Excited-state multiple proton transfer mechanism of 7-hydroxquinoline-$(H_2O)_3$ cluster

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Supporting Information:

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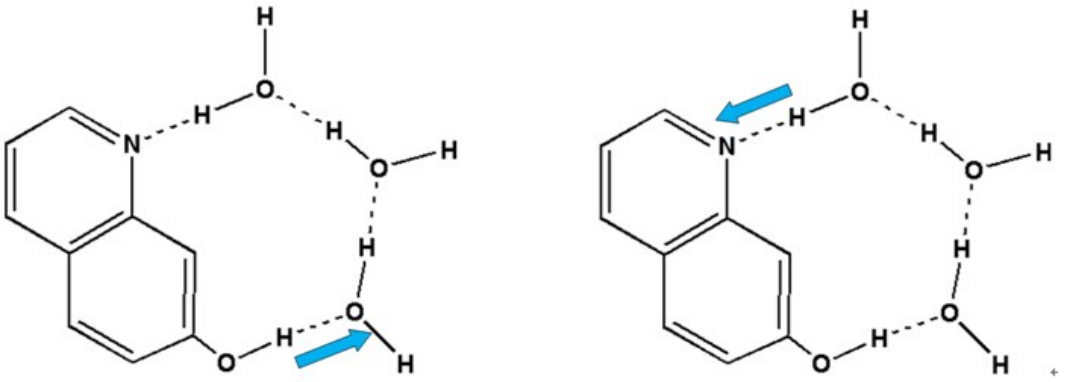
Table S1. The calculated primary bond lengths (Å) of **7HQ-$(H_2O)_3$** configuration involved in intermolecular hydrogen bonds in the S_0 state and S_1 state.

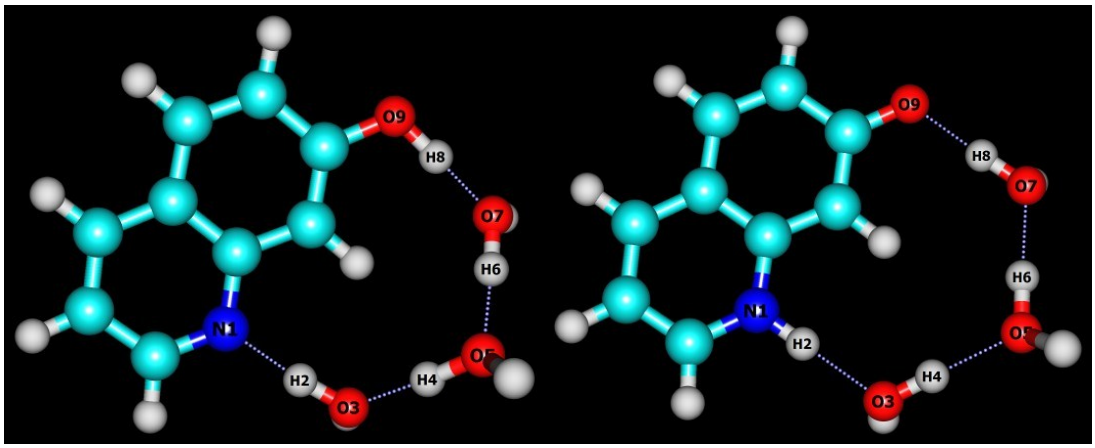
	$N_1\cdots H_2$	H_2-O_3	$O_3\cdots H_4$	H_4-O_5	$O_5\cdots H_6$	H_6-O_7	$O_7\cdots H_8$	H_8-O_9
S_0	**1.804**	**1.001**	**1.747**	**0.994**	**1.749**	**0.993**	**1.722**	**0.996**
S_1	**1.738**	**1.011**	**1.726**	**0.996**	**1.714**	**0.997**	**1.607**	**1.017**

Table S2. The calculated primary bond lengths (Å) of **7HQ-$(H_2O)_3$-PT** form involved in intermolecular hydrogen bonds in the S_0 state and S_1 state.

	N_1-H_2	$H_2\cdots O_3$	O_3-H_4	$H_4\cdots O_5$	O_5-H_6	$H_6\cdots O_7$	O_7-H_8	$H_8\cdots O_9$
S_0	**1.038**	**1.795**	**0.992**	**1.758**	**0.995**	**1.741**	**1.008**	**1.660**
S_1	**1.032**	**1.827**	**0.991**	**1.761**	**0.992**	**1.756**	**0.993**	**1.752**



Scheme S1 Two types of proton transfer reaction mechanism.



7HQ-$(H_2O)_3$ **7HQ-$(H_2O)_3$-PT**

Figure S1 Structures of **7HQ-$(H_2O)_3$** and its corresponding keto-tautomer **7HQ-$(H_2O)_3$-PT**.

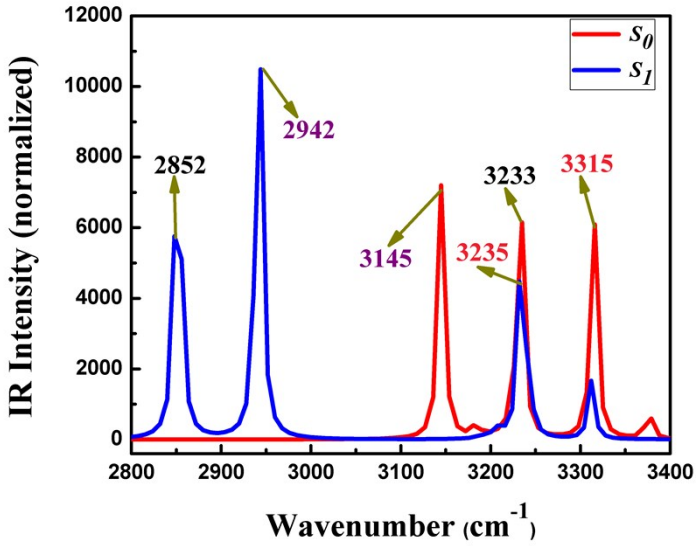


Figure S2 The calculated IR spectra of **7HQ-(H_2O)$_3$** structure in aqueous solvent at the spectral region of H_2-O_3(purple), H_8-O_9(black), H_4-O_5 and H_6-O_7 (pink) stretching bands.

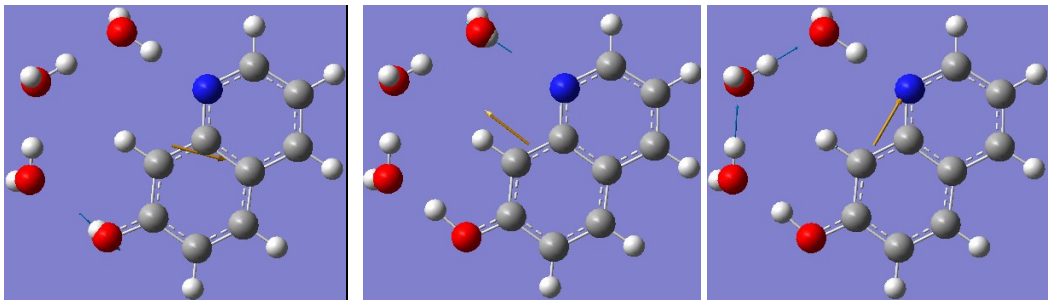
H_8-O_9	H_2-O_3	H_4-O_5 and H_6-O_7
		

Figure S3 Assignment of the different vibrational modes (both displacement vector and dipole derivative unit vector) of hydrogen-bonded 7HQ-$(H_2O)_3$ cluster at the spectral region of H_2-O_3, H_8-O_9 and the simultaneous H_4-O_5, H_6-O_7 stretching band.

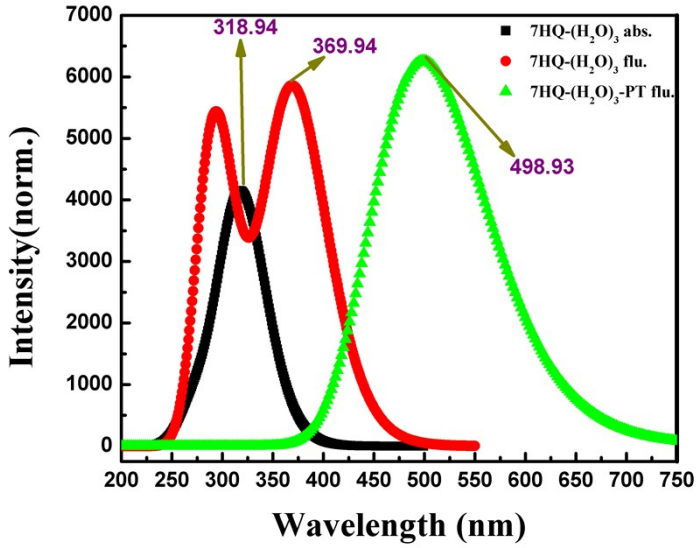
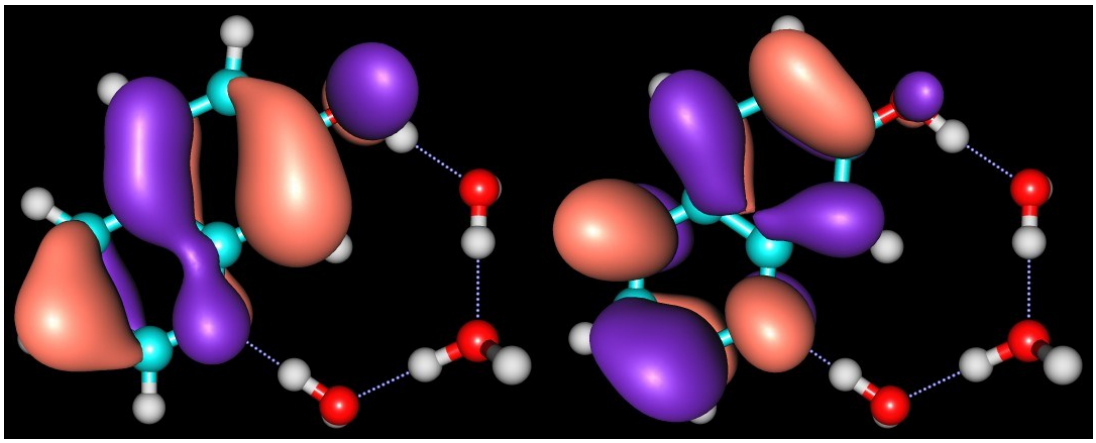


Figure S4 The calculated absorption and fluorescence spectra of **7HQ-$(H_2O)_3$** and **7HQ-$(H_2O)_3$-PT** forms based on the TDDFT/B3LYP/6-31+G(d)/IEFPCM (water) theoretical level.



HUMO **LUMO**

Figure S5 Frontier molecular orbitals (HOMO and LUMO) of **7HQ-$(H_2O)_3$** cluster.

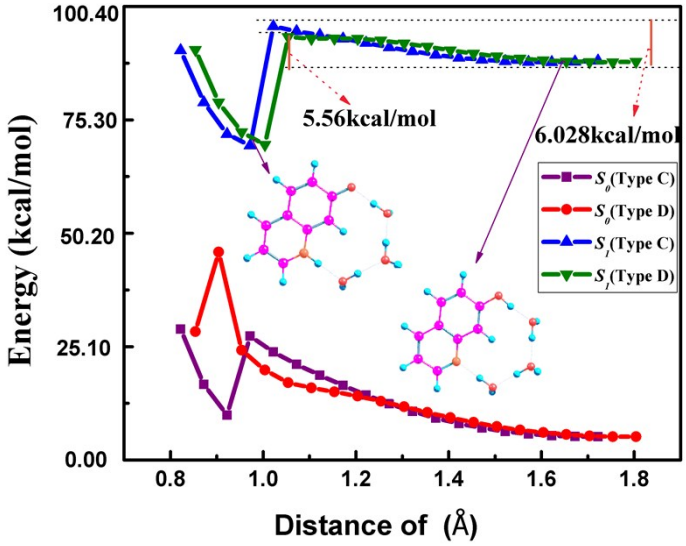


Figure S6 Potential energy curves of the S_0 and S_1 states for **7HQ-$(H_2O)_3$** cluster along with O_9-$H_8\cdots O_7$ (Type-C) and $N_1\cdots H_2$-O_3 (Type -D).