Guided Exploration of Halogen Bonding Interactions in Doped Graphitic Carbon Nitride Building Blocks with Vibrational Spectroscopy

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Herein we scrutinize the vibrational C-X and C≡C stretching modes and their local force constants (k^a) in a series of substituted bromo and iodoethynyl benzene halogen bond (XB) donors (F_5BABr, $(NO_2)_2$BABr, F_5BAI, and $(NO_2)_2$BAI). We also examine the shifts of these vibrational signatures and k^a that accompany XB formation between each donor and the doped graphitic carbon nitride building block, pnictogen and chalcogen substituted melamine ($C_3N_3(PH_2)_3$, $C_3N_3(OH)_3$, $C_3N_3(SH)_3$). Full geometry optimizations and harmonic vibrational frequency computations are performed on each XB donor, acceptor, and complex with the M06-2X density functional in conjunction with a double-ζquality correlation consistent basis set augmented with diffuse functions on all atoms and a psuedopotential for bromine and iodine centers (aug-cc-pVDZ for H, C, N, O and aug-cc-pVDZ-PP for Br, I; denoted aVDZ). To gain insight into the relationship between the strength of XB interaction and its C-X and C≡C stretching frequency, the magnitude of electron density transfer upon complexation and the local force constants of C-X, C≡C, and X-N is evaluated using full NBO and Local Mode Analyses (LModeA from the CATCO research group) on the M06-2X/aVDZ optimized geometries. Connections between select geometrical parameters, the energetics, the C-X, C≡C, and X-N local force constants, and the vibrational C-X and C≡C stretching modes of the XB donors and the complexes will be discussed.