

# Fluorescence turn-on and turn-off mechanisms of a dual-selective chemosensor of $\text{Bi}^{3+}$ and pH changes: Insights from a theoretical perspective

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## Abstract

The N-hydroxy 1,8-naphthalimide (LH) is an optical dual-selective chemosensor toward  $\text{Bi}^{3+}$  ions as well as pH changes. In specific, this sensor is selective to  $\text{Bi}^{3+}$  ions, which turn-on the fluorescence upon their interaction; otherwise, LH fluorescence is gradually turned-off when the pH of the medium rises to alkali values. We found that our theoretical and computational methodology through TD-DFT and multiconfigurational calculations approaches were able to elucidate both the CHEF (Chelation-Enhanced Fluorescence) observed by the interaction of the sensor with  $\text{Bi}^{3+}$ , by blocking the PET (Photoinduced Electron Transfer) in  $\text{L}^-$  and promoting the emissive deactivation of the excited state in  $\text{Bi}^{3+}/\text{L}$ . On the other hand, other ions such as  $\text{Al}^{3+}$  and  $\text{Ni}^{2+}$  were tested and no significative CHEF was observed. The metal-ligand interaction was studied via the Morokuma-Ziegler energy decomposition scheme and the NOCV (Natural Orbital of Chemical Valence). It was found that the electron pair of the deprotonated oxygen responsible for the PET in  $\text{L}^-$  is involved in the coordination of  $\text{Bi}^{3+}$ . Also, the luminescence decreasing in metal/sensor 1:2 relation was assessed. In pH sensing, our calculations confirmed that in the  $\text{L}^-$  (which is present in alkali medium), PET is strongly promoted by the deprotonated oxygen due to its strong contribution to the HOMO, leading to conclude that this mechanism is the responsible for the luminescence turn-off at basic pH values; the strength of the oscillator ( $f$ ) in the emissive transition and multiconfigurational calculations corroborates this statement. Furthermore, kinetic analysis through the  $k_{\text{et}}$  (rate of electron transfer process) and the  $k_{\text{rad}}$  (rate of the radiative process) were calculated and provided a quantitative prediction from the competition of PET with the radiative process. The employed methodology was able to explain the behavior of the dual-selective chemosensor and to evidence that to describe accurately this type of system, it is necessary to compute the properties of the  $S_0$  and excited states, together with the kinetic parameters in the charge transfer and emission channels.

## Author keywords

Chemosensor  
Dual sensor  
pH sensor  
Photoelectron transfer