

# Radiative decay channel assessment to understand the sensing mechanism of a fluorescent turn-on Al<sup>3+</sup> chemosensor

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The turn-on luminescent chemosensor [2-Hydroxy-1-naphthaldehyde-(2-pyridyl) hydrazone] (L), selective to Al<sup>3+</sup> ions, was studied by means of density functional theory (DFT) and time-dependent-DFT quantum mechanics calculations. The UV-Vis absorption and the radiative channel from the adiabatic S<sub>1</sub> excited state were assessed in order to elucidate the selective sensing mechanism of L to Al<sup>3+</sup> ions. We found that twisted intramolecular charge transfer (TICT) and photoelectron transfer (PET), which alter the emissive state, are responsible for the luminescence quenching in L. After coordination with Al<sup>3+</sup>, the TICT is blocked, and PET is no longer possible. So, the emission of the coordination complex is activated, and a fluorescence effect enhanced by chelation is observed. For compounds with Zn<sup>2+</sup> and Cd<sup>2+</sup>, the luminescence quenching is caused by PET, while for Ni<sup>2+</sup>, ligand to metal charge transfer is the prominent mechanism. To go into more detail, the metal-ligand interaction was analyzed via the Morokuma-Ziegler energy decomposition scheme and the natural orbital of chemical valence. ©

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CHEF

fluorescence

PET

TD-DFT

TICT

Charge transfer

Chemical analysis

Dynamic mechanical analysis

Excited states

Fluorescence

Ligands

Polyethylene terephthalates

Quantum theory

Quenching

CHEF

Ligand-to-metal charge transfers

Luminescence quenching

Metal-ligand interactions

Radiative decay channels

TD-DFT

TICT

Twisted intra-molecular charge transfers

Density functional theory