Supporting Information

Coherent Intermolecular Proton Transfer in Acid-Base Reaction of Excited State Pyranine

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Contents

Computational details of QM/EFP MD simulation

A spherical system of an HPTS and an acetate ion surrounded by 382 water molecules to form a water sphere of 17 Å radius was prepared for the QM/EFP-MD simulations. In the effective fragment potential method, the water solvent system is divided into multiple fragments and each fragment is described by a set of parameters deduced from *ab initio* calculations. In order to prevent evaporation of water molecules during long time simulations, we applied a harmonic restraint potential with force constant of 2 $\mathrm{kcal \cdot mol^{-1} \cdot Å^{-2}}$ for the boundary solvent molecules as implemented in CHARMM.[1] To equilibrate the system in the ground state, NVT runs of QM/EFP-MD simulation over 100 ps was initially performed at 300 K; note that time average of one step of random events is the same as ensemble average. Then, from the final structures after the equilibration we switched to the electronic state of HTPS from ground state to first excited state and 1 ps simulation was performed with a time step of 1 fs. Five snapshots of 100 ps equilibrated structures were chosen for the simulations. We have performed QM/EFP-MD simulation with a modified version of GAMESS.[2]

References

1. B. R. Brooks, R. E. Bruccoleri, B. D. Olafson, D. J. States, S. Swaminathan and M. Karplus, *J. Comput. Chem.*, 1983, **4**, 187-217.
2. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347-1363.

Figure S1. Optimized molecular structures of (a) HPTS in the ground state (PA) and (b) its conjugate base in the excited state (PB*). The C-S bond lengths are indicated.

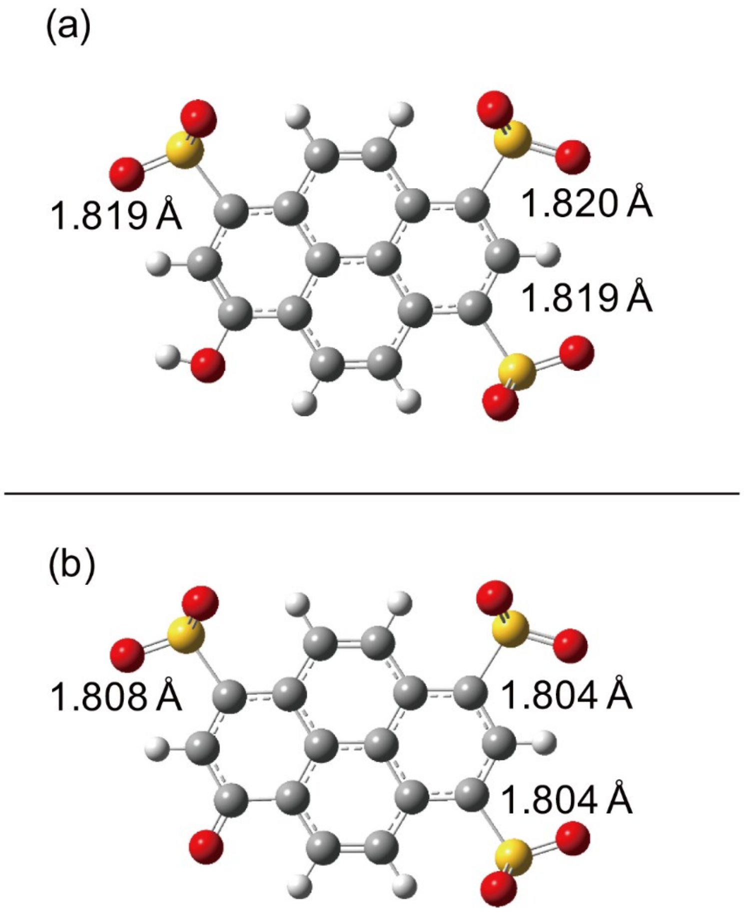

Figure S2. Normal mode of the 246 cm^{-1} band of PB*. The green arrow emphasizes the motion of the ketone group.

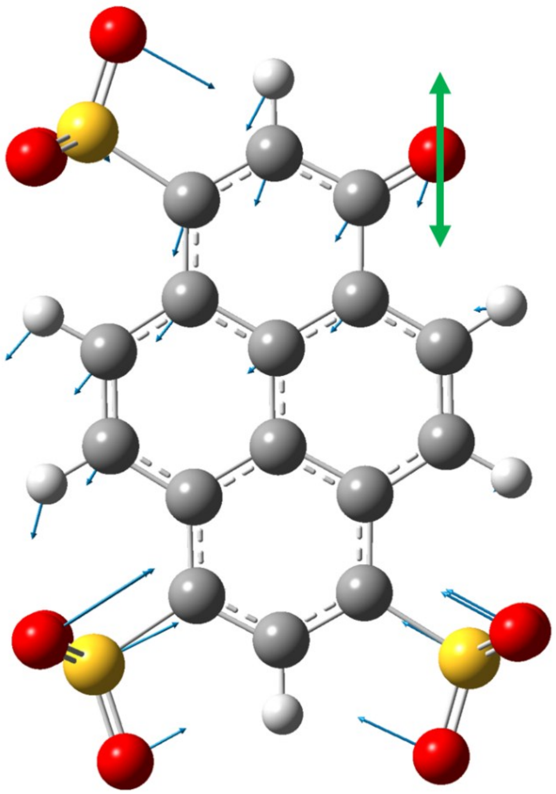

Figure S3. Optimized structure of HPTS-acetate complex from the QM/EFP MD.

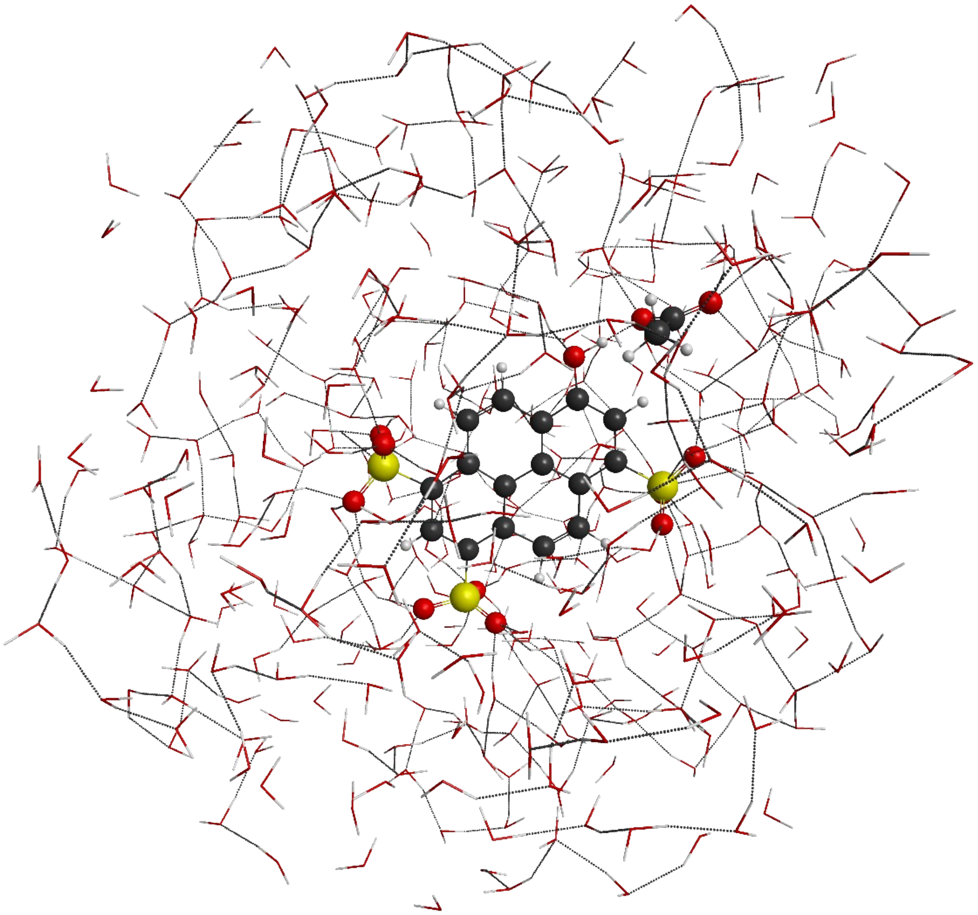

Figure S4. (a) Distance between the donor and acceptor oxygen atoms after the photoexcitation vs. time obtained from the QM/EFP MD. (b) Fourier transform of the data in (a) is compared with the VETF of PA*.