Sensing mechanism elucidation of a europium(III) metal?organic framework selective to aniline: A theoretical insight by means of multiconfigurational calculations

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A theoretical procedure, via quantum chemical computations, to elucidate the detection principle of the turn-off luminescence mechanism of an Eu-based Metal-Organic Framework sensor (Eu-MOF) selective to aniline, is accomplished. The energy transfer channels that take place in the Eu-MOF, as well as understanding the luminescence quenching by aniline, were investigated using the well-known and accurate multiconfigurational ab initio methods along with sTD-DFT. Based on multireference calculations, the sensitization pathway from the ligand (antenna) to the lanthanide was assessed in detail, that is, intersystem crossing (ISC) from the S1 to the T1 state of the ligand, with subsequent energy transfer to the 5D0 state of Eu3+. Finally, emission from the 5D0 state to the 7FJ state is clearly evidenced. Otherwise, the interaction of Eu-MOF with aniline produces a mixture of the electronic states of both systems, where molecular orbitals on aniline now appear in the active space. Consequently, a stabilization of the T1 state of the antenna is observed, blocking the energy transfer to the 5D0 state of Eu3+, leading to a non-emissive deactivation. Finally, in this paper, it was demonstrated that the host-guest interactions, which are not taken frequently into account by previous reports, and the employment of high-level theoretical approaches are imperative to raise new concepts that explain the sensing mechanism associated to chemical sensors.

antenna effect

CASSCF

lanthanide

metal-organic framework

Aniline

Antennas

Calculations

Chemical detection

Electronic states

Energy transfer

Ligands

Luminescence

Metal-Organic Frameworks

Molecular orbitals

Organometallics

Host guest interactions

Intersystem crossing

Luminescence mechanisms

Luminescence quenching

Multireference calculations

Quantum chemical computations

Sensing mechanism

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Europium compounds