Applications of Halogen Bonding to Supramolecular Chemistry, Organocatalysis and Phosphorescence Materials

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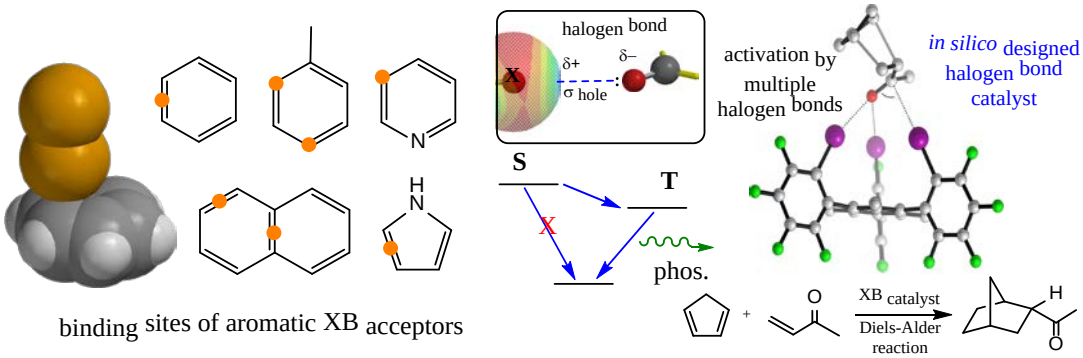
Halogen Bonding (XB) has become one of the most studied non-covalent interactions in the past two decades, owing to its wide range of applications in materials and biological and catalysis applications. Due to its bond strength and directionality, halogen bonds have great potential as supramolecular synthons in crystal engineering and rational catalyst and drug design. In this presentation, we will report our application studies on XB to supramolecular chemistry, organocatalysis and phosphorescence materials. Aromatic systems are potential halogen bond acceptors in supramolecular assemblies. Our updated statistical analysis of CSD survey of halogen bond contacts and *ab initio* studies involving several polycyclic aromatic hydrocarbons and *N*-heteroaromatic compounds revealed that XB generally forms at the rim of a phenyl ring with distinct site specificity. The nature of this type of XB interaction and origin of the rim specificity will be discussed. We envisage that the predicted XB site maps will be useful for materials and drug design involving this class of non-covalent interactions. In recent years, several groups have reported aromatic and heteroaromatic XB acceptors, such as phenanthrene, naphthalene and carbazole, exhibiting phosphorescence properties in XB assembled crystals. In an attempt to understand the application of XB on phosphorescence materials, we have carried out an ab initio study to address the fundamental questions on whether XB promotes intersystem crossing between excited states. We will report the important findings on several model systems on XB-induced phosphorescence materials. For catalysis application, we have examined the use of halogen-bond donors as noncovalent activators in Lewis acid catalysis. We performed *in silico* design on a halogen bonding based catalyst (triaryl benzene with multiple iodine-XB donors), and applied to Diels-Alder reaction, Claisen rearrangement and cope-type hydroamination. In collaboration with experimental study, we have demonstrated the halogen bonding activation of 2-iodoimidazolium triflate as XB catalyst for conjugate addition of α,β-unsaturated compounds with thiophene and its derivatives.



binding sites of aromatic XB acceptors