Supporting Information

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pH Assisted control over binding and relocation of acridine guest between a macrocyclic nanocarrier and natural DNA

Mhejabeen Sayed and Haridas Pal

Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India.
E-mail: msayed@barc.gov.in, hpal@barc.gov.in

Additional Figures:

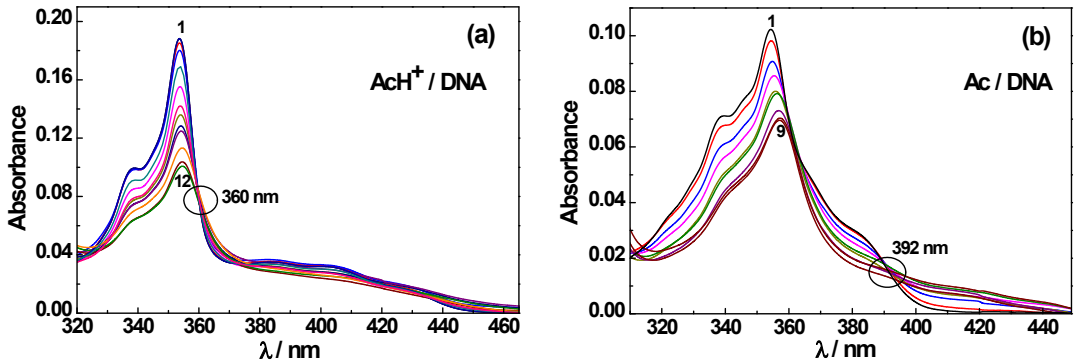

Fig. S1. Changes in the absorption spectra for **(a)** AcH^+/DNA system at pH 4 and (b) Ac/DNA system at pH 8.5. In panel **(a)**, for spectra 1–12, the AcH^+ concentration is 10.2 μM and DNA concentrations are: 0, 36, 78, 117, 172, 244, 296, 364, 429, 550, 694 and 800 μM. In panel **(b)**, for spectra 1–9, the Ac concentration is 10.53 μM and DNA concentrations are: 0, 69, 135, 209, 279, 364, 522, 667 and 800 μM.

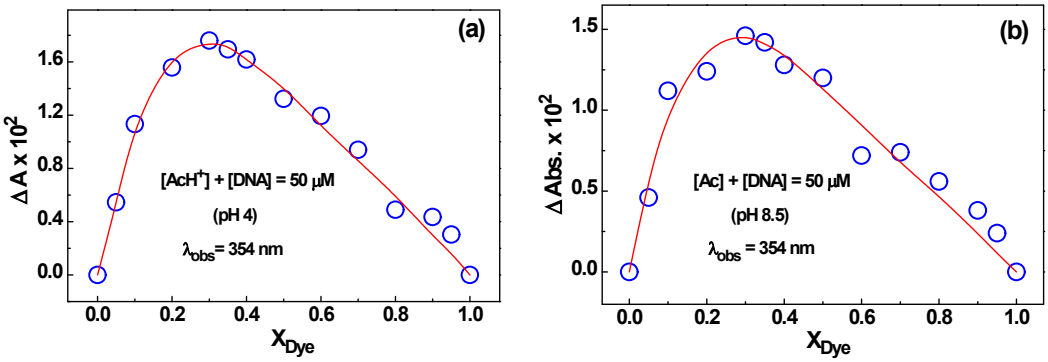

Fig. S2. Job's plots obtained for **(a)** AcH^+/DNA (pH 4) and **(b)** Ac/DNA (pH 8.5) systems following absorption changes, measured at 354 nm. In these measurements, the sum of the dye and the host concentrations in the solutions were kept constant at 50 μM.

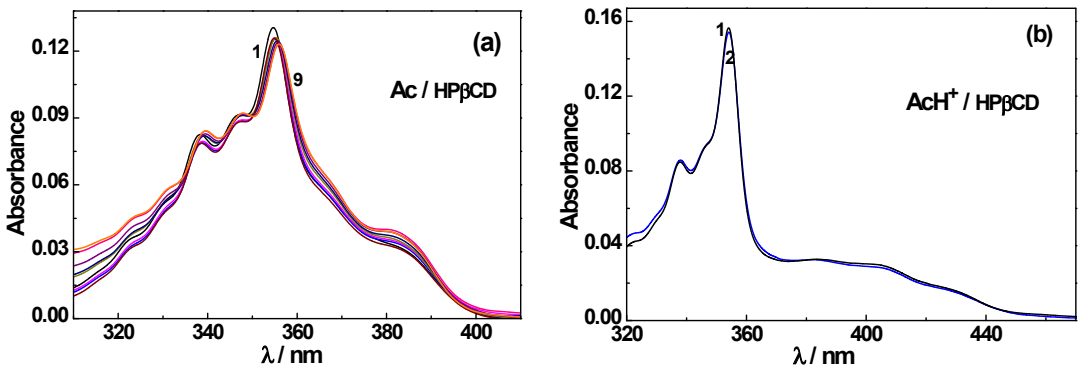

Figure S3. Changes in the absorption spectra for **(a)** Ac/HPβCD system at pH 8.5 and **(b)** AcH^+/HPβCD system at pH 4. In panel **(a)**, for spectra 1–9, the Ac concentration is 13.6 μM and HPβCD concentrations are: 0, 0.20, 0.43, 0.5, 0.81, 1.85, 3.9, 6.6, and 9.1 mM. In panel **(b)**, for spectra 1and 2, the AcH^+ concentration is 11 μM and HPβCD concentrations are: 0 and 10 mM.

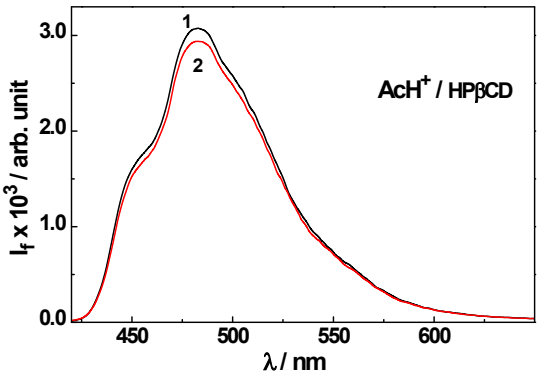

Figure S4. Changes in the steady-state fluorescence spectra of AcH^+/HPβCD system at pH 4. For spectra 1 and 2, the AcH^+ concentration is 11 μM and HPβCD concentrations are: 0 and 20 mM.

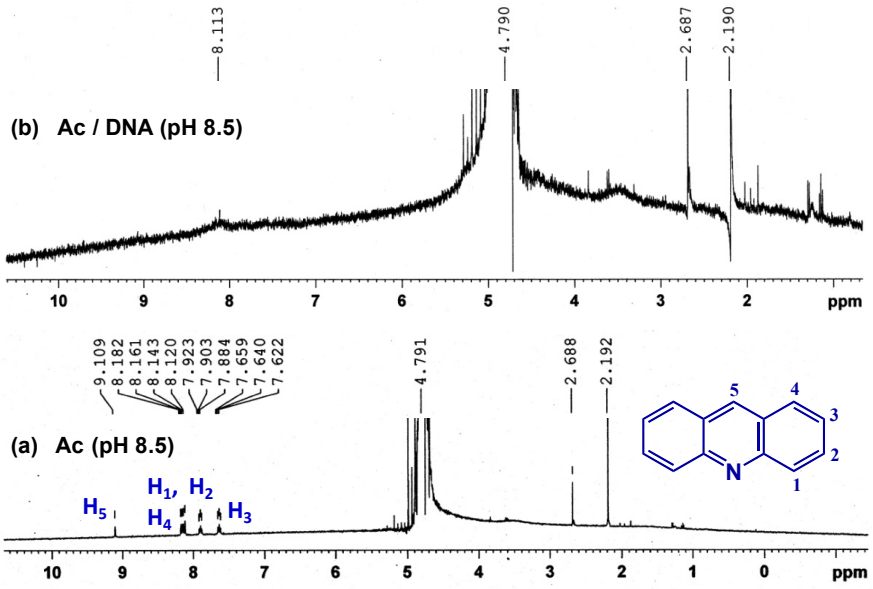

Figure S5: ^1H NMR spectra of **(a)** free Ac and **(b)** Ac-DNA systems obtained at pD 8.5. Concentrations of the components were: [Ac] = 150 μM and [DNA] = 300 μM.

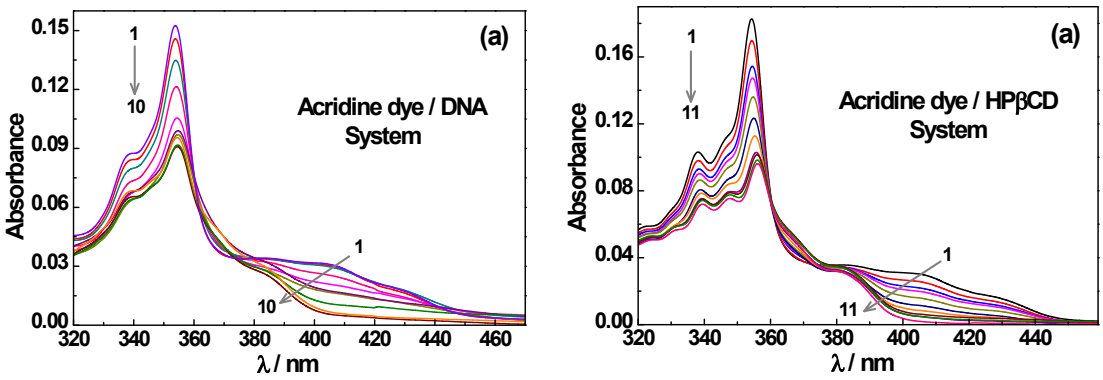

Figure S6. The pH dependent changes in the absorption spectra of the acridine dye in the presence of **(a)** DNA and **(b)** HPβCD hosts. In panel **(a)**, the dye and DNA concentrations are 10 μM and 800 μM, respectively, and for spectra 1-10 the pH are: 3.85, 4.3, 4.6, 5.1, 5.7, 6.2, 6.55, 7.0, 7.6 and 8.3. In panel **(b)**, the dye and HPβCD concentrations are 10 μM and 30 mM, respectively, and for spectra 1-11 the pH are: 3.0, 3.78, 4.16, 4.28, 4.51, 4.72, 5.03, 5.44, 5.84, 6.35 and 6.8.

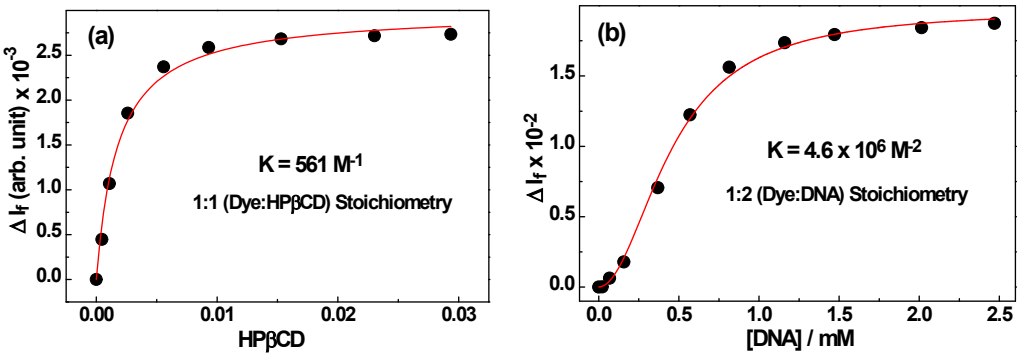

Figure S7. Fluorescence titration curves at pH 5.5 for **(a)** Ac/HPβCD only and **(b)** Ac/DNA system in the presence of 30 mM HPβCD.

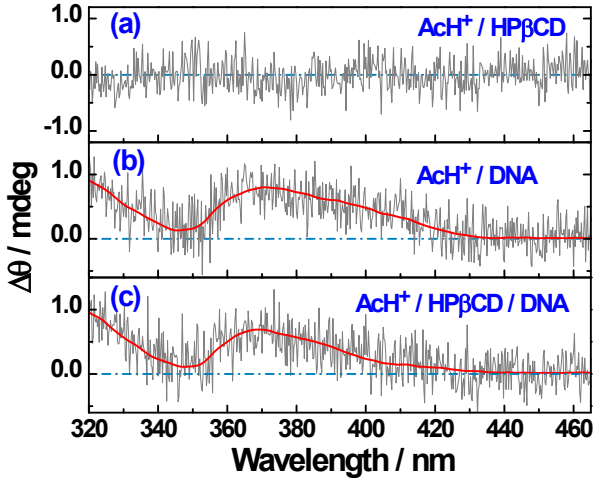

Figure S8: Circular dichroism spectra of (a) AcH^+/HPβCD, (b) AcH^+/DNA and (c) AcH^+/HPβCD/DNA systems (pH 8.5) as indicated in the figure. The concentrations of the analytes were: [Ac] = 50 μM, [HPβCD] = 20 mM and [DNA] = 1.2 mM.

***Note 1*:**

Fluorescence titration equation under the condition of $[B]_0 >> [D]_0$ when complexes are also fluorescent:

Let us consider that the dye D and the host B interact with each other to form complexes with 1:n stoichiometry. Then the formation of the complexes (C) can be presented by the following overall equilibrium.

$$D + nB \underset{}{\overset{K_{eq}}{\rightleftharpoons}} DB_n \text{ (Complex; C)} \quad (1)$$

where, $$K_{eq} = \frac{[C]_{eq}}{[D]_{eq}[B]_{eq}^{n}} \quad (2)$$

Let us follow this equilibrium by gradually increasing the concentration of B to a solution of D containing total D (sum of free and bound) concentration as $[D]_0$. For this system, under the condition that $[B] >> [D]_0$, one can approximately write $[B]_{eq} \approx [B]$. Therefore, the equilibrium concentration of the complex can be expressed as,

$$[C]_{eq} = K_{eq}[D]_{eq}[B]^{n} = K_{eq}\{[D]_0 - [C]_{eq}\}[B]^{n}$$

or, $$\frac{[C]_{eq}}{[D]_0} = K_{eq}[B]^{n} - K_{eq}[B]^{n}\frac{[C]_{eq}}{[D]_0}$$

or, $$\frac{[C]_{eq}}{[D]_0} = \frac{K_{eq}[B]^{n}}{1 + K_{eq}[B]^{n}} \quad (3)$$

For the studied system, if the complex is also fluorescent, the observed fluorescence intensity at any condition should be the sum of contributions of the free dye and the dye-host complex present in the solution. Considering the contributions of each species are proportional to their respective concentrations, we can write,

$$I_{obs} = k_D[D]_{eq} + k_C[C]_{eq} \quad (4)$$

where k_D and k_C are the proportionality constants for the contributions of the respective species. Assuming initial fluorescence intensity in the absence of B as I_D^0 and the final fluorescence intensity on complete complexation of the dye as I_C^∞, one can express these initial and final intensities as,

$$I_D^0 = k_D[D]_0 \quad \text{and} \quad I_C^\infty = k_C[D]_0 \tag{5}$$

Thus, eq. 4 can be rewritten as,

$$I_{obs} = I_D^0 \frac{[D]_{eq}}{[D]_0} + I_C^\infty \frac{[C]_{eq}}{[D]_0} = I_D^0 \frac{\{[D]_0 - [C]_{eq}\}}{[D]_0} + I_C^\infty \frac{[C]_{eq}}{[D]_0}$$

$$\text{or,} \qquad I_{obs} = I_D^0 - \left(I_D^0 - I_C^\infty\right) \frac{[C]_{eq}}{[D]_0}$$

$$\text{or,} \qquad \left(I_D^0 - I_{obs}\right) = \left(I_D^0 - I_C^\infty\right) \frac{[C]_{eq}}{[D]_0} \tag{6}$$

Substituting eq. 3 into eq. 6 we get the required fluorescence titration equation as,

$$\left(I_D^0 - I_{obs}\right) = \left(I_D^0 - I_C^\infty\right) \frac{K_{eq}\,[B]^n}{1 + K_{eq}[B]^n} \tag{7}$$

Eq. 7 in its simplified form can be written as,

$$\Delta I_f = \Delta I_f^\infty \frac{K_{eq}\,[B]^n}{1 + K_{eq}[B]^n} \tag{8}$$

This is exactly the same as eq. 1 given in the main paper.