The mechanism of Excited-State Multiple Protons Transfer Reaction for 3-Me-2,6-diazaindole in Aqueous Solution

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Table S1. The theoretical emission bands (nm) of **(2,6-aza)Ind**, **(2,6-aza)Ind +H_2O**, **(2,6-aza)Ind +$2H_2O$**, and **(2,6-aza)Ind +$3H_2O$** and their photo-tautomers predicted at different functionals (B3LYP, M06-2x, and PBE0) and experimental data of **(2,6-aza)Ind** monitored in aqueous solution (reference 14).

Complexes	B3LYP	M06-2x	PBE0	experimental
(2,6-aza)Ind	358	432	339	340
(2,6-aza)Ind +H_2O	331	443	323	
(2,6-aza)Ind +$2H_2O$	341	309	328	
(2,6-aza)Ind +$3H_2O$	333	307	324	
T-(2,6-aza)Ind	584	546	490	480
T-(2,6-aza)Ind +H_2O	465	415	445	
T-(2,6-aza)Ind +$2H_2O$	452	406	434	
T-(2,6-aza)Ind +$3H_2O$	445	401	429	

Computational Method

All electronic structure calculations were carried out with the Gaussian 09 program suite.[1] Geometry optimizations of the S_0 state and the S_1 state of **(2,6-aza)Ind**, **(2,6-aza)Ind + $2H_2O$**, **(2,6-aza)Ind + $3H_2O$** were implemented using DFT method and TDDFT method. For the accuracy of the theoretical method, we test the functionals B3LYP, PBE0 and M06-2X for the TDDFT computations, which is achieved by means of the absorption and fluorescence spectra of **(2,6-aza)Ind + nH_2O** that can be compared with the data reported earlier. The self-consistent field (SCF) convergence thresholds of the energy for both the ground state and excited state optimization were used the default setting (10^{-6}). The excited state Hessian was obtained by numerical differentiation of analytical gradients using central differences and default displacements of 0.02 Bohr. The infrared intensities were determined from the gradients of the dipole moment.[2] The geometry optimizations were performed without constraints on bond lengths, angles, or dihedral angles except constructing PES and PECs. The PES at S_0 state and the PECs at S_1 state of **(2,6-aza)Ind + L$3H_2O$** were constructed with the fixing of N_1-H_1 and/or O_2-H_2 distances at a series of values. All the local minima were confirmed by the absence of an imaginary mode in vibrational analysis calculations. To evaluate the solvent effect, H_2O was selected as the solvent in the calculations using the conductor-like screening model (COSMO) method. [3]

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(2) F. Furche and R. Ahlrichs, Journal of Chemical Physics, 2002, 117, 7433-7447.

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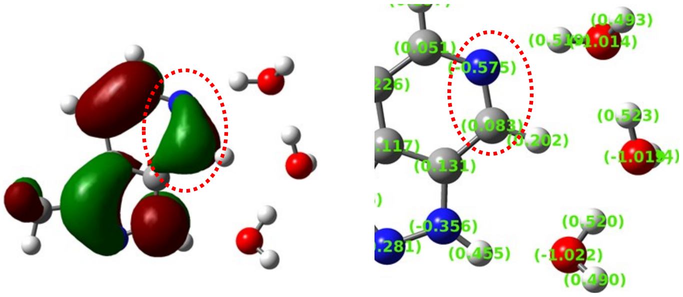
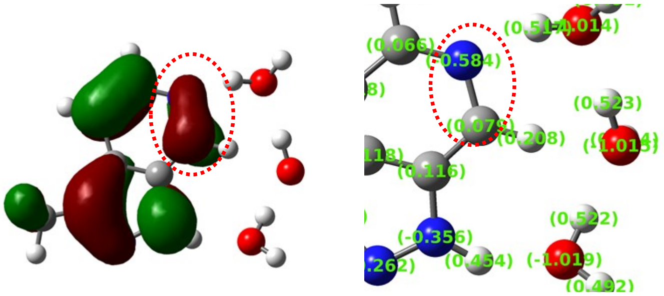


Ground State



First Exited State

Figure S1. The shapes of HOMOs of **(2,6-aza)Ind + L3H_2O** at S_0 and S_1 states; and natural bond orbital charge population on **(2,6-aza)Ind + L3H_2O** at S_0 and S_1 states.

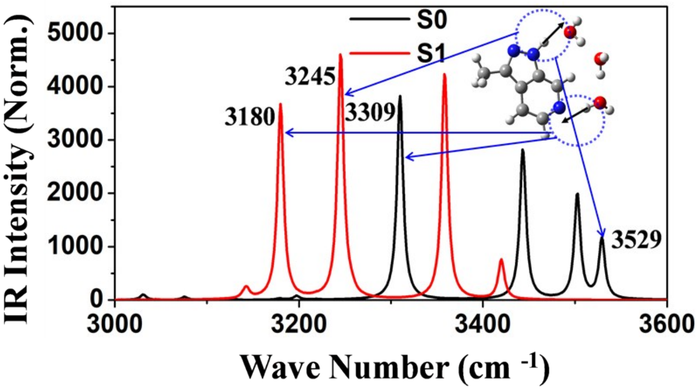


Figure S2. The calculated IR spectra of **(2,6-aza)Ind + L3H$_2$O** for the ground state (S$_0$) and first excited-state (S$_1$) in the spectral region of the N$_1$-H$_1$ and O$_2$-H$_2$ strengthening bands.