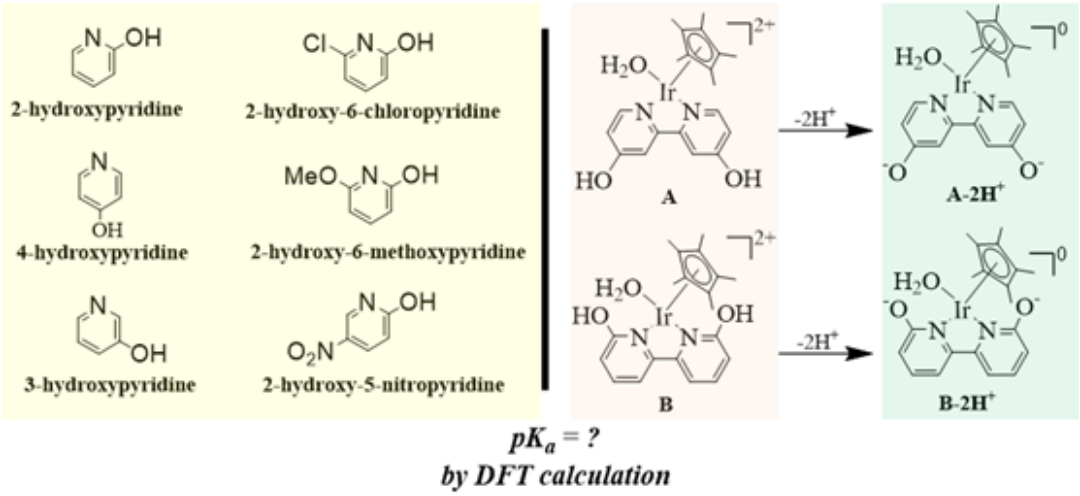
A DFT study of proton dissociation constant of hydroxypyridine derivatives and the proton-responsive Cp*Ir(III) complexes and their implication for CO_2 hydrogenation

Tanakorn Wonglakhon[1] and Panida Surawatanawong[1,2*]

[1]*Department of Chemistry, Faculty of Science, Mahidol University, Thailand*
[2]*Center of Sustainable Energy and Green Materials, Mahidol University, Thailand*

*e-mail: panida.sur@mahidol.edu

Proton dissociation constant (pK_a) is one of the fundamental properties of molecules that determines the degree of proton dissociation at a particular pH value. Hydroxypyridine derivatives are structurally related to drugs and biomolecules, such as nifedipine, quinine, etc. The accurate measurement of the pK_a of these compounds is thus of importance. We conducted the density functional study using M06/6-311++G(d,p)//B3LYP/6-31G(d,p) level of theory to calculate the pK_a of six hydroxypyridines. All calculations were performed in aqueous solution by employing the SMD and CPCM solvation models with Bondi, Pauling, and UAHF radii. The calculated pK_a values with the SMD solvation model have the lowest mean unsigned error of 1.1, which agrees well with the experimental values. In addition, this calculation model is applied to calculate the pK_a values of the proton-responsive Cp*Ir(III) complexes, the catalysts for CO_2 hydrogenation. The calculated pK_{a1} and pK_{a2} of complex **A** are 4.4 and 5.9, while those of complex **B** are 3.1 and 3.6, respectively, the error in comparison with the experiment is less than 1.0 pK_a unit. This indicates that when these two complexes are used for CO_2 hydrogenation at pH 8.3 according to the experimental condition, the active complexes are in the fully deprotonated form. This study could stimulate further the studies of acidity of the other proton-responsive Cp*Ir(III) complexes as well as their CO_2 hydrogenation mechanism.



Keywords: Proton dissociation constant; density functional study; proton-responsive Cp*Ir(III) complex; CO_2 hydrogenation