Electronic Supplementary Information

Features of partial encapsulation of an ESIPT probe 3-hydroxy-2-napthoic acid (3HNA) in the nano cavities of β and γ-cyclodextrin: comparative study with sequestered 3HNA in micelle and reverse micelle

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Cyclodextrine-3HNA binding study:

Binding constant from steady state anisotropy (Equation S1):

The steady state anisotropy of the ESIPT emission has been measured as a function of β-CD and γ-CD concentration. These data could be utilized to determine the binding constants of 3HNA-β-CD and 3HNA-γ-CD interactions by using the equation.

$$(r - r_f)/ R(r_b – r)=K_b[P] \quad (S1)$$

where, $R = Q_b/Q_f$; Q_f and Q_b are the quantum yield of the ESIPT emission of free 3HNA and 3HNA bound to β-CD or γ-CD respectively; r_f and r_b are the anisotropies observed for 3HNA and after complex formation of 3HNA bound to β-CD or γ-CD, respectively; [P] is the concentrations of cyclodextrins.

The binding constants and free energy changes (Table 5) associated with the complex formation determined from steady state anisotropy data match well with that determined from steady state fluorescence intensity data. Linearity in the plot of $(r – r_f) / R (r_b - r)$ vs concentration of β-CD/ γ-CD verifies the 1:1 complex formation. The binding constant is determined from the slope of the plot (Figure S2B, Table 5).

Binding constant from the time resolved emission studies (Equations S2 and S3):

The singlet state lifetimes of 3HNA as a function of concentration of β-CD and γ-CD were measured using λ_{exc}=370 nm (Figure 4, Table 2) at 298 K. The decay of free 3HNA fits nicely with one component having lifetime of 1.66 ns. The decay of 3HNA-CD complex exhibits two components of ~3.9 ns and 1.66 ns (Table 2). The percent contribution of the shorter component decreases gradually with the simultaneous increase of that of the longer component (Table 2). Thus the longer component is assigned as the lifetime of the complex. This trend of variation can be utilized to evaluate the binding constant of 3-HNA-CD complex. Assuming 1:1 CD-guest complex one can write

$$3HNA+CD = 3HNA\text{-}CD$$

With the corresponding equilibrium constant as

$$K= [3HNA\text{-}CD] /[3HNA][CD] \quad (S2)$$

Let C_0 is the initial concentration of 3HNA and C is the equilibrium concentration of the 3-HNA-CD complex.

Then from equation (S2) one can write,

$$K[CD]=C/C_0-C$$

After rearrangement the final expression takes the form as

$$C_0/C= 1+ 1/ K[CD] \quad (S3)$$

Since the concentrations of the cyclodextrins are much larger than that of the 3HNA, it may be assumed that the concentration of added cyclodextrins does not change much upon complex formation with 3HNA. Here C_0 is 20μM and the values of C obtained using lifetime measurements are given in Table 2. The plot of C_0/C vs. 1/[CD] gives a straight line (Figure S2C). From the slope, the binding constants have been evaluated (Table 5).

Table S1: Cavity diameter and molar volume of β- and γ-Cyclodextrin obtained from theoretical calculation:

Cyclodextrin	**Radius (in Å) of the**		**Molar volume ($cm^3\ mol^{-1}$)**
	Inner Rim	**Outer Rim**	
β	7.3	13.5	852.6
γ	9.8	16.2	783.4

Table S2A: Distance table for interactions of the inclusion complex of β-CD-3HNA.

Interactions	Distance (Å)
O_{131}-H_{141}	1.76
O_{59}-H_{132}	1.88
O_{9}-H_{118}	2.64
O_{63}- H_{71}	1.90
O_{131}-H_{116}	4.11
O_{140}-H_{108}	4.40

Table S2B: Distance table for interactions of the inclusion complex of γ-CD-3HNA.

Interactions	Distance (Å)
O_{40}-H_{183}	1.82
O_{184}-H_{121}	2.13
O_{184}-H_{119}	2.48
O_{185}-H_{91}	2.36
O_{185}-H_{93}	2.25

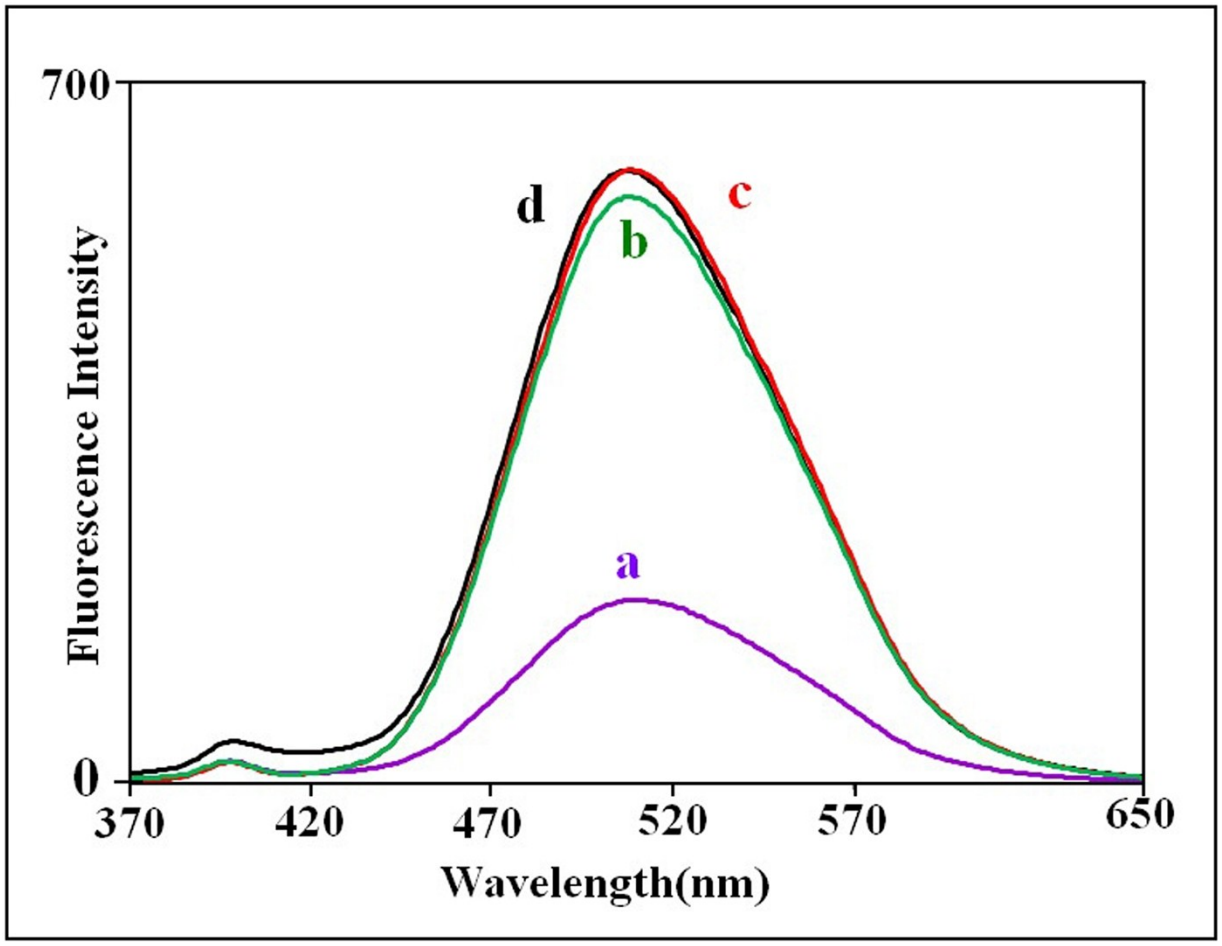

Figure-S1 Fluorescence spectra of 3HNA (20 μM) at 298 K in aqueous medium; (a) in pure water, (b) in 4mM TTAB, (c) in 1mM CTAB, (d) in 20mM Triton-X; λ_{exc} = 350 nm; Excitation band pass 10 nm, and emission band pass = 5 nm.

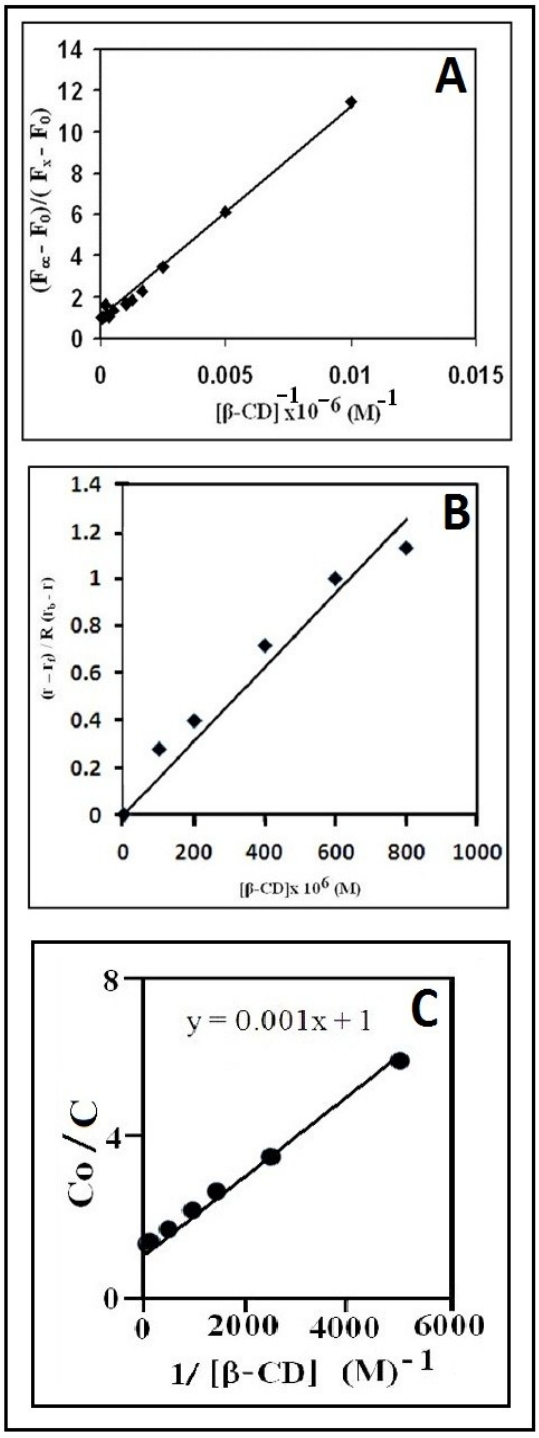

Figure S2: (A) The plot of $(F_\infty - F_0)/(F_x - F_0)$ against $[\beta\text{-CD}]^{-1}$;(B) Plot of $(r - r_f) / R\ (r_b - r)$ against $[\beta\text{-CD}]^{-1}$; (C) Plot of C_0/C vs. $1/[\beta\text{-CD}]$.

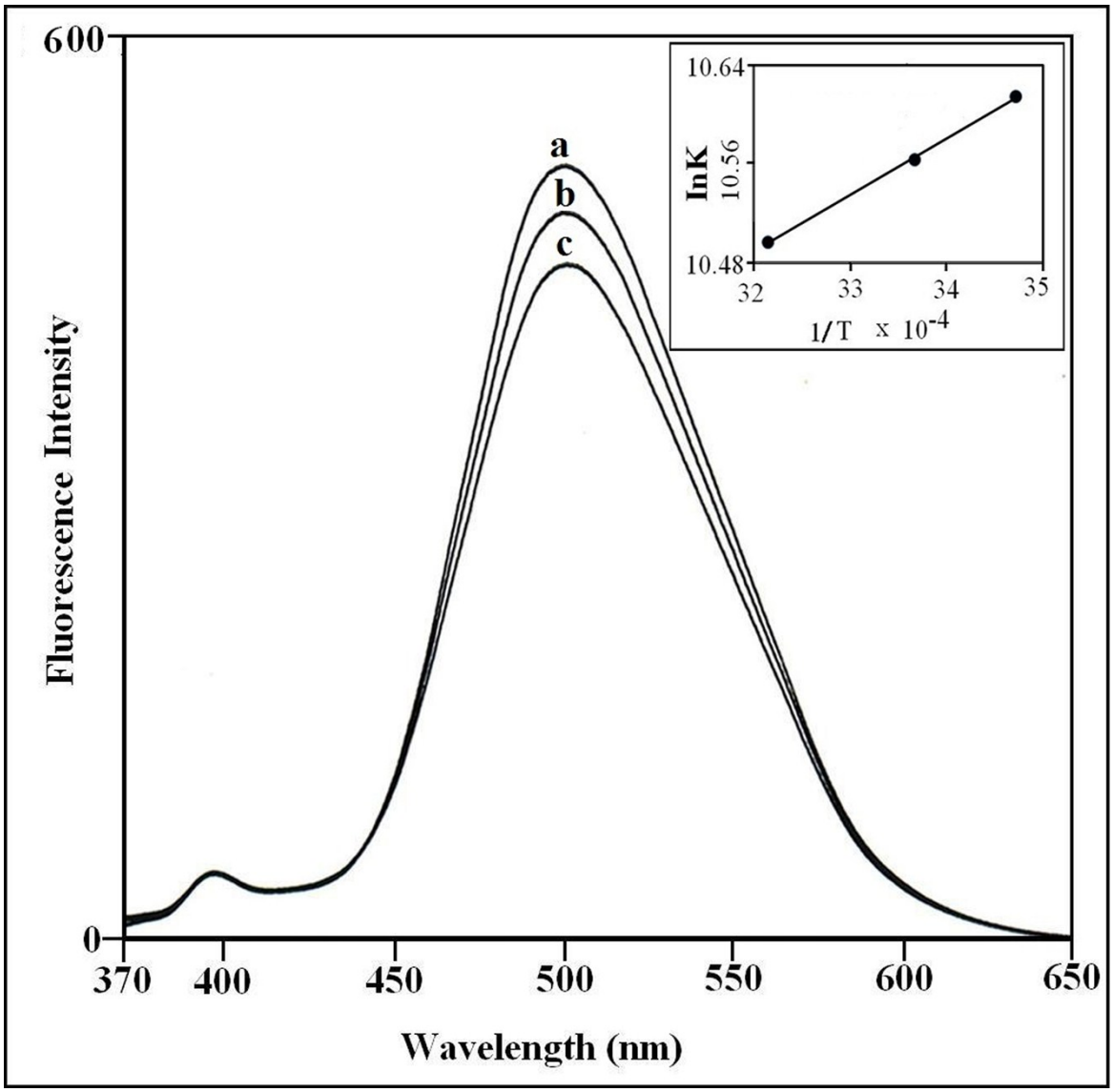

Figure-S3 Fluorescence spectra of 3HNA (20 μM) in aqueous buffer solution of β-CD (6mM) (pH 7) with varying temperature: (a) 15 ºC, (b) 24 ºC, (c) 34 ºC; λ_{exc} = 350 nm; Excitation band pass 10 nm, and emission band pass = 5 nm. *Inset:* The plot of ln K vs. 1/T.

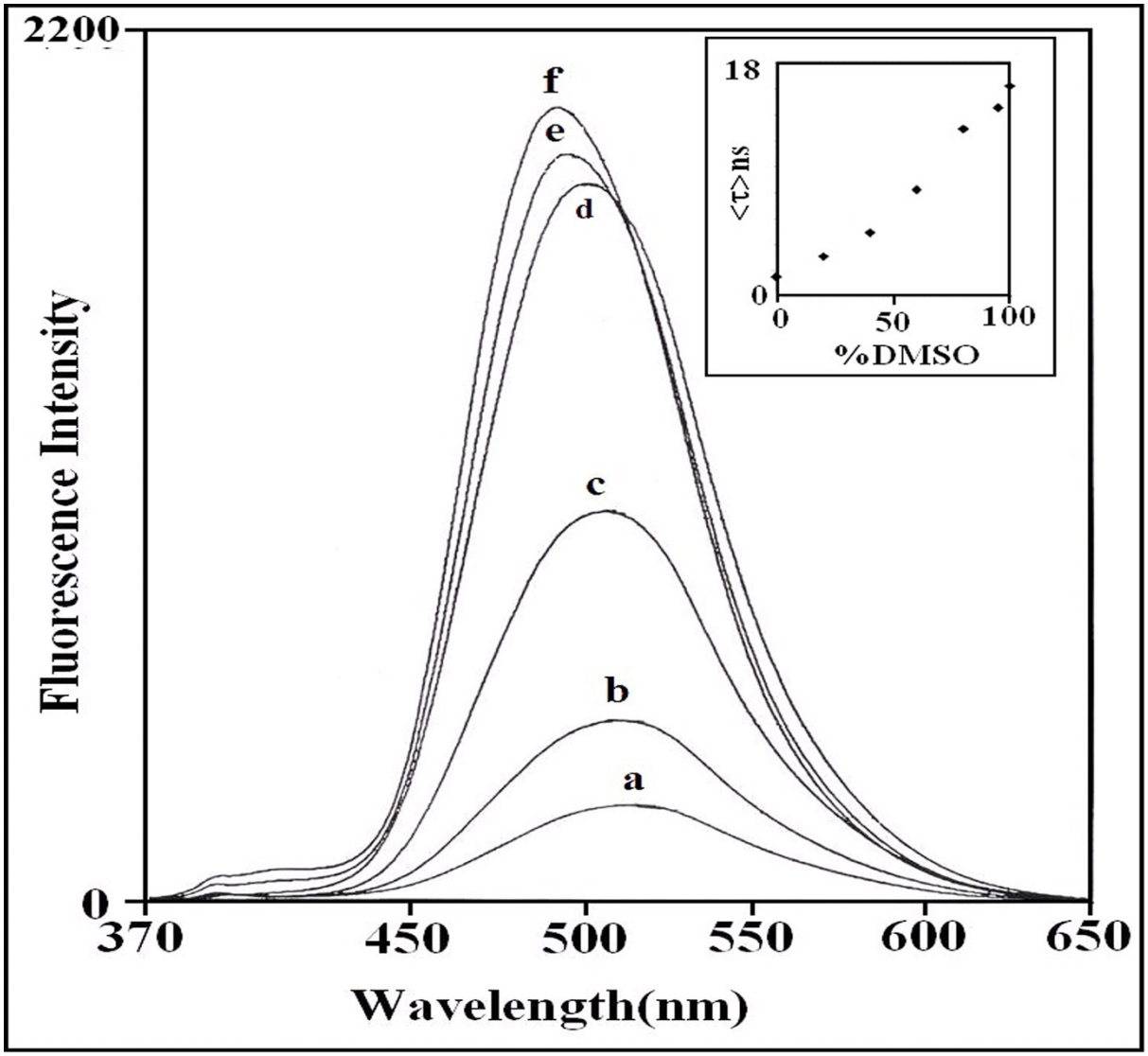

Figure S4: Fluorescence spectra of 3HNA (20 μM) in DMSO and water mixtures at 298 K. Curves (a–f) represents 20%, 40%, 60%, 80%, 95% and 100% DMSO, respectively. λ_{exc} = 350 nm; excitation and emission band pass = 10 nm each. **Inset:** Plot of τ (ns) of 3HNA at 298 K in DMSO–water mixed solvent against the % volume of DMSO in the mixed solvent.

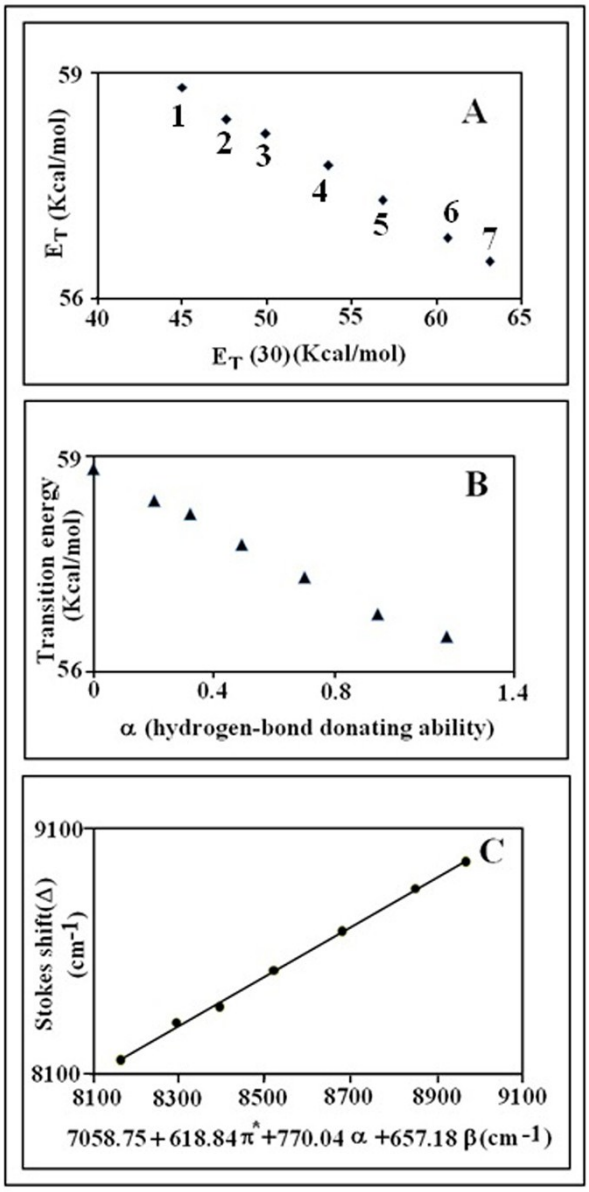

Figure S5: (A) Plot of transition energy (E_T in kcal/mol) of ESIPT emission of 3HNA (20 μM) in different mixed solvents of water and DMSO against the solvent polarity index E_T(30)-scale (kcal/ mol): (1) DMSO, (2) 90% DMSO, (3) 80% DMSO, (4) 60% DMSO, (5) 40% DMSO, (6) 20% DMSO, (7) Water; λ_{exc} = 350 nm; excitation band pass = 10nm and Emission band pass = 5 nm. (B) Plot of transition energy (kcal/mol) of ESIPT emission of 3HNA in different mixed solvents of water and DMSO against the hydrogen bond donating acidity parameter alfa (α). (C) Plot of Stokes shift (Δ) (cm-1) vs Eq. (6) for different mixed solvents of water and DMSO.

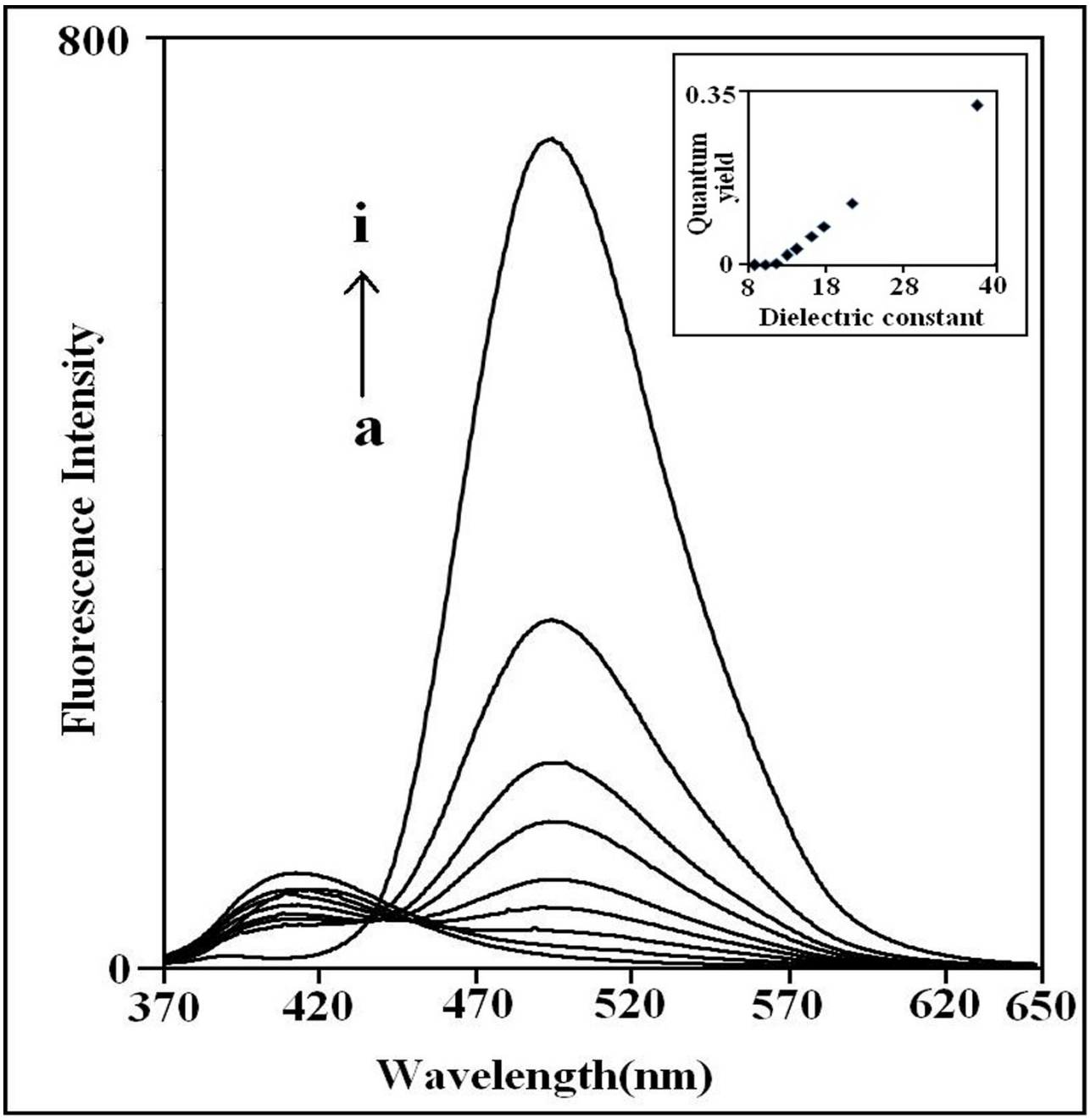

Figure S6: Fluorescence spectra of 3HNA (20 μM) in DCM-ACN mixed solvents at 298 K. Curves (a–i) represents 0%, 4%, 8%, 12%, 16%, 22%, 27%, 39% and 100% ACN respectively. λ_{exc} = 350 nm; excitation band pass = 10 nm and emission band pass=5 nm. **Inset:** Plot of dielectric constant of ACN/DCM mixtures against λ_{max} of 3HNA (20 μM) emission on those mixtures.