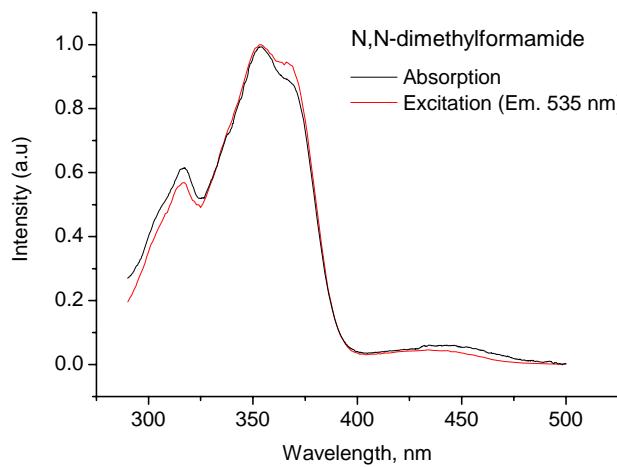
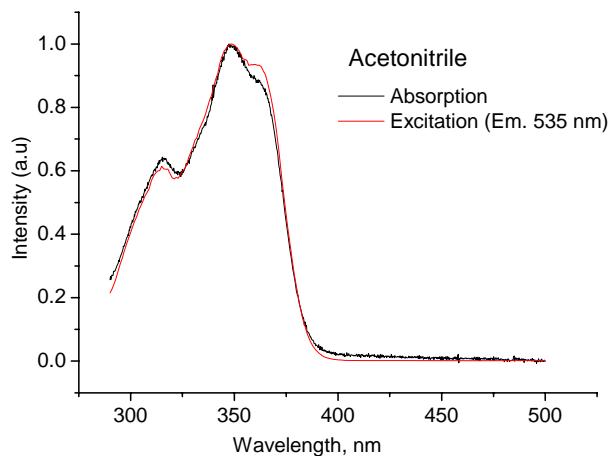


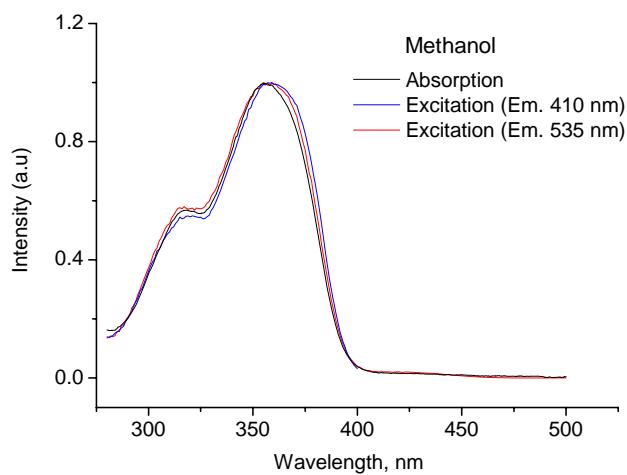
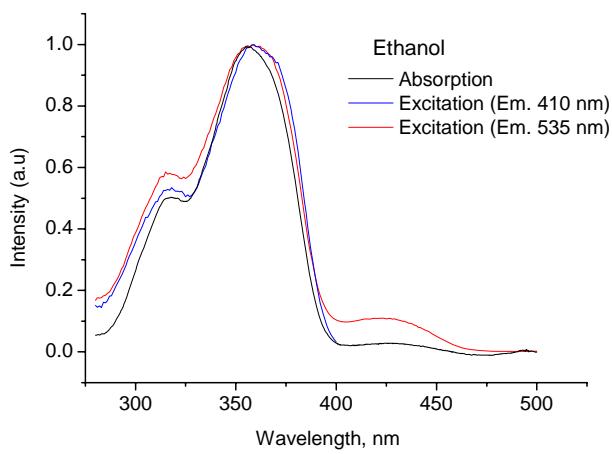
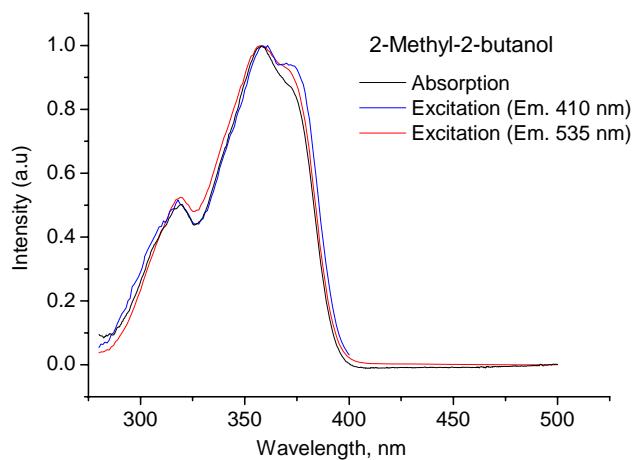
Electronic supplementary information (ESI)

An unusually slow proton transfer dynamics of a 3-hydroxychromone dye in protic solvents

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1. Spectroscopic data.





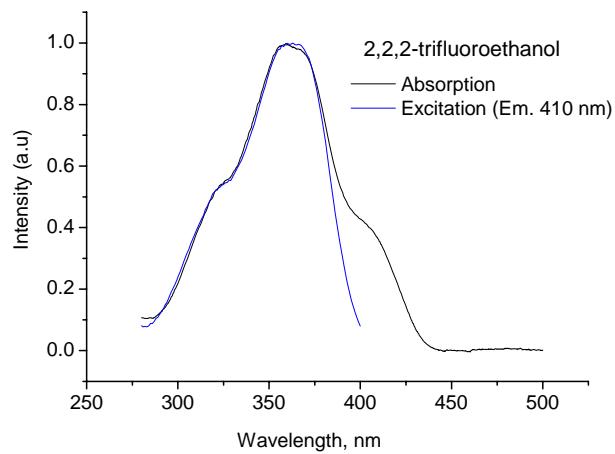
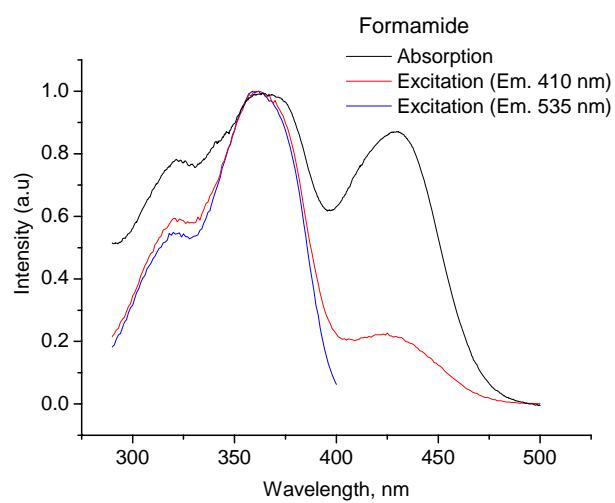
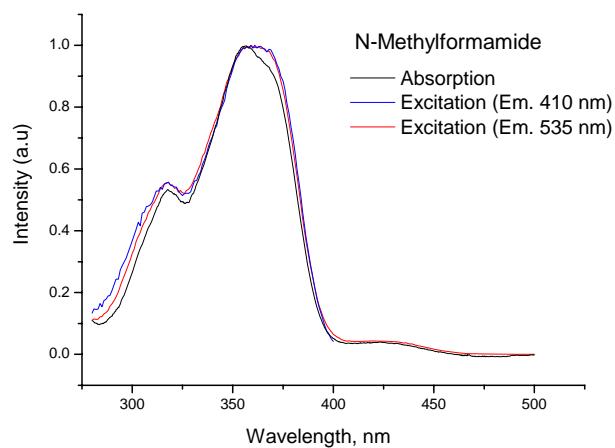


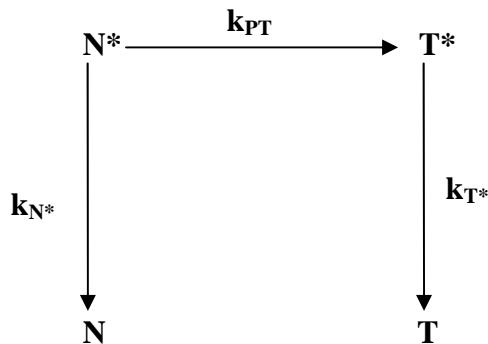
Fig. S1. Absorption and fluorescence excitation spectra of dye FHC in different organic solvents.

For comparison, all the spectra were normalized at the maximum.

2. Models of ESIPT Dynamics

A. Model of irreversible ESIPT.

The model of an irreversible ESIPT reaction²⁶ is illustrated in Scheme.2, where the rate constant for the reverse proton transfer (k_{PT}) is neglected for an excited-state reaction between the N^* and T^* forms and it is also assumed that once the excited tautomer (T^*) species is formed, only radiative ($k_R^{T^*}$) or nonradiative ($k_{NR}^{T^*}$) processes will depopulate this excited state.



Scheme S1. k_{PT} : rate constant for the ESIPT reaction ; k_{N^*} and k_{T^*} are the decay rate constants of the N^* the T^* excited forms respectively

The time-dependent populations of N^* and T^* are given by

$$d[N^*]/dt = - (k_{N^*} + k_{PT}) [N^*] = - (k_R^{N^*} + k_{NR}^{N^*} + k_{PT}) [N^*] \quad (1)$$

$$d[T^*]/dt = - k_{T^*} [T^*] + k_{PT} [N^*] = - (k_R^{T^*} + k_{NR}^{T^*}) [T^*] + k_{PT} [N^*] \quad (2)$$

where $k_R^{N^*}$, $k_{NR}^{N^*}$, $k_R^{T^*}$, $k_{NR}^{T^*}$ are the radiative and non-radiative decay rate constants for the N^* and T^* excited forms, respectively, and k_{PT} is the rate constant for the forward intramolecular proton transfer reaction.

Solution of Eqs (1) and (2) using appropriate boundary conditions yields the observed monophasic N^* and biphasic T^* emission decay kinetics described by Eqs (3) and (4) respectively.

$$[N^*(t)] = [N^*]_0 \exp(-t/\tau_1) \quad (3)$$

$$[T^*(t)] = [N^*]_0 (k_{PT}/k_{T^*} - k) [\alpha \exp(-t/\tau_1) + \beta \exp(-t/\tau_2)] \quad (4)$$

where $\alpha = -\beta = (k_{PT}/k_{T^*} - k)$, $k = k_{N^*} + k_{PT}$, and τ_1 and τ_2 are the fast and slower decay times, respectively. The decay times are expressed in the following manner.

$$\tau_1 = 1/k = 1/(k_R^{N^*} + k_{NR}^{N^*} + k_{PT}) \quad (5) \quad ; \quad \tau_2 = 1/(k_R^{T^*} + k_{NR}^{T^*}) \quad (6)$$

The expressions of quantum yields for the N^* and T^* emission bands are:

$$\varphi_{N^*} = k_R^{N^*} \tau_1 \quad (7)$$

$$\varphi_{T^*} = k_R^{T^*} \tau_2 (k_{PT} \tau_1) \quad (8)$$

φ_{N^*} and τ_1 are determined from the steady-state fluorescence emission spectra and time-resolved fluorescence decay measurements, respectively which enable us to obtain the values of $k_R^{N^*}$ from Eqn 1 for 2FHC in alcohols and amides (Table-3). The sum of the nonradiative and ESIPT rate constant are obtained from the following equation

$$k_{NR}^{N^*} + k_{PT} = (1 - \varphi_{N^*})/\tau_1 \quad (9)$$

For the estimation of k_{PT} , the rate constant for the ESIPT reaction (Scheme.2), we used a method described in details elsewhere.²⁶ The values of k_{PT} can be obtained directly from the sum of $k_{NR}^{N^*}$ and k_{PT} if $k_{PT} \gg k_{NR}^{N^*}$. The ratio $k_{PT}/k_{NR}^{N^*}$ for a particular solvent 1 is expressed as:

$$k_{PT}^1/k_{NR}^{N^*1} \approx a / b-a \quad (10)$$

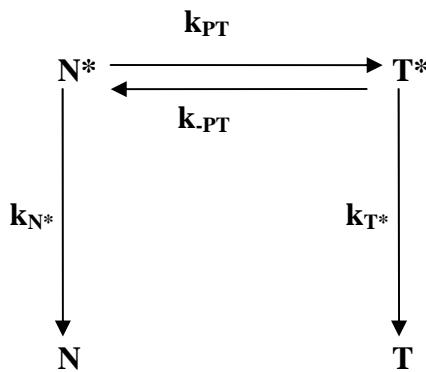
$$\text{where } a = k_{PT}^1 / k_{PT}^2, \quad b = (k_{NR}^{N^*1} + k_{PT}^1) / (k_{NR}^{N^*2} + k_{PT}^2)$$

k_{PT}^1, k_{PT}^2 are the ESIPT rate constants in the first and second solvent, respectively; $k_{NR}^{N^*1}$ and $k_{NR}^{N^*2}$ are the nonradiative decay rate constants for the N^* excited form in the first and second solvent, respectively.

The ratio $k_{PT}/ k_{NR}^{N^*}$ for 2FHC in alcohols and amides was estimated to be > 2.5 using Eq 10. In consequence, $k_{PT} > 0.7(k_{NR}^{N^*} + k_{PT})$, so that the value of k_{PT} varies between $0.7(k_{NR}^{N^*} + k_{PT})$ and $(k_{NR}^{N^*} + k_{PT})$, which enables us to estimate the magnitude and error in the estimation of k_{PT} (Table 3).

B. Model of reversible ESIPT

The following model (Scheme-3) of a reversible ESIPT reaction²⁷ between N^* and T^* species is used for evaluating the kinetic parameters associated with the reversible proton transfer process of 2FHC in N-methylformamide.



Scheme S2. k_{PT} , $k_{.PT}$ are the rate constants for the forward and reverse ESIPT reactions, respectively ; k_{N^*} , k_{T^*} are the decay rate constants of the N^* and T^* forms respectively

For such a reversible ESIPT reaction (Scheme-2), the time-dependent populations of the N^* and T^* forms are described by:

$$d[N^*]/dt = - (k_R^{N^*} + k_{NR}^{N^*} + k_{PT}) [N^*] + k_{.PT} [T^*] \quad (11)$$

$$d[T^*]/dt = - (k_R^{T^*} + k_{NR}^{T^*}) [T^*] + k_{PT} [N^*] \quad (12)$$

where $k_{N^*} = k_R^{N^*} + k_{NR}^{N^*}$ and $k_{T^*} = k_R^{T^*} + k_{NR}^{T^*}$

Solution of Eqn (11) and (12) using appropriate boundary conditions yield the observed biphasic N^* and T^* emission decay kinetics described by Eqs (13) and (14), respectively.

$$[N^*(t)] = [N^*]_0 [\alpha_1^{N^*} \exp(-t/\tau_1) + \alpha_2^{N^*} \exp(-t/\tau_2)] \quad (13)$$

$$[T^*(t)] = [N^*]_0 [\alpha_1^{T^*} \exp(-t/\tau_1) + \alpha_2^{T^*} \exp(-t/\tau_2)] \quad (14)$$

The decay times, τ_1 and τ_2 are described by

$$\alpha_1^{N^*} = (\gamma_{N^*} - \gamma_2) / (\gamma_1 - \gamma_2) \quad (15)$$

$$\alpha_2^{N^*} = (\gamma_1 - \gamma_{N^*}) / (\gamma_1 - \gamma_2) \quad (16)$$

$$\text{where } \gamma_1, \gamma_2 = (\tau_1)^{-1}, (\tau_2)^{-1} = \frac{1}{2} \{(\gamma_{N^*} + \gamma_{T^*}) \pm [(\gamma_{N^*} - \gamma_{T^*})^2 + 4 k_{PT} k_{-PT}]^{1/2}\} \quad (17)$$

$$\text{with } \gamma_{N^*} = k_R^{N^*} + k_{NR}^{N^*} + k_{PT} \text{ and } \gamma_{T^*} = k_R^{T^*} + k_{NR}^{T^*} + k_{-PT} \quad (18)$$

Further, the γ_{N^*} and γ_{T^*} were estimated from Eqs 17-19 by

$$\gamma_{N^*} = \gamma_2 + \alpha_1^{N^*} (\gamma_1 - \gamma_2) \quad (19)$$

$$\gamma_{T^*} = \gamma_1 - \alpha_1^{N^*} (\gamma_1 - \gamma_2) \quad (20)$$

Moreover, assuming that the rates of forward and reverse ESIPT reactions are much faster than the rate of radiative and nonradiative deactivation processes (i.e., k_{PT} , and $k_{-PT} \gg k_{N^*} + k_{T^*}$). As a result Eq 18 can be simplified as :

$$\gamma_{N^*} \approx k_{PT} \text{ and } \gamma_{T^*} \approx k_{-PT} \quad (21)$$