CHAPTER 5

Conclusions

Theoretical study of HBX and APBT derivatives by using time-dependent density functional theory (TD-DFT/TD-B3LYP/6-311+G(d,p) level). This research is well prepared to report the effects of hetero nitrogen substitution of HBX derivatives and substituent effect of APBT derivatives on the geometry, photophysical, photochemical properties and ESIPT of HBX derivatives. Starting from the effect of hetero nitrogen inserted in the benzene ring of benzimidazole (HBI), benzoxazole (HBO) and benzothaizole (HBT) moieties of HBX derivatives. Calculated spectra of HBI derivatives were systematically investigated by the method of choice at TD-DFT/TD-B3LYP/6-311+G(d,p) level, which was validated by a good agreement of calculated maximum wavelengths of HBI with the available experimental data. Adding the hetero nitrogen in HBX derivatives does not affect the planarity of these derivatives but significantly affect their photophysical properties. The absorption spectra of hetero nitrogen disubstitution are more red shift than hetero nitrogen monosustitution, particularly, the absorption spectra of 1,4- and 3,4-disubstitution of HBX derivatives exhibit more red shift than other positions because the lone pair electron in the substituted hetero nitrogen might stabilize the π-conjugated system of benzimidazole, benzoxazole and benzothaizole ring of HBX derivatives. Furthermore, the chance of ESIPT is found to be in the order of HBT > HBI > HBO. The selected derivatives substituted with hetero nitrogen at 1,4 and 3,4 position of HBX derivatives could facilitate ESIPT process due to the nitrogen substitution makes O–H bond of selected derivatives weaker than those of HBX and the N– H distance of selected derivatives become stronger in the excited state.

Furthermore, the effect of electron donating and withdrawing group are substituted on absorption and emission spectra of APBT derivatives was studied. The calculated absorption wavelength of APBT derivatives are in agreement with the experimental data. The result of the study revealed that these patterns of substitutions are likely to give fluorescent APBT-derived dyes with large Stokes' shifts including a strong EDG at R_2 position and a strong EWG at R_3 position, a push-pull architecture consisting of a strong EWG at R_1 position and a strong EDG at R_3 position and solely a strong EDG at R_2 position. These rough generalised ideas, along with in depth understanding of the fluorescent of APBT.

Therefore, the obtained information in this present study particularly on prediction of photophysical properties of new designed fluorescent dyes will be very useful guideline toward the design of other fluorescent probes for this application for chemists who are interested in developing the novel and effective ESIPT fluorescent dyes.