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A: Spectroscopy, Molecular Structure, and Quantum Chemistry

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New Sensitive and Selective Chemical Sensors for Ni²⁺ and Cu²⁺ ions, Sensing Mechanism Insights Through DFT Methods

Manuel A. Treto-Suárez^a, Jorge Tapia^{b,f}, Yoan Hidalgo-Rosa^{a,f}, Dayan Páez-Hernández^{a,e*}, Elies Molins^c, Ximena Zarate^{d*} and Eduardo Schott^{b,f*}.

^aDoctorado en Fisicoquímica Molecular, Universidad Andres Bello. Ave. República #275, Santiago de Chile, Chile. <u>dayan.paez@unab.cl</u>, <u>mtretosuarez@gmail.com</u>.

^bDepartamento de química inorgánica, UC Energy Research Center, Facultad de Química y de Farmacia, Pontificia Universidad Católica de Chile, Vicuña Mackenna 4860, Macul, Santiago, Chile. maschotte@gmail.com

^cInstitut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra. Spain. elies.molins@icmab.es

^dInstituto de Ciencias Químicas Aplicadas, Theoretical and Computational Chemistry Center, Facultad de Ingeniería, Universidad Autónoma de Chile, Av. Pedro de Valdivia 425, Santiago, Chile. ximena.zarate@uautonoma.cl

^eCenter of Applied Nanosciences (CANS), Chile República #275, Santiago de Chile, Chile.

^fMillennium Nuclei on Catalytic Processes towards Sustainable Chemistry (CSC), Chile.

Corresponding Author

Ximena Zarate^{c*}: <u>ximena.zarate@uautonoma.cl</u> and Eduardo Schott^{b,d}: <u>maschotte@gmail.com</u>

Abstract

We report the synthesis and theoretical study of two new colorimetric chemosensors with especial selectivity and sensitivity to Ni²⁺ and Cu²⁺ ions over other metal cations in CH₃CN/H₂O 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 to explain the selective sensing of the ions. For all the systems studied, the absorption band is characterized by a $\pi \rightarrow \pi^*$ transition centered in the ligand. Instead of Ni²⁺ and Cu²⁺ ions, the transition is set towards the σ^* molecular orbital with a strong contribution of $3d_x^2-y^2$ 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.

Introduction

The detection of metals either *in situ* or *in vivo* in a simple, sensible and selective way is challenging due to the complexity of the different biological and environmental matrices^{1–7}. This topic has inspired scientists to implement diverse methods to accomplish these aims^{8,9}. There are many analytical methods for the qualitative and quantitative determination of metal ions^{10–13}. The most employed are atomic absorption spectroscopy, chromatography, inductively coupled plasma atomic emission spectrometry, among others^{13–15}, which need sophisticated and expensive equipment^{10–13}. In this regard, chemosensors have been proven as promising devices for the detection of analytes due to their simplicity, sensitivity and selectivity^{12–16}. This analysis procedure can be performed *in vivo*, and *in situ*^{12–16}.

Optical sensors are chemosensors that detect analytes through measurable changes in properties such as absorbance, luminescence, light polarization, etc^{8,17}. They are excellent for the detection of analytes as distinct optical properties can be generated, increased, or diminished upon the incorporation of the analyte, which makes the signal easily detectable^{8,17–20}. Absorbance is the principle behind the colorimetric sensors. The analyte produces a change in the UV-Vis absorption spectra profile of the sensor, eventually leading to a color change. This is a clear advantage to design devices with accessible cost and rapid tracking of analytes *in vivo* and *in situ*. These peculiarities have increased the interest of researchers, notably in medical, biological and environmental science^{13–16,21,22}.

The nature of change in the UV-Vis absorption spectra is determined by the interaction of the metal ion with the acceptor or donor group in the sensor¹³. If a rich-electron metal ion interacts with an acceptor group of the sensor (with low-lying empty orbitals), the Metal to Ligand Charge Transfer (MLCT) mechanism can be activated. This mechanism causes a red-shift (bathochromic shift) of the bands in the absorption spectra and the oxidation of the metal. If the orbitals of the metal cation are empty or partially filled, they can interact with a donor group (with relatively high-energy lone pairs) of the sensor. Therefore, the Ligand to Metal Charge Transfer (LMCT) can occur and a hypsochromic shift (blue-shift) of the absorption bands is observed as well as the reduction of the metal¹³.

The development of chemical sensors for Cu²⁺ and Ni²⁺ ions has been rather slow compared to other metal ions¹³. Copper is the third most abundant metal in the Earth's crust, one of the most used metal in daily life and a vital nutrient for living organisms^{13,23}. This metal has a significant role in many physiological processes as it participates in the formation and performance of brain tissues, the heart, and other organs^{13,24}. However, when copper concentrations are deficient, less 100 mg in an adult person, or become excessive, they can produce alterations for the organism mainly hematological, and also leukopenia and neuro disorders such as Wilson's, Menke's, Alzheimer's and Parkinson's disease, among others^{13,23}. For this reason, the determination of serum ceruloplasmin concentration is used as a control method of this metal ion.^{25–27}. Nickel, unlike Copper, is required in very small amounts for the metabolic and synthetic processes in the organisms. However, like Copper, the excess of Nickel can produce serious effects, such as

disorders in the respiratory system, in the central nervous system, in the dermis, or even cancer, among others^{28–31}.

The development of synthetic colorimetric sensors involves expensive and prolonged synthetic protocols¹³. To reach this goal more efficiently, rational molecular engineering is a protocol to design molecular systems holding predetermined photophysical-properties. In this regard, as colorimetric sensors performance depends on the electronic properties, the theoretical and computational characterization constitutes a very helpful tool to explain the transduction mechanism principle^{32,33}.

Density Functional Theory (DFT) is the most common theoretical approach implemented to study metal ions sensors. The most consistent results are obtained by mixing Density Functional Theory (DFT) and the adiabatic approximation through the Time-Dependent Density Functional Theory (TD-DFT)^{34–38}. In this sense, it is necessary to obtain the geometry of the energy minimum of the sensor before and after the interaction with the analyte in the ground state. The vibrational frequencies analysis is performed for all the optimized structures to confirm that they are minima on the Potential Energy Surface (PES) and to analyze the coordination process^{34–37}.

In this framework, two colorimetric sensors with high selectivity and sensitivity towards Ni^{2+} and Cu^{2+} ions over other metal cations (Ag⁺, Ba²⁺, Pb²⁺, Zn²⁺, Co²⁺, Fe²⁺, and Mg²⁺) in acetonitrilewater (8:2) solution were synthesized and characterized. Metals show distinguishable chemistry properties and characteristics, i.e. the electronic structure of alkaline earth metals (Mg²⁺ and Ba²⁺) is different from metals with open-shell d orbitals (Cu²⁺, Ni²⁺, Co²⁺, and Fe²⁺) and with others with closed-shell d¹⁰ (Ag⁺, Pb²⁺, and Zn²⁺). These differences allow relating the behavior of the sensors with the characteristics of metal ions, which were deeply analyzed through a theoretical methods^{32,33}.

2. Experimental Section

2.1. General

For the measurement of sensitivity, perchlorate salts with different cations were used. The measured solutions contained concentrations of 10 μ M for ligands and 50 μ M of the perchlorate

of the respective metal (Ag⁺, Ba²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Zn²⁺, Co²⁺, Fe²⁺, and Mg²⁺). The sensor solution was made in an 8:2 mixture of acetonitrile-buffer (50 mM HEPES at pH 7.2), while the metal and capacity solutions of the measured solutions were made with an 8:2 acetonitrile-water mixture. The stoichiometry of the generated complex was determined through the Jobs method, stock solutions of 10 mM concentration of metal and ligand were used, increasing the molar fraction of the ligand from 0-1. The competition experiments were carried out with the mixtures already mentioned, the concentration of the ligation used was 10 µM and the concentration of the metals used was 20 µM for both the sensor metal and the competitor metal.

Synthesis of N,N-bis(pyridin-2-ylmethyl)aniline. The synthesis of N,N-bis(pyridin-2-ylmethyl) aniline was performed with a modification of the method described by Hrishikesan and Kannan³⁹. In summary, in a reflux system and nitrogen atmosphere, a 2-neck round bottom flask equipped with an addition funnel and condenser, 13 g (0.075mol) of K₂HPO₄ and 25 mL of dry acetonitrile were added. The solution was stirred at 0°C and 2.4 mL (0.026 mol) of aniline were added dropwise, the solution was kept under stirring for half an hour after the addition was finished. Afterward, 11.42 g (0.07mol) of picolyl chloride is added in small portions through the addition funnel. The final mixture is kept under reflux for 3 days. The solution is cooled, filtered, and washed with ethyl acetate. The solid is discarded and the solution is concentrated under vacuum up to 1/3 of its original volume. 10 mL of distilled water are added, and the pH increased to 8 using 3M NaOH. The extractions are performed with DCM (3 times 50mL) and the organic layer is dried with anhydrous sodium carbonate. The obtained red solution is dried under vacuum and the obtained solid is recrystallized with hot ethanol.

Synthesis of 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). The respective nitroaniline (10.2 mmol) was dissolved in 10 mL of THF and a solution of 0.523 g (7.58 mmol) of NaNO2 in 10mL of water is added. This solution is cooled to 0 °C and 1 mL of concentrated HCl is added dropwise under stirring during 30 min. The resulting solution is added gradually to a solution of 20 mL of THF, 20 mL of water and 1.87g (6.8 mmol) of N, N-bis

(pyridin-2-ylmethyl) aniline under stirring and at 0 ° C. The resulting mixture should be kept under stirring and at 0 °C for 3 days. The compound is purified on a silica flash column using hexane and ethyl acetate in polarity gradient (using each time 400mL of hexane:ethyl acetate in the following proportions=1:0;9:1;8:2;7:3;6:4;1:1;4:6;3:7;2:8;1:9;0:1). The obtained solid is recrystallized using hot methanol. It is possible to monitor the formation of product by TLC, differentiating the precursor and the products with similar RF using the vanadate sulfide reagent presenting gray and pink tones caused by the change to acidic pH, respectively⁴⁰. Compound A: 64% yield, dark red semi-translucent crystals. Elemental Analysis: C, 67.91; H, 4.75; N, 19.80; O, 7.54. The mass calculated for: C₂₄H₂₀N₆O₂: 424.46. Mass found: 425.0. The numeration and assignation of the protons and carbos can be found in the SI. ¹H NMR (400 MHz, Chloroform-d) δ 8.62 (d, J = 4.9 Hz, 2H, H-6, H-12), 7.84 (s, 1H, H-25), 7.82 (s, 1H, H-14), 7.80 (s, 1H, H-16), 7.68 – 7.61 (m, 2H, H-1, H-2, H-10, H-11), 7.59 (t, J = 7.7 Hz, 1H, H-26), 7.46 – 7.42 (m, 1H, H-27), 7.25 (d, J = 7.9 Hz, 2H, H-3, H-9), 7.20 (d, J = 4.6 Hz, 1H, H-28)), 6.82 (d, J = 9.2 Hz, 2H, H-13, H-17), 4.94 (s, 4H, H-21, H-22). ¹³C NMR (101 MHz, Chloroform-d) δ 157.6 (C-4, C-8), 151.9 (C-18), 150.0 (C-6, C-12), 147.3 (C-24), 146.0 (C-29), 144.8 (C-15), 137.1 (C-2, C-10), 132.8 (C-26), 129.0 (C-27), 126.2 (C-14, C-16), 123.9 (C-25), 122.5 (C-28), 120.9 (C-3.9), 118.7 (C-1, C-11), 112.5 (C-13, C17), 57.4 (C-21, C-22). Compound B: Yield 53%, orange crystals. Elemental Analysis: C, 67.91; H, 4.75; N, 19.80; O, 7.54. The mass calculated for: C₂₄H₂₀N₆O₂: 424.46. Mass found 424.6. The numeration and assignation of the protons and carbos can be found in the SI. ¹H NMR (400 MHz, Chloroform-d) δ 8.62 (s, 1H, H-29), 8.60 (d, J = 2.3 Hz, 2H, H-6, H-14), 8.18 (d, J = 6.4 Hz,1H, H-25), 8.11 (d, J = 6.8 Hz, 1H, H-27), 7.83 (d, J = 8.5 Hz, 2H, H-2, H-12), 7.66 -7.63 (m, 2H, H-18, H-20), 7.59 (t, J = 8.0 Hz, 1H, H-26), 7.25 (d, J = 7.9 Hz, 2H, H-3, H-11), 7.20 (dd, J = 7.5, 4.9 Hz, 1H, H-1, H-13), 6.83 (d, J = 8.9 Hz, 2H, H-17, H-21), 4.93 (s, 4H, H-7, H-21), 4.93 (s, 4H, H-7), 4.93 (s, 4H, H-7)H-9). ¹³C NMR (101 MHz, Chloroform-d) δ 157.6 (C-16) , 153.7(C-24) , 151.8(C-4,C-10) , 150.0(C-29), 149.1 (C-28), 144.2 (C-19), 137.1 (C-3, C-11), 129.8(C-26), 128.8 (C-27), 125.8 (C-2, C12), 123.5(C-25), 122.5(C-1, C-13), 120.9 (C-18,C-20), 116.5 (C-6, C-14), 112.5(C-17, C-21), 57.4(C-7, C-9).

Data Collection. Single crystals for A and B were obtained from the slow evaporation of ethanol solutions. Single-crystal X-Ray diffraction data sets were collected at 294 K for A and B up to a max 2 θ of ca. 61° on a Bruker APEX II diffractometer, using monochromatic MoK α radiation, λ = 0.71073 Å and a 0.3° separation between frames. Data integration was performed using SAINT V6.45A and SORTAV (Blessing, 1995) in the diffractometer package⁴¹. Table 1 shows a selection of bond lengths and angles, and torsion angles (A_c and B_c). The data collection and structural refinement parameters are given in Table S1. The structures were solved by direct methods using SHELXT-2014 (Sheldrick, 2014) and Fourier's difference methods, and refined by least-squares on F2 using SHELXL-2014/7 (Sheldrick, 2014) inside the WinGX program environment (Farrugia, 2012). Anisotropic displacement parameters were used for non-H atoms and the H-atoms were positioned in calculated positions and refined riding on their parent atoms. Figure 5a and b exhibit ORTEP views of both compounds. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, CCDC No. 1998031 and 1998032 for A and B, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336 033. E-mail: data request@ccdc.cam.ac.uk. Web page: http://www.ccdc.cam.ac.uk.

2.2. Computational Details.

We inform a set of calculations that account the structure and optical properties of the free sensors (**A** and **B**) and coordinated with metals of interest (**A**/M and **B**/M). All the S₀ state geometries were optimized with ORCA 4.0 code at the Density Functional Theory (DFT) level with a B3LYP functional and def2-TZVPP basis set for all atoms⁴². The structures were optimized to study the change in the UV-Vis spectra, through TD-DFT computations^{43,44}. The optical properties were analyzed through the Coulomb attenuating method (CAM-B3LYP) functionals, which was developed to minimize deviations in charge-transfer excitation energies^{43,44}. The solvation effects were considered via a Conductor–like Screening Model (CPCM) using the parameters of acetonitrile/water as solvents (\mathcal{E} =36.6 and refraction=1.344)⁴⁵. The coordination number was included explicitly, considering the most probable for each metal ion^{46–51}, as perchlorate or water

ligands. Due to Pb²⁺, Ba²⁺ and Mg²⁺ ions do not form coordination bonds, there were not considered. In all cases, the frequencies were calculated for showing that the geometries obtained are at a global minimum.

The nature of the interaction A/M and B/M is studied through the Morokuma-Ziegler decomposition scheme. The interaction energy (ΔE_{Int}) was analyzed by across fragments approximation to the molecular structure and the decomposition of the ΔE_{Int} (Equation 1)^{52–54} \Box .

$$\Delta E_{Int} = \Delta E_{Pauli} + \Delta E_{dis} + \Delta E_{Elec} + \Delta E_{Orb} \quad (1)$$

The ΔE_{Pauli} has a destabilizing role in the interaction and represents the contribution in energy due to the antisymmetric of the wave function result. The ΔE_{dis} is related to the distortion term and characterizes the quantity of energy required to promote the separated fragments from their equilibrium geometry to the structure until it will occupy in the combined molecule. The ΔE_{Elec} is associated with the electrostatic interaction nucleus–electron. The ΔE_{Orb} is originated from the relaxation of the system because of the mixing of occupied and unoccupied orbitals. This parameter can involve donor-acceptor interactions, charge-transfer, polarization, or electron-pair bonding. The ΔE_{Orb} is investigated through the Natural Orbital of Chemical Valence (NOCV) methodology proposed by Mitoraj^{54,55} \Box . The calculations of the Morokuma-Ziegler decomposition scheme were carried out using the Amsterdam Density Functional (ADF) code⁵⁶. Agree to this scheme, A/M and B/M systems were studied as two fragments that make up all system: M (Metal with ions perchlorate or water as coordination sphere) and sensor (A and B) (see Figure 1).



Figure 1. a) Molecular structure of A and B. b) Molecular structures of A/M and B/M systems with M: Ag⁺, Ba²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Zn²⁺, Co²⁺, Fe²⁺, and Mg²⁺.

3. Results and Discussion

3.1. General

As shown in Table 1, a good agreement between the experimental and theoretical results was obtained. A small deviation is observed in the torsion angle of the methylbenzene portion of the molecule. The crystallization of the sensors bounded to the studied metals was not possible. Experiments using metal-ligand concentrations 5:1 have demonstrated the chemosensing ability of compounds **A** and **B** of Cu^{2+} and Ni^{2+} cations. Furthermore, there is a drastic color change from yellow to colorless, which allows the effortless detection of the presence of the mentioned metals (see SI, Figure S1). This color change is explained as in the UV-Vis measurements one of the absorption bands of the sensors at 428 and 420 nm, for **A** and **B** respectively, decreases its intensity in the presence of Cu^{2+} and Ni^{2+} (see Figure 2). Furthermore, a new absorption band belonging to the sensor/metal interaction is observed. This absorption band has in all cases a hypsochromic shift to the characteristic signal of the free sensors. In the case of Fe^{2+} , a new band is also observed for the sensor/metal interaction, however, the color does not vanish, as for the two-other metal, due to the small shift of the mentioned band, thus there is no pronounced change in color.



Figure 2. UV-Vis absorption spectra of sensor **a**) **A** and **b**) **B** $[1 \times 10^{-5}$ M in CH₃CN/H₂O (80:20, v/v)] in the presence of different cations (5 equiv.) of Ag⁺, Ba²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Zn²⁺, Co²⁺, Fe²⁺, Mg²⁺ ions.

The determination of the sensor stoichiometry was performed for the metals Cu^{2+} and Ni^{2+} ; on the other hand, Fe^{2+} cation was not considered as the new absorption band does not allow for a color change, additionally, it presents a small difference between the signals. The sensor/metal stoichiometry was analyzed using the Jobs chart methodology, where the absorbance v/s molar fraction is plotted. For both studied metals, it was determined that the λ_{max} of the bands of each sensor-metal complex were reached in the solution with 0.5 molar fraction, which corresponds to a ratio of sensor/metal 1:1 (see Figure 3 and S2).



Figure 3. Job plot of a 1:1 complex of sensor **A** and Ni²⁺ ion, where the absorption was 345nm and was plotted against the mole fraction of the metallic ions at an invariable total concentration of 10 μ M in CH₃CN/H₂O (80:20, v/v).

Furthermore, selectivity is one of the most important characteristics of a sensor, as it determines its utilization efficiency in a real sample. Thus, to explore the practical applicability of **A** and **B** as Cu^{2+} and Ni^{2+} selective sensors, competition experiments were also performed in 2.0 equiv. of Cu^{2+} or Ni^{2+} mixed with 2.0 equiv. of background metal cations such as Ag^+ , Ba^{2+} , Cu^{2+} , Ni^{2+} ,

Pb²⁺, Zn²⁺, Co²⁺, Fe²⁺, and Mg²⁺. The absorbance was measured at the λ_{max} sensor-metal in the UV-Vis spectrum. The $\Delta A(A-A_0)$ parameter is used because the free sensors has still small absorbance in λ_{max} , and this procedure eliminates the signal of absorbance of the free sensor, which allows a better interpretation of the cation's interference. As can be observed in Figure 4, the largest interference was observed for Fe²⁺ and Co²⁺ for both studied sensors. As discussed before, the UV-Vis profile of the sensor-Fe²⁺ complex has a hypsochromic shift of the λ_{max} , however, there is no visual change upon sensor-metal interaction, thus competition is observed. In the case of Pb²⁺, when sensor **A** is used a decrease in the absorption band of the complexes with Cu²⁺ and Ni²⁺ is observed (see Figure 4 and S3). In contrast, sensor **B** does not show Pb²⁺ interference (see Figure S3).





The crystal structure for both studied sensors was determined in its free state. ORTEP views of both structures are shown in Figure 5. Compound A crystallizes as two molecules per asymmetric unit with similar but not identical conformations. As could be observed both structures show an almost planar structure on the phenyl azo ring portion. Based on the crystal structure analysis and theoretical calculations, a series of angles, torsion angles and bond lengths of interest are analyzed (see Table 1). As compound A crystallizes in two molecules per asymmetric unit, he conformational magnitudes in Table 1 are given as the average of both. On the other hand, the skeleton of the B molecule exhibits a disorder following an approximate binary axis with unequal populations of 62:38; in this case, only the major component has been listed. Table 1 shows good agreement between the experimental and theoretical data for the structures. The variation is only significant for the C_1 - N_4 - C_3 - C_6 of the B_C and C_1 - N_4 - C_2 - C_4 to both (A_C and B_C). This difference is due to the freedom degrees of rotation which these angles have in solution. Root Mean Square Deviations (RMSD) provide a quantitative evaluation of the differences between two structures, based on their atomic positions. Per this parameter, the differences are $\sim 4\%$ and $\sim 6\%$ to A and B, respectively. Furthermore, a comparison between the PXRD pattern from the crystal and the bulk sample was performed. Both samples show the same PXRD pattern, showing that both samples have the same composition, see SI (Figure S14).



Figure 5. ORTEP diagrams with 50% of probability ellipsoids for compounds a) **A**, and b) **B**. Optimized structure of sensors c) **A** and d) **B**.

Table 1. Structural parameters obtained through X-ray crystal structure analysis ($^{*}A_{C}$ and B_{C}) and theoretical calculated (A_{T} and B_{T}).

System	A _T	A _C	B _T	B _C
$d(C-N_1)$	1.472	1.463(5)	1.477(4)	1.448
$d(C-N_2)$	1.408	1.4605(4)	1.414(4)	1.455
$d(C-N_3)$	1.396	1.46(4)	1.396(5)	1.441
$d(C_1-N_4)$	1.375	1.373(5)	1.375(4)	1.364
$d(C_2-N_4)$	1.452	1.456(5)	1.452(5)	1.450
$d(C_3-N_4)$	1.453	1.4455(5)	1.453(5)	1.453
$d(C_4-N_5)$	1.334	1.2995(5)	1.333(5)	1.331
$d(C_5-N_5)$	1.332	1.3615(6)	1.332(6)	1.335
$d(C_6-N_6)$	1.337	1.3225(5)	1.337(5)	1.335
$d(C_7-N_6)$	1.331	1.353(7)	1.331(6)	1.331

$d(N_2=N_3)$	1.255	1.216(4)	1.255(4)	1.238
$\alpha(C-N_2=N_3)$	114.7°	109.7(3)°	114.9(4)°	112.6
$\alpha(N_2=N_3-C)$	116.1°	112.0(3)°	116.3(4)°	112.5
$\alpha(N_1-C-C)$	120.7°	120.4(4)°	118.8(3)°	118.5
γ(C-N=N-C)	177.1°	178.75(3)°	-179.6(4)°	-179.8
$\gamma(N_4-C_2-C_4-N_5)$	37.5°	-66.95(5)°	36.2(4)°	157.8
$\gamma(N_4-C_3-C_6-N_6)$	176.9°	10.6(4)°	177.1(4)°	174.8
$\gamma(C_1-N_4-C_2-C_4)$	91.0°	77.6(5)°	81.3(5)°	76.7
$\gamma(C_1-N_4-C_3-C_6)$	81.4°	79.2(5)°	91.1(5)°	76.9

*Where α and γ are bond angles, and *d* is the bond lengths in Å. A_c is the average for the two molecules per asymmetric unit

3.2. Optical properties and sensing mechanisms

The UV-Vis absorption spectra of **A** and **B** are experimentally characterized by two bands at ~260-428 nm and ~260-420 nm, respectively. The UV-vis absorption spectra show a blue-shift (~ 90 nm) of the maximum absorption peak upon the interaction with Cu²⁺ and Ni²⁺ ions. To design more efficient and effective systems in the future, the rationalization of the sensing mechanisms of metal ions is important. In this sense, quantum chemical computations were also carried out for structures of **A**, **B**, and metal complex **A**/M and B/M, (where M: Ag⁺, Ba²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Zn²⁺, Co²⁺, Fe²⁺, Mg²⁺) in the ground state (S₀). The structure geometries were optimized in the ground state (S₀) states and where the input data to calculate the excitations that constitute the UV-Vis absorption spectra. The optimized geometries are shown in figures from 5 to 7.

The coordination of the metal is quasi-planar square for the Cu^{2+} and Ni^{2+} ions, trigonal planar for the Ag⁺ ions, hexagonal for the Co²⁺ and Fe²⁺ ions, and tetrahedral for other metals ions (see Figure 6 and 7). The coordination obtained are characteristic of these metal ions^{46,47,49,51,57}. When **A** and **B** interact with the metal ions, a structural change in the S₀ state of these sensors is observed. As this change is produced in all systems (although de sensors lose-more planarity in the complexes with Cu²⁺ and Ni²⁺ ions) (see Figures 6 and 7), it is not possible to directly correlate this change with the marked differences in their absorption spectra only through this analysis. In this sense, a time-dependent analysis (TDDFT) was performed to see the nature of the transitions.



Figure 6. Optimized structures of the A/M (M: Ag⁺, Ba²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Zn²⁺, Co²⁺, Fe²⁺, Mg²⁺) complexes in S₀ states.



Figure 7. Optimized structures of the B/M (M: Ag⁺, Ba²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Zn²⁺, Co²⁺, Fe²⁺, Mg²⁺) complexes in S₀ states.

TDDFT allowed to reproduce the two main absorption bands observed experimentally for A and **B** at \sim 260 and \sim 420 nm (these transitions are tabulated in Tables 2 and 3). As can be observed, there is a small difference with the experimental values, around ~ 30 nm, which is within the error range reported for TDDFT computations^{34,58}. The experimentally blue-shift of the maximum UVvis absorption band (~ 90 nm) induced by the interaction of A and B with Cu^{2+} and Ni^{2+} ions are also well reproduced. The smallest blue-shift of the absorption band in the case of Fe^{2+} (~30 nm) systems are reproduced as well (see Table 2 and 3). In the **B**/M systems, a blue-shift can be seen for other metal ions (Zn^{2+} , Mg^{2+} , and Pb^{2+}) (see Table 3, Figure S4 and S5), although this behavior is not experimentally evidenced. However, the calculated absorption band is characterized by the $\pi \rightarrow \pi^*$ transition centered on the ligand for all systems (see Figure from S4 to S6), except for the complexes with Cu²⁺ and Ni²⁺ ions. For these systems, the transition is characterized by a σ^* molecular orbital with a strong contribution of the $3d_{x^{2}-y^{2}}$ transition for the Cu²⁺ and Ni²⁺ ions (see Table 2, Figure 8 and 9). These absorptions imply a ligand to metal charge transfer (LMCT) that results in a blue-shift in the absorption band, as experimentally evidenced. The blue-shift is characteristic of the LMCT transition¹³ and is very common in transition-metal complexes^{47,59,60}. This charge transfer can be established by the

Table 2. Singlet \rightarrow Singlet absorption data in A and A/M considering the solvent effect (Acetonitrile, ε =3	36.6
and refraction=1.344).	

availability of its d orbitals for accepting electrons from some ligand rich in electrons^{46,59}.

		CAM-B	3LYP	B3LYP					
Systems	ems $^*\lambda_a$ f Active		Active MOs	Α	λ_a f		Active MOs	Α	
Α	336.8	0.240	H→L+1	$\pi \rightarrow \pi^*$	393.9	1.099	H→L+1	$\pi \rightarrow \pi^*$	
	222.7	0.103	H - 2→L+2	$\pi { ightarrow} \pi^*$	264.9	0.128	$H\rightarrow L+7$	$\pi {\rightarrow} \pi^*$	
A /TNT•7+	297.6	1.020	H-1 \rightarrow L+3	$\pi \rightarrow 3d_{x^2-y^2}$	320.9	0.436	H-1 \rightarrow L+3	$\pi \rightarrow 3d_{x^2-y^2}$	
A/INI-*	248.8	0.130	H - 3→L+1	$\pi {\rightarrow} \pi^*$	266.7	0.165	H-3→L+1	$\pi {\rightarrow} \pi^*$	
A/Cu ²⁺	295.3	0.356	H_{β} -1 \rightarrow L_{β} +1	$\pi \rightarrow 3d_{x^{2}-y^{2}}$	302.7	0.435	H_{β} -1 \rightarrow L_{β} +1	$\pi \rightarrow 3d_{x^2-y^2}^2$	
	222.8	0.130	H_{β} -3 \rightarrow L_{β} +1	$\pi { ightarrow} \pi^*$	264.1	0.240	H_{β} -3 \rightarrow L_{β} +1	$\pi {\rightarrow} \pi^*$	
A/Co ²⁺	309.8	0.727	$H_{\alpha} \rightarrow L_{\alpha}$	$\pi { ightarrow} \pi^*$	412.8	0.545	H_{α} -1 \rightarrow L _{\alpha} +1	$\pi { ightarrow} \pi^*$	

	251.3	0.103	H_{α} -4 \rightarrow L_{α}	$\pi \rightarrow \pi^*$	239.1	0.046	H_{α} -3 \rightarrow L _{α} +2	$\pi \rightarrow \pi^*$
A /7 ?+	303.7	0.845	H→L	$\pi { ightarrow} \pi^*$	404.0	0.632	H-1→L	$\pi \rightarrow \pi^*$
A/20	249.9	0.129	H-3→L	$\pi { ightarrow} \pi^*$	260.4	0.109	H-4→L+1	$\pi { ightarrow} \pi^*$
A /IE - 2+	328.8	0.564	H_{α} -1 \rightarrow L_{α}	$\pi { ightarrow} \pi^*$	367.5	0.160	H_{α} -1 \rightarrow L_{α}	$\pi \rightarrow \pi^*$
AITC	225.1	0.100	H_{α} -1 \rightarrow L_{\alpha}+2	$\pi { ightarrow} \pi^*$	243.3	0.279	H_{α} -1 \rightarrow L_{\alpha}+5	$\pi {\rightarrow} \pi^*$
$\Lambda / \Lambda \sigma^+$	362.6	0.962	$H \rightarrow L+1$	$\pi { ightarrow} \pi^*$	401.4	0.689	H-2→L+1	$\pi \rightarrow \pi^*$
A/Ag	225.6	0.138	H-4→L	$\pi {\rightarrow} \pi^*$	268.2	0.124	H-4→L+2	$\pi {\rightarrow} \pi^*$
Λ/Ma^{2+}	296.1	0.694	H→L	$\pi { ightarrow} \pi^*$	367.5	0.284	H-1→L	$\pi \rightarrow \pi^*$
A/Mg	249.3	0.132	H-3→L	$\pi { ightarrow} \pi^*$	304.8	0.539	H-1→L+1	$\pi {\rightarrow} \pi^*$
A /Bo ²⁺	361.2	0.245	H→L	$\pi { ightarrow} \pi^*$	391.2	0.484	$H \rightarrow L+1$	$\pi {\rightarrow} \pi^*$
A/Da	319.2	0.326	H-1→L	$\pi {\rightarrow} \pi^*$	269.4	0.197	H-5→L+1	$\pi { ightarrow} \pi^*$
A /Ph2+	320.4	0.132	H→L	$\pi {\rightarrow} \pi^*$	384.5	0.183	H-1→L	$\pi \rightarrow \pi^*$
A/ r 0-	301.5	0.887	H-1 \rightarrow L+2	$\pi {\rightarrow} \pi^*$	314.3	0.178	H-1→L+2	$\pi {\rightarrow} \pi^*$

*Where λ_a is the theoretical absorption wavelength in nm, A is the assignment of transitions, *f* is the oscillator strength, H (HOMO) and L (LUMO).

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Table 3. Singlet \rightarrow Singlet absorption data in B and B/M considering the solvent effect (Acetonitrile, ϵ =36.6 and refraction=1.344).

		CAM-I	B3LYP	B3LYP				
Systems	*λ _a	f	Active MOs	Α	λ_{a}	f	Active MOs	А
В	379.9	1.114	H→L	$\pi \rightarrow \pi^*$	407.4	1.420	H→L+1	$\pi \rightarrow \pi^*$
	239.5	0.168	$H\rightarrow L+4$	$\pi {\rightarrow} \pi^*$	262.3	0.193	$H\rightarrow L+7$	$\pi {\rightarrow} \pi^*$
D/NI;2+	295.5	1.318	$H \rightarrow L+1$	$\pi \rightarrow 3d_{x^2-y^2}^2$	325.5	0.890	H-1→L+1	$\pi \rightarrow 3d_{x^2-y^2}$
D/INI-	216.5	0.203	$H \rightarrow L+2$	$\pi {\rightarrow} \pi^*$	251.0	0.111	H - 4→L+2	$\pi {\rightarrow} \pi^*$
$\mathbf{D}/\mathbf{C}\mathbf{w}^{2+}$	308.1	0.215	H_{β} -1 \rightarrow L_{β} +1	$\pi \rightarrow 3d_{x^{2}-y^{2}}^{2}$	311.2	0.663	H_{β} -1 \rightarrow L_{β} +1	$\pi \rightarrow 3d_{x^2-y^2}^2$
D/Cu⁻	249.5	0.241	H_{β} -5 \rightarrow L_{\beta}+3	$\pi {\rightarrow} \pi^*$	231.9	0.061	H_{β} -5 \rightarrow L_{\beta}+3	$\pi {\rightarrow} \pi^*$
$\mathbf{P}/\mathbf{C}\mathbf{o}^{2+}$	319.5	1.157	$H_{\alpha} \rightarrow L_{\alpha}$	$\pi \rightarrow \pi^*$	347.9	0.291	$H_{\alpha} \rightarrow L_{\alpha} + 1$	$\pi {\rightarrow} \pi^*$
B/C0 ²⁺	254.1	0.263	H_{α} -6 \rightarrow L _{α} +1	$\pi {\rightarrow} \pi^*$	275.0	0.132	H_{α} -4 \rightarrow L _a +1	$\pi {\rightarrow} \pi^*$
D/7 2+	297.0	1.370	$H\rightarrow L+2$	$\pi \rightarrow \pi^*$	336.9	1.257	$H \rightarrow L+1$	$\pi \rightarrow \pi^*$
D/ Z.11 ⁻	233.6	0.352	$H\rightarrow L+5$	$\pi {\rightarrow} \pi^*$	268.7	0.180	H - 4→L+1	$\pi {\rightarrow} \pi^*$
$\mathbf{D}/\mathbf{E}_{2}^{+}$	321.5	1.030	$H_{\alpha} \rightarrow L_{\alpha}$	$\pi \rightarrow \pi^*$	371.6	0.208	H_{α} -2 \rightarrow L_{α}	$\pi {\rightarrow} \pi^*$
D/TC	254.1	0.295	H_{α} -7 \rightarrow L_{α}	$\pi {\rightarrow} \pi^*$	235.8	0.607	H_{α} -2 \rightarrow L _a +1	$\pi {\rightarrow} \pi^*$
$\mathbf{P}/\mathbf{A}\mathbf{a}^+$	362.7	1.187	H→L	$\pi \rightarrow \pi^*$	412.3	0.839	H→L	$\pi \rightarrow \pi^*$
D/Ag	238.5	0.144	$H\rightarrow L+6$	$\pi {\rightarrow} \pi^*$	257.4	0.159	H - 1→L+8	$\pi {\rightarrow} \pi^*$
B/M _a 2+	310.2	1.163	$H \rightarrow L+1$	$\pi \rightarrow \pi^*$	336.4	1.236	$H \rightarrow L+1$	$\pi {\rightarrow} \pi^*$
D/Mg	165.5	0.178	H-2→L+4	$\pi {\rightarrow} \pi^*$	187.7	0.165	H-4→L	$\pi {\rightarrow} \pi^*$
B/Ba ²⁺	333.7	1.261	H→L	$\pi \rightarrow \pi^*$	372.9	1.171	$H \rightarrow L+1$	$\pi \rightarrow \pi^*$
D/Da	234.5	0.237	H-2→L+1	$\pi {\rightarrow} \pi^*$	272.4	0.279	H-4→L+1	$\pi {\rightarrow} \pi^*$
B/Dh2+	308.2	1.182	H→L	$\pi { ightarrow} \pi^*$	328.1	1.064	H-1→L+2	$\pi {\rightarrow} \pi^*$
D/ P U-	255.3	0.364	H-4→L	$\pi {\rightarrow} \pi^*$	265.5	0.102	H-4→L+2	$\pi {\rightarrow} \pi^*$

*Where λ_a is the theoretical absorption wavelength in nm, A is the assignment of transitions, *f* is the oscillator strength, H (HOMO) and L (LUMO).

On the other hand, when the solvent effect is not considered, the relative energy of the transitions displays significant change and the λ_a are not closer to the experimental wavelength (Table S4 and

S5). The computed data using B3LYP functional resemble the experimental results more than by CAM-B3LYP values in terms of the relative energy of the transition (see Tables 2 and 3).



Figure 8. Molecular orbital diagram based on the S₀ state (absorption) in the free sensors (A and B), in the A/Ni²⁺ and B/Ni²⁺. Where λ_a is the theoretical absorption wavelength and *f* is the oscillator strength.

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Figure 9. Molecular orbital diagram based on the S₀ state (absorption) in the A/M and B/M (M: Cu²⁺ and Co²⁺) complexes in S₀ states. Where λ_a is the theoretical absorption wavelength and *f* is the oscillator strength.

The analysis of the Morokuma-Ziegler decomposition schema provides the compression of the composition of the interaction energy. According to this method, the electron transfer is established from the ligand to metal and the metal to ligand (Figures 10 and S7 to B/M). The interaction does not exhibit a marked difference between orbital or electrostatic character. Only, results for Ni²⁺, Cu²⁺ and Ag⁺ ions, show a large electrostatic character. This implies that the LMCT can be more favored in these systems than in the others (see it in Tables 4, S4 and S5).

Table 4. Morokuma-Ziegler EDA (contribution to the ΔE_{Int} in %)*.

Systems	ΔE_{Int}	ΔE _{Pauli}	ΔE_{Elec}	ΔE_{Orb}	ΔE_{Disp}	%E _{elec}	%E _{orb}	%E _{disp}	k
A/Ni ²⁺	-226.6	259.0	-242.2	-228.4	-15.0	50	47	3	-120.0
A/Cu ²⁺	-184.0	196.6	-203.2	-161.8	-15.6	53	43	4	-70.4
B/Ni ²⁺	-237.9	236.3	-240.4	-218.3	-15.5	51	46	3	-104.3
B/Cu ²⁺	-185.5	196.7	-201.9	-1617	-15.6	53	43	4	-70.1



Figure 10. Contours of the NOCV deformation density (ρ) for A with metals.

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4. Conclusions

Two new chemosensors were experimentally developed, they show high selectivity and sensitivity to Cu²⁺ and Ni²⁺ ions over other metal cations in CH₃CN/H₂O solution. These sensors exhibit a drastic color change from yellow to colorless, which allows the detection of the presence of the mentioned metals. The sensor/metal interaction, to Cu²⁺ and Ni²⁺ ions, induced a new absorption band with a hypsochromic shift respect to the characteristic signal of the free sensors. For both studied metals correspond a ratio of sensor/metal of 1:1. The theoretical research has enabled us to rationalize the behaviors of the two sensors. The blue-shift of the maximum UV-vis absorption band (~ 90 nm), by the interaction of the sensors with Cu^{2+} and Ni^{2+} ions, are reproduced through the TDDFT. The smallest blue-shift of the absorption band in the Fe^{2+} (~30 nm) systems is reproduced too. As the systems B/M (M: Zn²⁺, Mg²⁺, and Pb²⁺) theoretically show also a blue shift in the absorption band, it is necessary to analyze the nature of the transitions to correctly explain the experimental behavior of the sensors. For all systems, except for complex with Ni²⁺ and Cu²⁺ ions, the absorption band is characterized by the $\pi \rightarrow \pi^*$ transition centered in the ligand. Instead of Ni²⁺ and Cu²⁺ions, the transition is set towards the σ^* molecular orbital with a strong contribution of $3d_{x^{2}-y^{2}}^{2}$ transition for Ni⁺² and Cu⁺² ions. These absorptions imply an LMCT mechanism that results in the blue shift in the absorption band of these systems. When the solvent effect is not considered, the relative energy of the transition displays significant change. The computed data using B3LYP functional resemble the experimental results more than by CAM-B3LYP values in terms of the relative energy of the transition. According to the Morokuma-Ziegler decomposition schema, the electron transfer is established from the ligand to metal and the metal to ligand for all systems. This interaction does not present a marked orbital or electrostatic character. Only for the Ni²⁺, Cu²⁺ and Ag⁺ ions are shown a large electrostatic character. This result entails that the LMCT can be more favored in these systems than the others.

Supporting Information

Crystal data and structure refinement, job plots for all studied sensors, competition measurements, TDDFT results, molecular orbital diagram for the studied sensors, Morokuma-Ziegler EDA, NMR spectra, Mass spectra and PXRD.

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"TOC Graphic"

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