

Proton diffusion dynamics along a diol as a proton-conducting wire in a photo-amphiprotic model system

(Center for Soft and Living Matter, Institute for Basic Science (IBS)^a, Department of Chemistry, School of Natural Science, Ulsan National Institute of Science and Technology (UNIST)^b)

Ye-Jin Kim^{a, b} (gne1019@unist.ac.kr), Kyeong Eun Mun (mke3321@unist.ac.kr), and Oh-Hoon Kwon^{a, b} (ohkwon@unist.ac.kr)

We investigated the dynamics of excited-state proton transfer (ESPT) of photo-amphiprotic 7-hydroxyquinoline (7HQ) in the presence of a hydrogen (H)-bond bridging diol in a polar aprotic medium. The formation of 1 : 1 H-bonded complexes of 7HQ with various diols of different alkane chain lengths was revealed using steady-state electronic spectroscopy. With femtosecond-resolved fluorescence spectroscopy, cyclic H-bonded 1 : 1 complexes were found to undergo facile ESPT from the acidic enol to the basic imine group of 7HQ *via* the H-bond bridge. Through quantum chemical calculations, we found that the proton-transfer rate of the well-configured H-bonded complex correlated with the intramolecular H-bond length of a H-bond wiring diol molecule. Noncyclic, singly H-bonded 7HQ with a diol molecule was observed to undergo ESPT once another diol molecule diffuses to the noncyclic complex and accomplishes the formation of a reactive cyclic H-bonded 7HQ-(diol)₂ complex, which was evidenced by the observation that the overall proton-transfer rate constant decreases when a longer-chain diol was used as the bridging wire part. The kinetic isotope effect on the proton relay was investigated to confirm that the nature of the activation barrier for the proton diffusion along the wire is isotope-sensitive proton tunnelling, while for the non-cyclic configuration, the isotope-insensitive H-bond bridge formation is a prerequisite for ESPT.

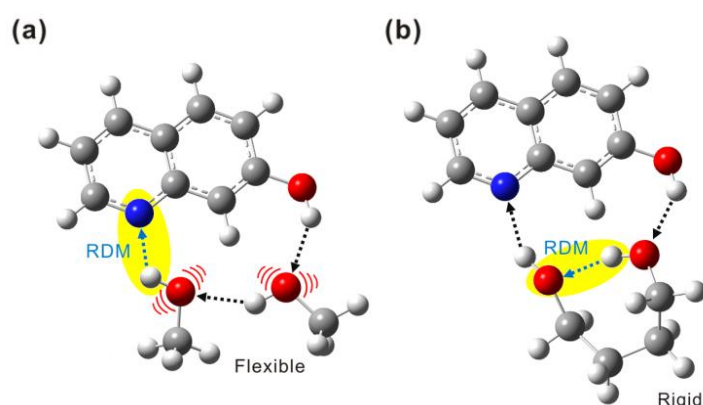


Figure Transition of the reaction coordinate for the ESPT of cyclic H-bond bridged complexes of 7HQ. (a) H-bonded complex with two alcohol molecules as a H-bond bridge. (b) H-bond complex with one diol molecule as the bridge. RDM denotes the rate-determining step.