Supporting Information

Reductive Quenching of Pyridine linked Porphyrins by Phenol: A Case of Proton Coupled Electron Transfer

S. Prashanti and Prakriti Rnajan Bangal

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Uppal road, Tarnaka, Hyderabad 500607 , India

All three ms-pyridylporphyrins (TpyPs) were purchased from Porphyrin System, Germany and used as received. 4-methoxyphenol and 4-ethoxyphenol were purchased from Aldrich Chemical, USA and spectroscopic grade dichloromethane is purchased from Merck, Germany.

Absorption Studies: All Uv/vis spectra were recorded using Cintra 10e UV/VIS spectrophotometer (GBC). Spectroscopic titrations were done taking micromolar solutions of respective porphyrins in DCM and phenol concentrations were kept upto 0.5 molar. Equilibrium constant K_{HB}, for the formation of hydrogen-bond complexes were calculated from the change in absorbance at given wavelength on added reagent (respective phenol) using the relation given by Mataga andTsuno.

$$(1-d_0/d)/[Q]=-K_{HB} + (\varepsilon_C/\varepsilon)K_{HB}\ (d_0/d);$$

where ε_C and ε respectively, denote the extinction coefficient of the complex and free molecule and d_0 and d are absorbance in absence and present of bonding agent{Q is different phenol} whose total concentration is much greater than that of probes. The intercept of the plot $(1-d_0/d)/[Ql]$ Vs $(\varepsilon_C/\varepsilon)K_{HB}\ (d_0/d)$ is $-K_{HB}$. Two steps plot corresponds to the two types of equilibrium, First one for low concentration(below 0.1 M) of bonding agent which is due to H-boning of phenol with pyridyl end ($^1K_{HB}$) and second one for higher concentration of bonding agent which corresponds to H-boning of phenol to pyrrole end ($^2K_{HB}$).

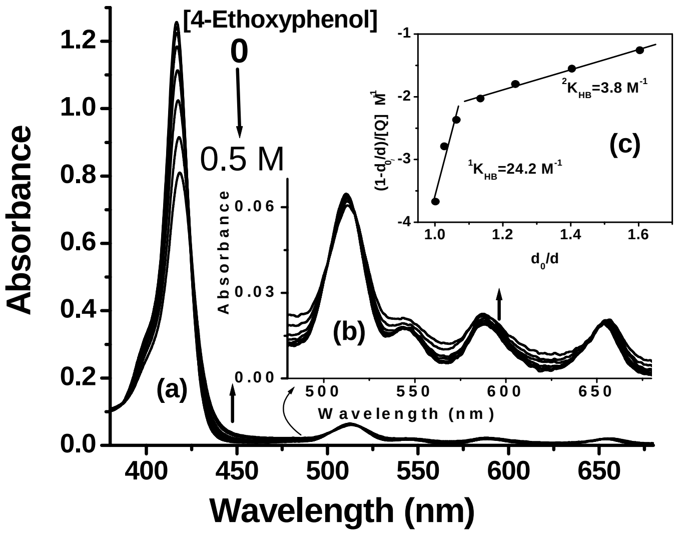

Figure 1S. (a)Absorption spectra of TpyP(2) in DCM as function of 4-ethoxyphenol. (b) Enlarge portion of Q band (c)Mataga and Tsuno plot at the peak of the Soret band.

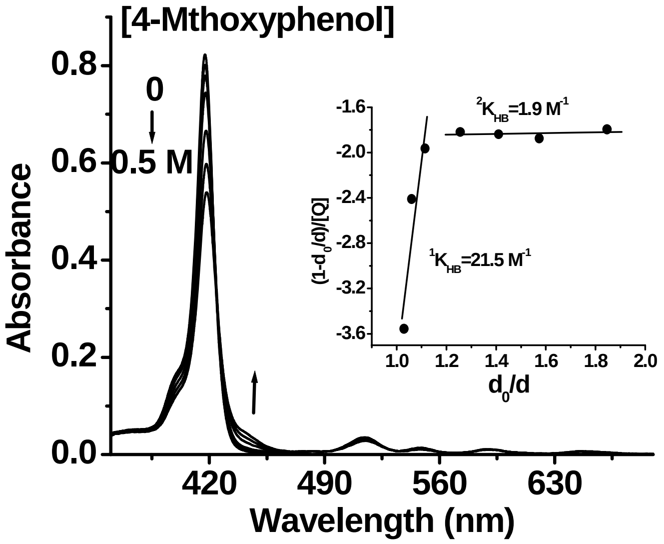

Figure 2S. Absorption spectra of TpyP(3) in DCM as function of 4-methoxyphenol. Insert is Mataga and Tsuno plot at 417 nm (Soret band peak)

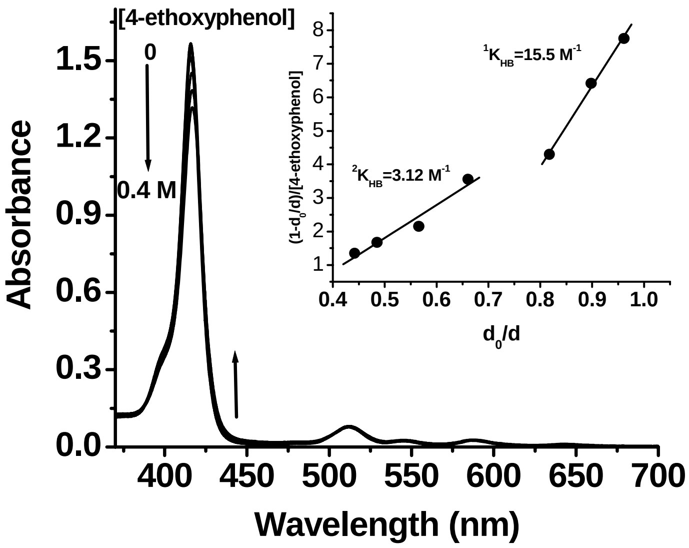

Figure 3S. Absorption spectra of TpyP(4) in DCM as function of 4-ethoxyphenol. **Insert**: Mataga and Tsuno plot at 448 nm. At 448 nm od increases as phenol concentration increases resulting different look of Mataga and Tsuno plot.

Fluorescence Spectra;

All steady state fluorescence spectra were recorded at room temperature by Fluorolog-3 spectrofluorometer of Horiba Jobin Yvon exciting on any of the Q-band where variation of absorbance is less due to added H-bonding agent. Lifetime measurements were done by Fluoro Cube of Horiba Jobin Yvon with 490 nm LED at 300^0 K. The normal lifetime (τ_0) of TpyP(4) =7.7 ns. TpyP(3) =7.0 ns, TpyP(2) = 7.5 ns. All quenching (steady state and time resolved) experiments were done in DCM solvent with ~2x10^{-5} M concentration of porphyrin. Fluorescence quantum yield (φ) is determined using secondary standard method described elsewhere taking Tpetraphenylporphyrin as reference (φ = 0.13). The measure yield (φ) of TpyP(4) =0.08, TpyP(3) =0.07 and TpyP(2) = 0.1

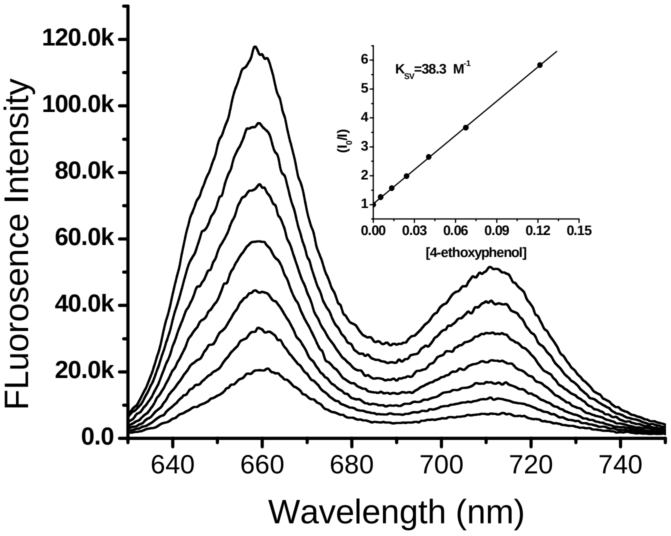

Figure 4S. Quenching of fluorescence of TpyP(2) by 4-ethoxyphenol. Insent: S-V plot based on fluorescence intensity.

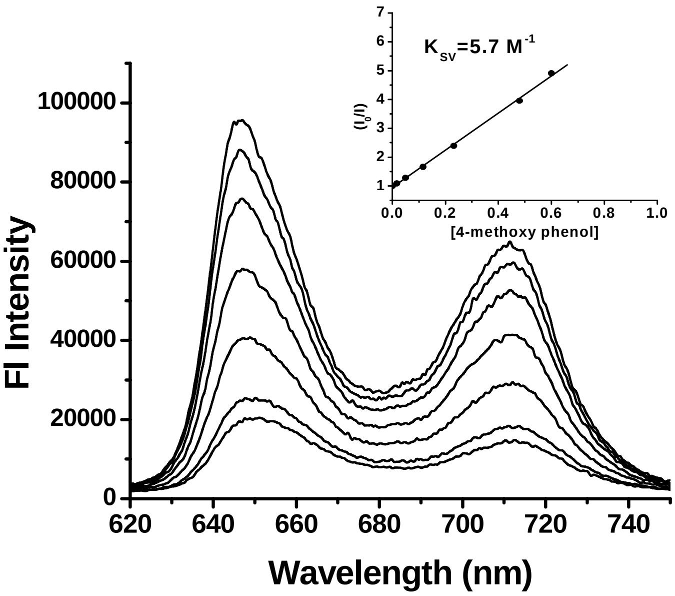

Figure 5S. Quenching of fluorescence of TpyP(4) by 4-methoxy phenol. Insent: S-V plot based on fluorescence intensity.

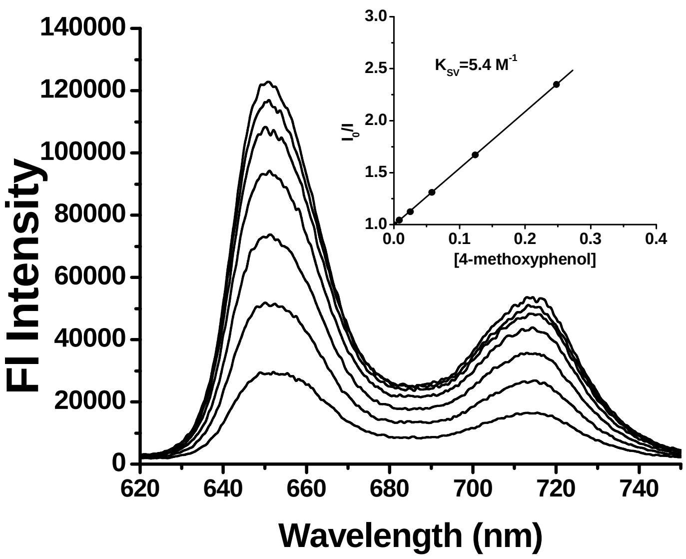

Figure 6S. Quenching of fluorescence of TpyP(3) by 4-methoxyphenol. Inset: S-V plot based on fluorescence intensity.

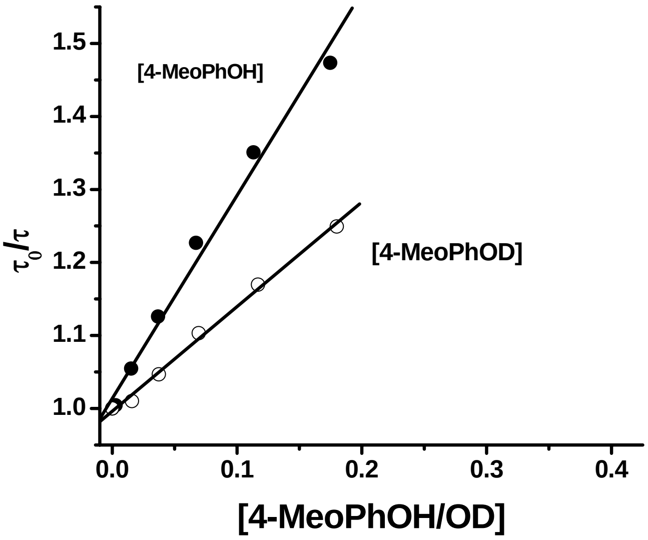

Figure 7S. Kinetic isotope effect: S-V plot for TpyP(3) based on lifetime change as function of 4-Methoxyphenol and deuterated 4-methoxy phenol.

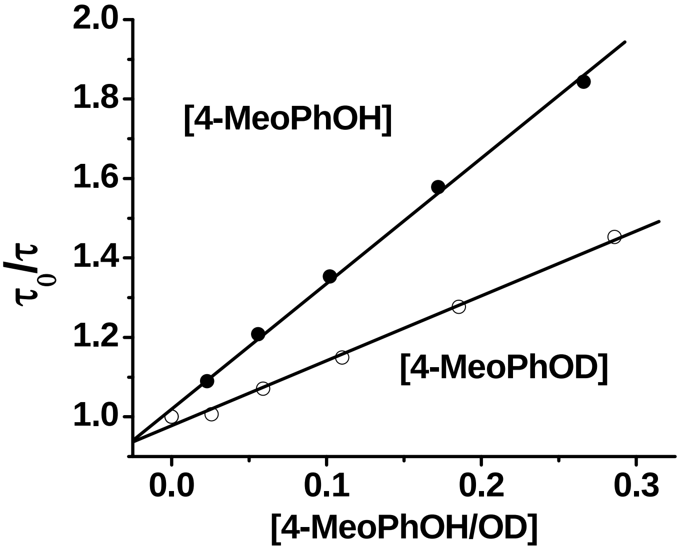

Figure 8S. Kinetic isotope effect: S-V plot for TpyP(4) based on lifetime change as function of 4-Methoxyphenol and deuterated 4-methoxyphenol.

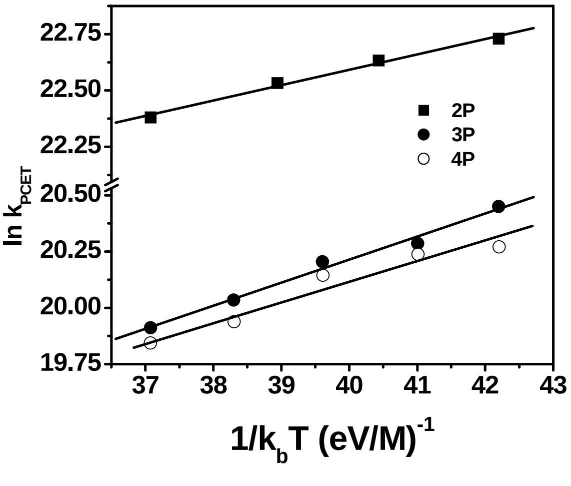

Figure 9S. Temperature dependence of proton coupled electron transfer rate constant for TpyP isomers with 4-ethoxyphenol.

Semi-empirical Calculation:

All the molecular modeling computations were performed in semi-empirical level by using the Gaussian 03, revision B.03 package39 implemented on Intel Pentium-4 PC machines. The optimization of the geometries of the 1:1 H-bonded complexes of TpyPs and 4-methoxyphenol were carried out using AM1 Hamiltonian following the tight convergence criteria implemented in Gaussian 03 program package and sufficient numbers of suitable redundant coordinates were chosen in order to have optimized structures of the complexes.

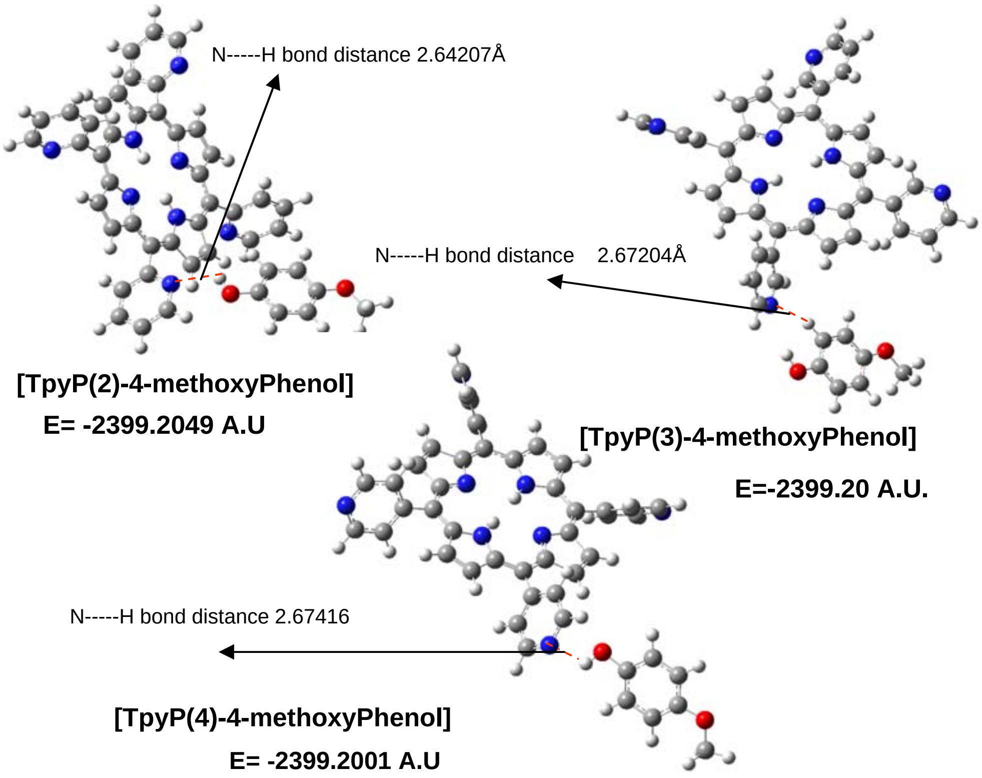

Figure 10s. Optimized geometries for different [TpyPs-Phenol] H-bonded complex.