

# New Sensitive and Selective Chemical Sensors for Ni<sup>2+</sup> and Cu<sup>2+</sup> Ions: Insights into the Sensing Mechanism through DFT Methods

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We report the synthesis and theoretical study of two new colorimetric chemosensors with special selectivity and sensitivity to Ni<sup>2+</sup> and Cu<sup>2+</sup> ions over other metal cations in the CH<sub>3</sub>CN/H<sub>2</sub>O solution. Compounds (E)-4-((2-nitrophenyl)diazenyl)-N,N-bis(pyridin-2-ylmethyl)aniline (A) and (E)-4-((3-nitrophenyl)diazenyl)-N,N-bis(pyridin-2-ylmethyl)aniline (B) exhibited a drastic color change from yellow to colorless, which allows the detection of the mentioned metal cations through different techniques. The interaction of sensors with these metal ions induced a new absorption band with a hypsochromic shift to the characteristic signal of the free sensors. A theoretical study via time-dependent density functional theory (TD-DFT) was performed. This method has enabled us to reproduce the hypsochromic shift in the maximum UV-vis absorption band and explain the selective sensing of the ions. For all of the systems studied, the absorption band is characterized by a  $\pi \rightarrow \pi^*$  transition centered in the ligand. Instead of Ni<sup>2+</sup> and Cu<sup>2+</sup> ions, the transition is set toward the  $\pi^*$  molecular orbital with a strong contribution of the 3d<sub>x<sup>2</sup>-y<sup>2</sup></sub> transition ( $\pi \rightarrow 3d_{x^2-y^2}$ ). These absorptions imply a ligand-to-metal charge transfer (LMCT) mechanism that results in the hypsochromic shift in the absorption band of these systems.