancement is due to the fencing of PET by the inclusion of the nonconjugated donor group in the β-CD nanocavity.

Supporting information

From the molecular modeling studies, we inferred that the mode of inclusion complex between ADD-2 and β-CD, is similar to the ADD-1/β-CD complex (Figure 4). But there is no absorption and emission spectral change is observed on increasing the concentration of β-CD with ADD-2. This confirms that the fluorescence enhancement observed in ADD-1 is due to the fencing of PET between the donor and acceptor by the inclusion of donor group in the β-CD nanocavity.

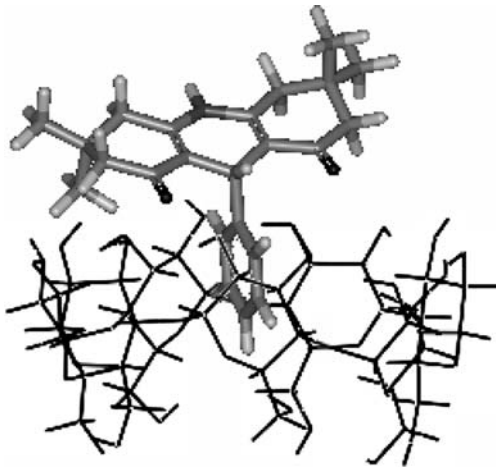


Figure 4. Optimised plausible binding mode for 1:1 host-to-guest complexation of ADD-2 with β-CD.

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