Sensing mechanism elucidation of a chemosensor based on a metal-organic framework selective to explosive aromatic compounds

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Theoretical elucidation of the turn-off mechanism of the luminescence of a chemosensor based on a metal-organic framework (MOF) [Zn2(OBA)4(BYP)2] (BYP: 4,4?-bipyridine; H2OBA: 4,4?-oxybis[benzoic acid]), selective to nitrobenzene (NB) via quantum chemical computations, is presented. The electronic structure and optical properties of Zn-MOF were investigated through the combination of density functional theory (DFT) and time-dependent DFT methods. Our results indicate that the fluorescence emission is governed by a linker (BPY)-to-linker (OBA) charge transfer (LLCT) involving orbitals ?-type. Next, the interaction with the analyte was analyzed, where very interesting results were obtained, that is, the lowest unoccupied molecular orbital is now composed of orbitals from NB, which changes the emissive state of the Zn-MOF. This suggests that the LLCT process is blocked, inducing the fluorescence quenching. Otherwise, the Morokuma-Ziegler energy decomposition and natural orbitals for chemical valence on the Zn-MOF-NB interactions were studied in detail, which illustrate the possible channels of charge transfer between Zn-MOF and NB. Finally, we believe that this proposed methodology can be applied to different chemosensor-analyte systems to evidence the molecular and electronic factors that govern the sensing mechanisms.

luminescence MOFs

nitroaromatic compounds

PET

TD-DFT

Benzoic acid

Charge transfer

Electronic structure

Fluorescence

Metal-Organic Frameworks

Molecular orbitals

Optical properties

Organometallics

Quenching

Electronic factors

Electronic structure and optical properties

Energy decomposition

Fluorescence emission

Lowest unoccupied molecular orbital

Quantum chemical computations

Time-dependent DFT

Turn-off mechanisms

Density functional theory