

Insights into the selective sensing mechanism of a luminescent Cd(II)-based MOF chemosensor toward NACs: roles of the host–guest interactions and PET processes

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Abstract

The structural and photophysical properties of the $[\text{Cd}_2(\text{H}_2\text{L})_2(\text{H}_2\text{O})_5] \cdot 5\text{H}_2\text{O}$ (where H_4L is the ligand 5,5'-(thiophene-2,5-dicarbonyl)bis(azanediyl))diisophthalic acid labeled as Cd-MOF), as well as the elucidation of the selective turn-off luminescent sensing mechanism toward 4-nitroaniline (pNA) were addressed, using quantum chemical methods. To reach this aim, the structures of the ground state (S_0) and first excited state (S_1) Cd-MOF/analyte system were assessed. We found that after the interaction a photoinduced electron transfer (PET) from the Cd-MOF to pNA is responsible for the fluorescence quenching in this system. For this purpose, a study was performed based on TD-DFT and multireference calculations to corroborate that an excited state exists with the adequate electronic configuration for PET process in the interacting system Cd-MOF/analyte. Intermolecular interaction between the Cd-MOF and analyte was studied by means of Morokuma–Ziegler energy decomposition analysis, natural orbitals of chemical valence, ab initio molecular dynamics (AIMD) calculations and non-covalent interactions (NCI) index. These results showed that intermolecular interactions via hydrogen bond are considerably strengthened in the excited state for the Cd-MOF/pNA, which favor the non-radiative deactivation channels of the chemosensor. In addition, the overlap of absorption spectra of Cd-MOF and pNA indicates that the loss of fluorescence is also due to internal filter effect (IFE). The most noteworthy aspect of this methodology is to consider the relative energies of the S_0 and S_1 states of MOF/analyte system to explaining the experimental behavior of Cd-MOF toward 4-nitroaniline, proving to be a robust tool in the accurate elucidation of the sensing mechanism in the MOF chemosensor. Graphical abstract: [Figure not available: see fulltext.] Ab initio methods along with TD-DFT have been used to elucidate the selective turn-off luminescent sensing mechanism of nitroaromatic compounds by a Cd-based metal–organic framework (MOF). The role of the host–guest interaction has been pointed out using different theoretical descriptors. A theoretical protocol is given to get more insights into the MOF design and selectivity for nitroaromatic compounds. © 2021, The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature.

