Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementry Information

Diffusive and Non-diffusive Photo-induced Proton Coupled Electron Transfer from hydrogen bonded phenols to meso-tetrakis-5,10,15,20-Pentafluorophenyl Porphyrin

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Derivation of modified Stern-Volmer equation

Case.1: Quenching is competitive process to the fluorescence, $K_Q \neq 0$

$$\frac{I_0}{I} = 1 + \frac{(K_{QB} - K_Q) * K_{HB} * [Q]_0 * [B]_0}{1 + K_{HB} * [B]_0} \quad (5)$$

where I_0& I are fluorescence intensities in the absence and presence of quencher respectively. K_{QB}& K_Q are Stern-Volmer constants of hydrogen bonded phenol and free phenol respectively. Q and B represents corresponding phenol and pyridine base respectively and K_{HB} is the hydrogen bond equilibrium constant between phenol and base.

Using Stern-Volmer equation, the fluorescence quenching of $H_2F_{20}TPP$ by both free and hydrogen bonded phenol is given by eq.1

$$\frac{I_0}{I} = 1 + K_Q[Q] + K_{QB}[QB] \rightarrow \quad (1)$$

where QB is the hydrogen bonded complex and other terms have their usual meaning. Hydrogen bond equilibrium(K_{HB})for the complex formation can be calculated as follows,

$$Q + B \rightleftarrows QB$$

$$\Rightarrow K_{HB} = \frac{[QB]}{[Q] * [B]} \rightarrow \quad (2)$$

and again $[Q]_0 = [Q] + [QB]$, $[B]_0 = [B] + [QB]$ → (3)
where $[Q]_0$,$[B]_0$are the total concentration of phenol and base respectively. substituting the values from (3) in to (2),

$$(2) \Rightarrow K_{HB} = \frac{[QB]}{([Q]_0 - [QB]) * ([B]_0 - [QB])} \Rightarrow K_{HB}\{([Q]_0 - [QB]) * ([B]_0 - [QB])\} = [QB]$$

$$\Rightarrow K_{HB}([Q]_0 * [B]_0 - [Q]_0 * [QB] - [B]_0 * [QB] + [QB]^2) = [QB] \rightarrow \quad (4)$$

since$[QB]$ is very small, so $[QB]^2$ can be neglected

$$(4) \Rightarrow K_{HB}([Q]_0 * [B]_0 - [Q]_0 * [QB] - [B]_0 * [QB]) = [QB]$$

$$\Rightarrow K_{HB} * [Q]_0 * [B]_0 - K_{HB} * [QB]([Q]_0 + [B]_0) = [QB]$$

$$\Rightarrow K_{HB} * [Q]_0 * [B]_0 = K_{HB} * [QB]([Q]_0 + [B]_0) + [QB]$$

$$\Rightarrow K_{HB} * [Q]_0 * [B]_0 = = \{K_{HB} * ([Q]_0 + [B]_0) + 1\} * [QB]$$

$$\Rightarrow [QB] = \frac{K_{HB} * [Q]_0 * [B]_0}{1 + K_{HB} * ([Q]_0 + [B]_0)} \rightarrow \quad (5)$$

on the condition that total concentration of added base much exceeds that of phenol, $[Q]_0 << [B]_0$, $[Q]_0$ in the denominator can be neglected in eq.5.

$$(5) \Rightarrow [QB] = \frac{K_{HB} * [Q]_0 * [B]_0}{1 + K_{HB} * [B]_0} \rightarrow (6)$$

now eq.1 $\Rightarrow \frac{I_0}{I} = 1 + K_Q[Q] + K_{QB}[QB]$

$\Rightarrow \frac{I_0}{I} = 1 + K_Q([Q]_0 - [QB] + K_{QB}[QB]$, using $[Q] = [Q]_0 - [QB]$

$$\Rightarrow \frac{I_0}{I} = 1 + K_Q * [Q]_0 + (K_{QB} - K_Q) * [QB] \rightarrow (7)$$

inserting eq.6 in eq.7

$$\Rightarrow \frac{I_0}{I} = 1 + K_Q * [Q]_0 + (K_{QB} - K_Q) * \frac{K_{HB} * [Q]_0 * [B]_0}{1 + K_{HB} * [B]_0}$$

Case.2: Here quenching is not competitive process tothe fluorescence,

$K_Q \rightarrow 0$ *or too small*

$$\frac{I_0}{I} = 1 + K_{QB} * \frac{K_{HB} * [Q]_0 * [B]_0}{1 + K_{HB} * [B]_0} \quad (6)$$

Using Stern-Volmer equation, the fluorescence quenching of $H_2F_{20}TPP$ by both free and hydrogen bonded phenol is given by eq.1

$$\frac{I_0}{I} = 1 + K_Q[Q] + K_{QB}[QB] \rightarrow (1)$$

but in this case$H_2F_{20}TPP$ fluorescence is not quenched by added phenol, So $K_Q = 0$ *or twoo small*. Hence eq.1 transforms as

$$\Rightarrow \frac{I_0}{I} = 1 + K_{QB}[QB] \rightarrow (2)$$

$$using\ relation, [QB] = \frac{K_{HB} * [Q]_0 * [B]_0}{1 + K_{HB} * [B]_0}$$

$$(2) \Rightarrow \frac{I_0}{I} = 1 + K_{QB} * \frac{K_{HB} * [Q]_0 * [B]_0}{1 + K_{HB} * [B]_0}$$

$$so\ the\ final\ eq\ is \Rightarrow \frac{I_0}{I} = 1 + K_{QB} * \frac{K_{HB} * [Q]_0 * [B]_0}{1 + K_{HB} * [B]_0}$$

Some figures relating to steady state and time resolved titration:

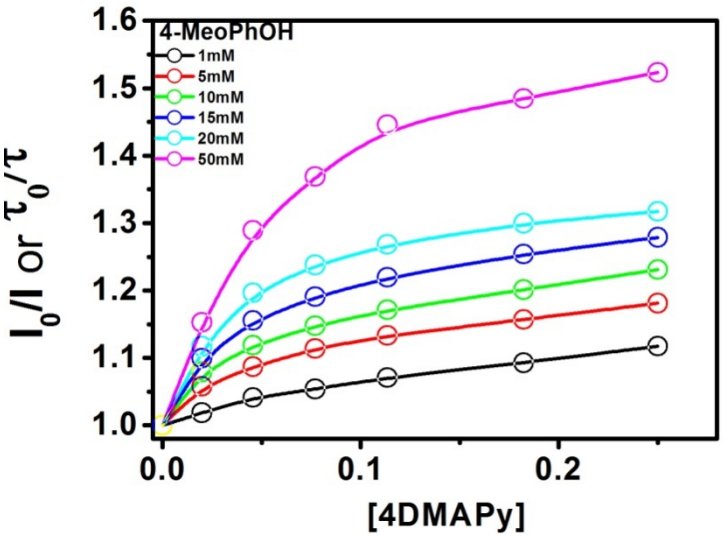

Fig.S1 S-V plot as a function of 4DMAPy concentration when 4-MeoPhOH concentration is parameter

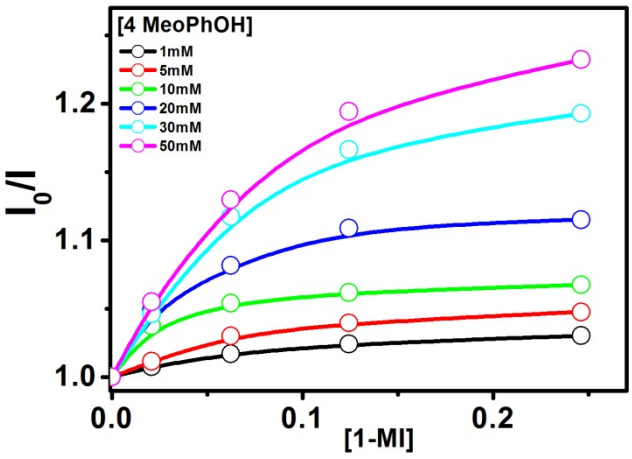

Fig.S2 S-V plot as a function of 1-Methyl Imidazole concentration when 4-MeoPhOH concentration is parameter

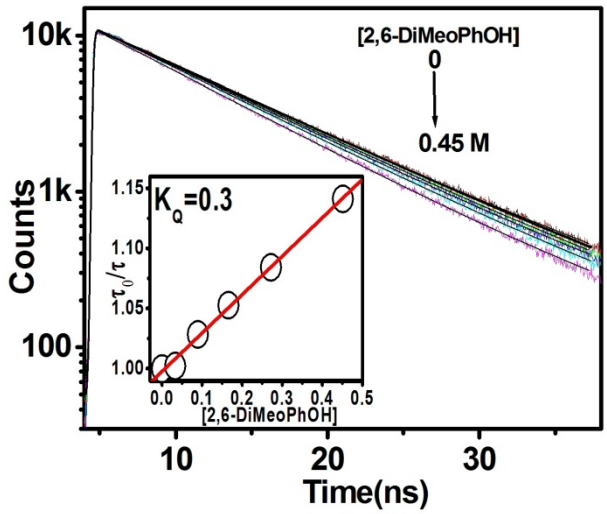

Fig. S3 Fluorescence decay profile of $H_2F_{20}TPP$ as a function of 2,6DiMeoPhOH. Inset shows the S-V plot

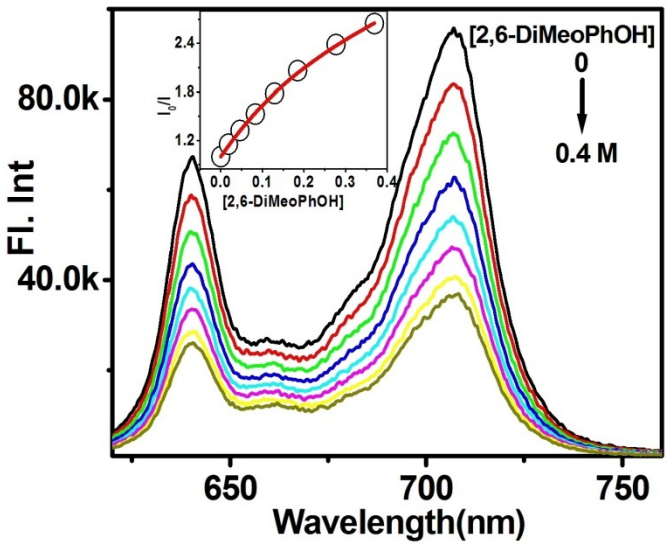

Fig.S4 Change of fluorescence intensity of $H_2F_{20}TPP$ (20 μM) following successive addition of 2,6-DiMeoPhOH in DCM solvent in presence of 0.1M 4DMAPy, λ_{ex}=590 nm. Inset shows the S-V plot

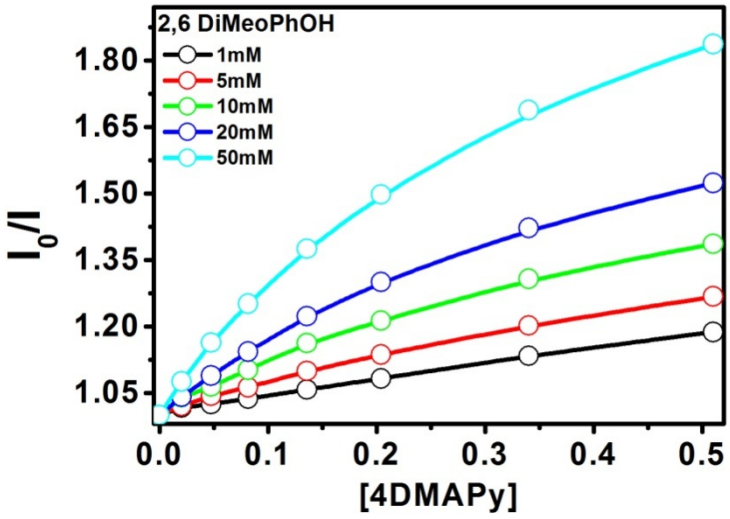

Fig. S5. S-V plot as a function of 4-DMAPy concentration when 2,6- DiMeoPhOH concentration is parameter.

Fluorescence Up-Conversion Data

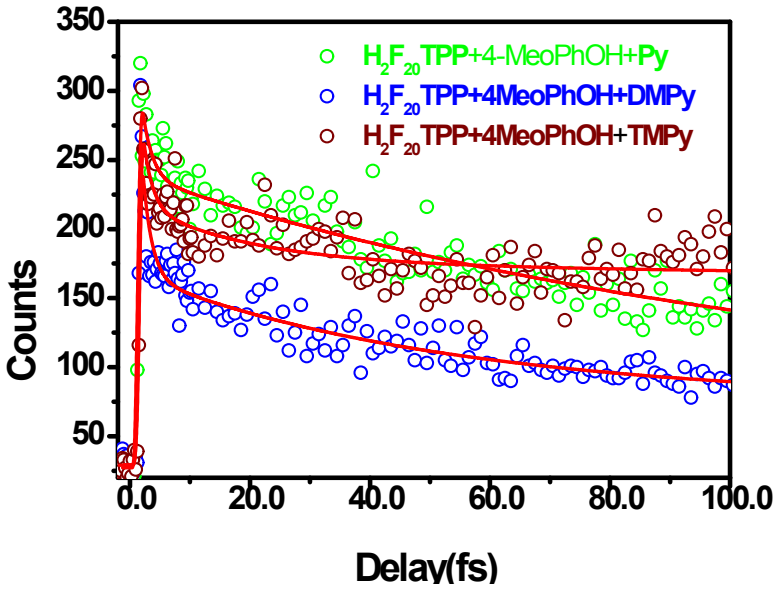

Fig. S7 Fluorescence Up-Conversion decay profile of $H_2F_{20}TPP$ in presence of 0.5 M 4-MeoPhOH and 0.5M of various pyridines (Py, DMPy, TMPy) on excitation at 410 nm. Smooth solid lines are fits of experimental data.

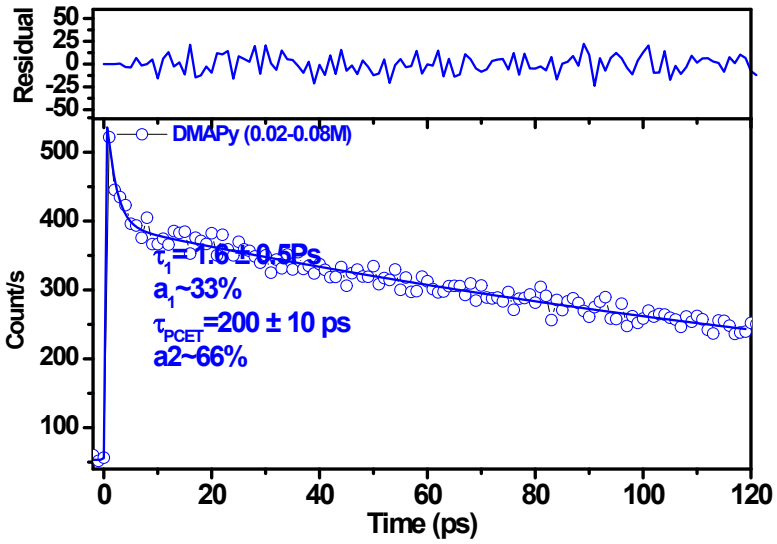

Fig. S8:Fluorescence Up-Conversion decay profile of $H_2F_{20}TPP$ inpresence of 0.5 M 2,6-DiMeoPhOH and (0.02-.08M) 4DMAPy on excitation at 410 nm. Smooth solid lines are fits of experimental data.