Decoding Photoluminescent Sensing in Metal Organic Frameworks

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Luminescent metal organic frameworks (MOFs) are an emerging material in the sensing field due to their relative ease of synthesis, selectivity of adsorption, and oftentimes reversible nature of the sensing mechanism. For example, mesoporous metal organic frameworks (MMOFs) can detect the explosive compounds DNT, a derivative of TNT, and DMNB, a taggant used in plastic explosives, by lessening the intensity of the MMOF photoluminescence within seconds of exposure. Upon heating, the adsorbed molecule is released and the material is recyclable. This has substantial implications in the cost effectiveness of explosive detection and ease of use. The two main processes of sensing in MOFs involve quenching, which lessens or completely eliminates the photoluminescence, and enhancement, which can involve either turning the MOF from "off" to "on" (in terms of emitting light) or increase the intensity of already existing luminescence. However, questions remain concerning the exact atomic scale processes which drive these sensing mechanisms. We investigate these questions by implementing recent advances in optical property calculations and studying the electron relaxation via a density matrix formalism. The focus of this study is on Zn-containing MOFs to focus on the organic linker driven photoluminescence, which is altered via guest molecule adsorption.

Two models are studied: the photoluminescent mesoporous metal organic framework (MMOF) $Zn_2(bpdc)_2(bpee)$, known to be a selective quencher of explosive compounds, and an entangled porous coordination polymer framework (PCP) $Zn_2(bdc)_2(dpNDI)$, which exhibits enhanced luminescence upon addition of aromatic analytes [bpdc = 4,4$'$-biphenyldicarboxylate; bpee = 1,2-bipyridylethene; bdc = 1,4-benzenedicarboxylate; dpNDI = N,N$'$-di(4-pyridyl)- 1,4,5,8-naphthalenediimide]. These models have been well studied experimentally, which provides a benchmark to compare the reliability of our results. Experimentally, DNT quenches the MMOF luminescence by 84% and the computationally calculated quenching is 77%. For the enhancement, the PCP luminescence is enhanced by a factor of 2.5 when benzene is adsorbed in the MOF, and computationally we calculate the enhancement factor to be 3.2.

Our results capture the atomic-scale process of guest-induced luminescent quenching and enhancement. Calculations were performed at the density functional theory level in VASP with the vdW-DF exchange-correlation functional in order to incorporate the long-range van der Waals interactions between MOFs and guest molecules. Atomic displacement parameters and electron/hole relaxation pathways were calculated by implementing *ab initio* molecular dynamics (AIMD); the luminescence was calculated via the corresponding oscillator strength throughout the AIMD trajectory. Finally, electron (and hole) relaxation was studied by calculating non-adiabatic couplings between each time step of the AIMD and forming a reduced density matrix. By using these tools, a full analysis on the guest-MOF interactions was performed and the atomistic mechanisms of guest-induced sensing in the Zr-MOFs is explained.