Electronic Supplementary Information

Zn^{2+} and Cu^{2+} complexes of a Fluorescent Scorpiand-type Oxadiazole Azamacrocycle Ligand: Crystal Structures, Solution Study and Optical Properties

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Paoli, Patrizia Rossi, Enrique García-España and Mario Inclán

Table S1. Crystallographic data and refinement parameters for compounds [Zn**L**]$(ClO_4)_2$ and [Cu**L**]$(ClO_4)_2$

Figure S1 ORTEP-3 view of $[Cu\mathbf{L}]^{2+}$ as found in the solid state structure of [Cu**L**]$(ClO_4)_2$. Ellipsoids are drawn at 15% probability.

Figure S2. Side (left) and top (right) views of the $[Zn\mathbf{L}]^{2+}$ cation as found in the X-ray structures of [Zn**L**]$(ClO_4)_2$ (all atoms ball and stick) superimposed to **FUTPIV (**stick, green**)** and **ZUHPAV** (stick, red). Structures are superimposed by the atoms labelled with asterisk.

Figure S3. Absorption (**a**) and emission (**b**) spectra of **L**, as a function of pH in aqueous solution. [**L**]=$7.8\cdot10^{-5}$ M, λ_{ex}=275 nm.

Figure S4. Distribution diagram of the species (−), [**L**] = $5.0\cdot10^{-6}$, ([Zn^{2+}] = $7.5.0\cdot10^{-6}$, I = 0.15 M $NaClO_4$, T = 298.1 K

Figure S5. ESI-MS spectra of (A) a 20 μM solution of L and (B) a solution containing 20 μM of L and 200 μM of Zn^{2+}.

Figure S6. Absorption (**a**) and emission (**b**) spectra of **L**-Zn(II) system, as a function of pH in aqueous solution. [**L**]= [Zn^{2+}] = $1.8\cdot10^{-5}$ M, λ_{ex}=275 nm

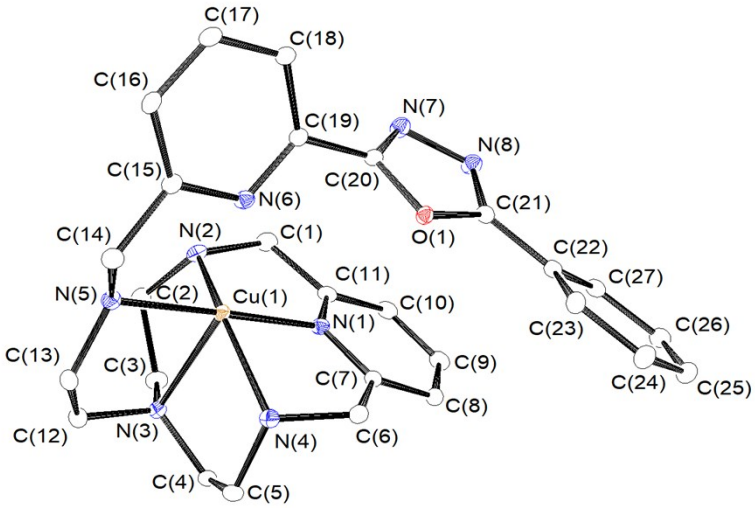
Figure S7. Absorption (**a**) and emission (**b**) spectra of **L**-Zn(II) system, as a function of pH in aqueous solution; **L** to Zn(II) 1:1 (− line); **L** to Zn(II) 2:3 (- - - line). [**L**]= $4.8\cdot10^{-6}$ M, λ_{ex}=275 nm.

Figure S8. (a) Absorption and **(b)** emission spectra of the Cu^{2+}/**L** system in an aqueous buffer (HEPES, 0.5 M) solution at pH = 7.4; obtained by adding several amounts of Cu^{2+} up to 2 equivalents.

Figure S9. Absorption spectra of the Zn^{2+}/**L** system in acetonitrile solution obtained by adding several amounts of Zn^{2+} up to 2 equivalents with respect to **L**; [L] = 1.0 x 10^{-5} M.

Table S1. Crystallographic data and refinement parameters for compounds [Zn**L**]$(ClO_4)_2$ and [Cu**L**]$(ClO_4)_2$.

	[Zn**L**]$(ClO_4)_2$	[Cu**L**]$(ClO_4)_2$
Empirical formula	$C_{27}H_{32}Cl_2ZnN_8O_9$	$C_{27}H_{32}Cl_2CuN_8O_9$
Formula weight	748.87	747.04
Temperature (K)	100	110
Wavelength (Å)	1.54184	1.54184
Crystal system, space group	Orthorhombic, Pbca	Orthorhombic, Pbca
Unit cell dimensions (Å)	a = 12.4453(2) b = 14.3947(3) c = 33.7578(4)	a = 12.3325(3) b = 14.5161(4) c = 33.7255(7)
Volume ($Å^3$)	6047.6(2)	6037.5(3)
Z, D_c (mg/cm^3)	8, 1.645	8, 1.644
μ (mm^{-1})	3.352	3.249
F(000)	3088	3080
Crystal size (mm)	0.35x0.28x0.25	0.28x0.24x0.23
θ range (°)	8.828 – 143.798	8.884-144.158
Reflections collected / unique	22850 / 5793	16740 / 5774
Data / parameters	5793 / 520	5774 / 520
Goodness-of-fit on F^2	1.068	1.053
Final R indices [$I>2\sigma(I)$]	R1 = 0.0432, wR2 = 0.1127	R1 = 0.0381, wR2 = 0.0991
R indices (all data)	R1 = 0.0659, wR2 = 0.1287	R1 = 0.0495, wR2 = 0.1086



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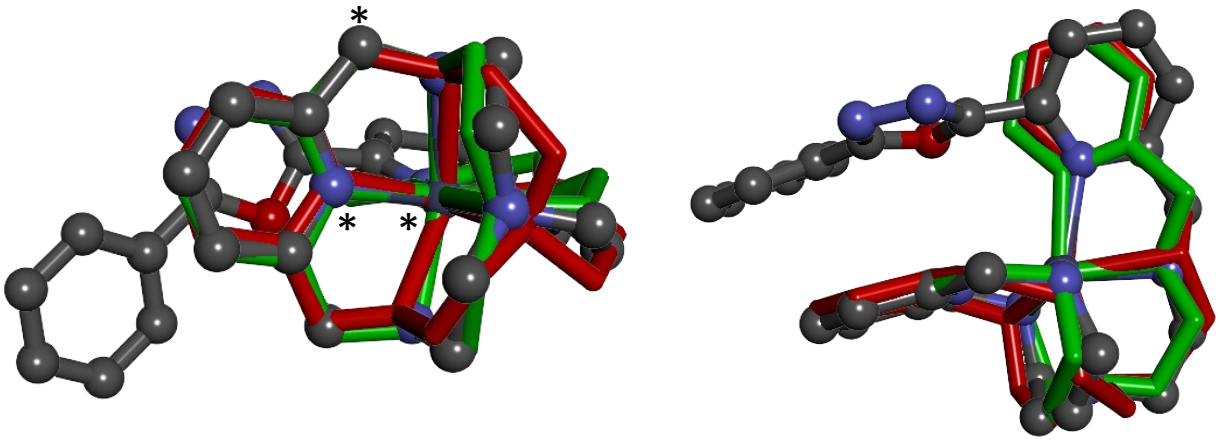

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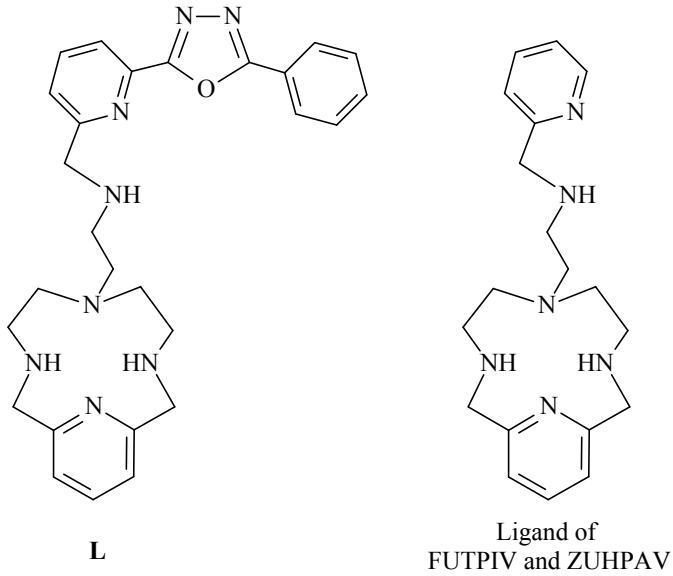
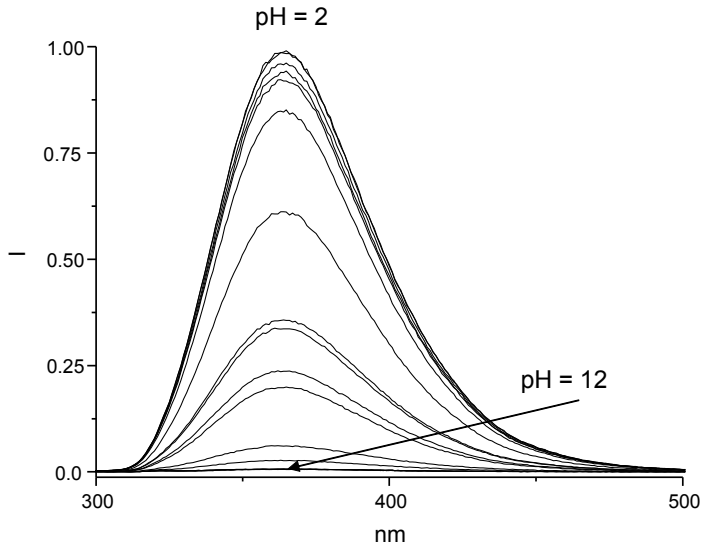


a)

Figure S2. (**a**) Schematic drawing of **L** and related ligand. (**b**) Side (left) and top (right) views of the $[Zn\mathbf{L}]^{2+}$ cation as found in the X-ray structures of $[ZnL](ClO_4)_2$ (all atoms ball and stick) superimposed to **FUTPIV** (stick, green) and **ZUHPAV** (stick, red). Structures are superimposed by the atoms labelled with asterisk.



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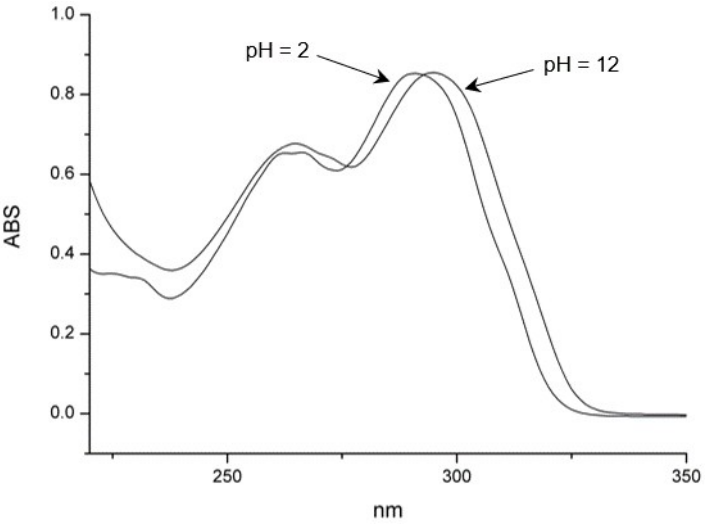

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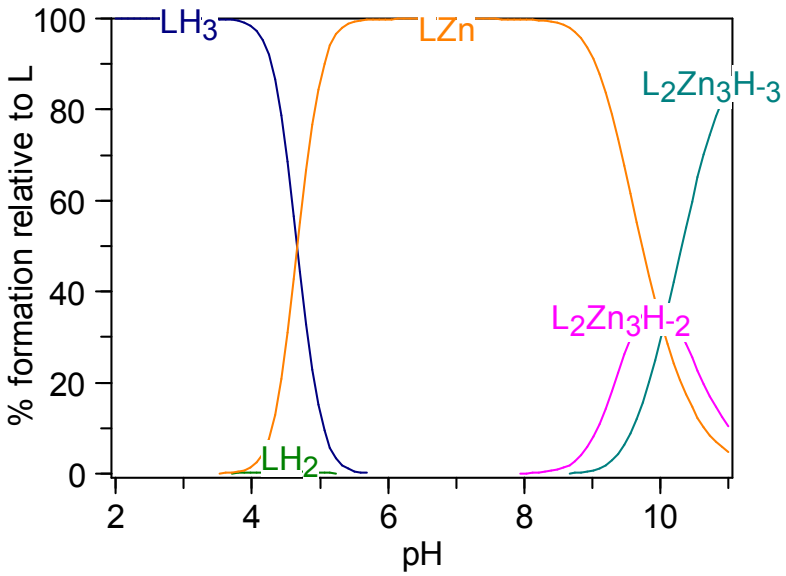

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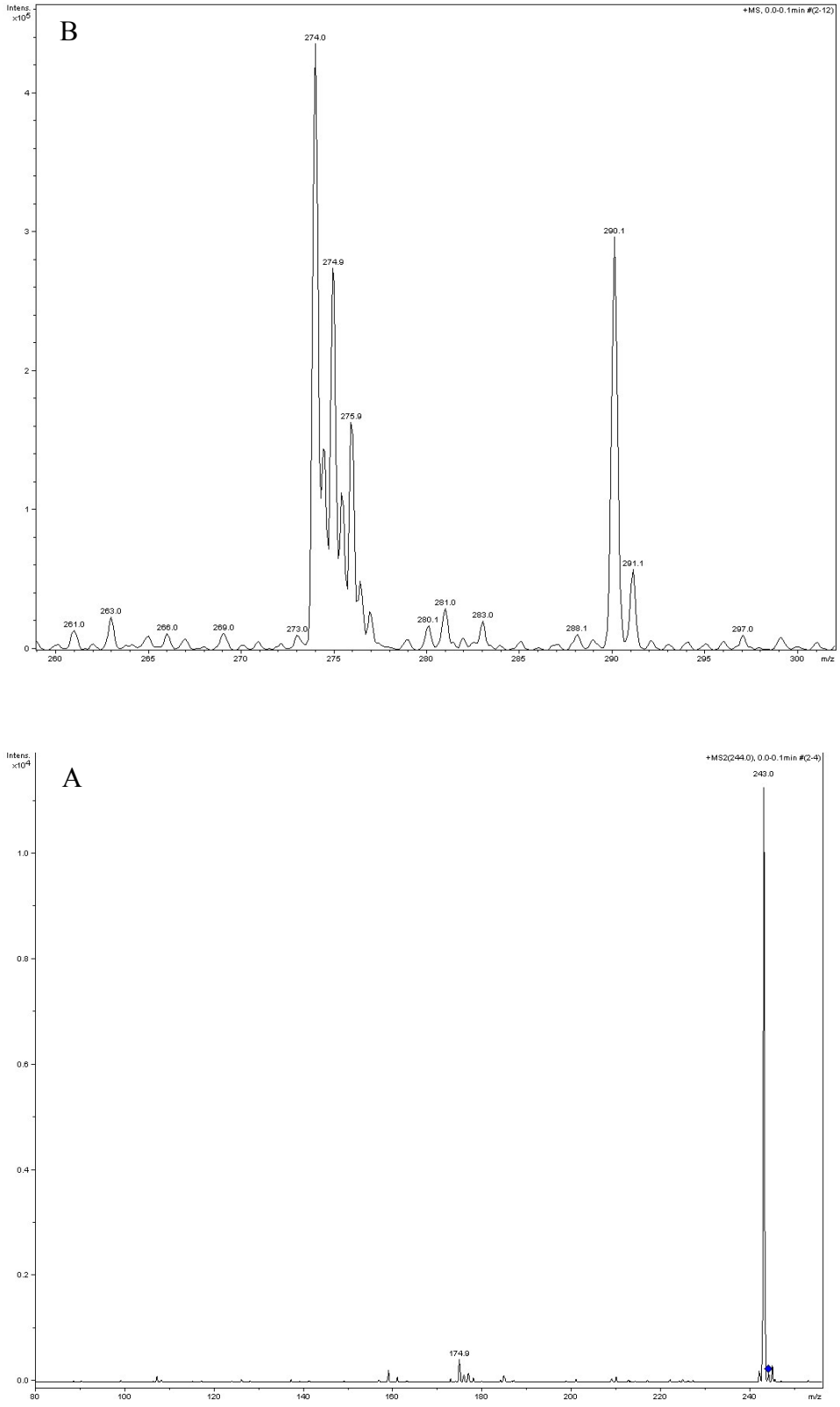

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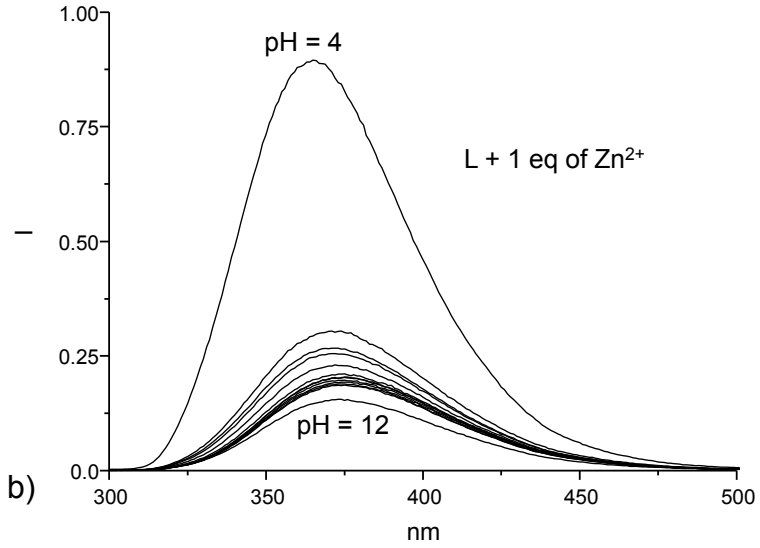

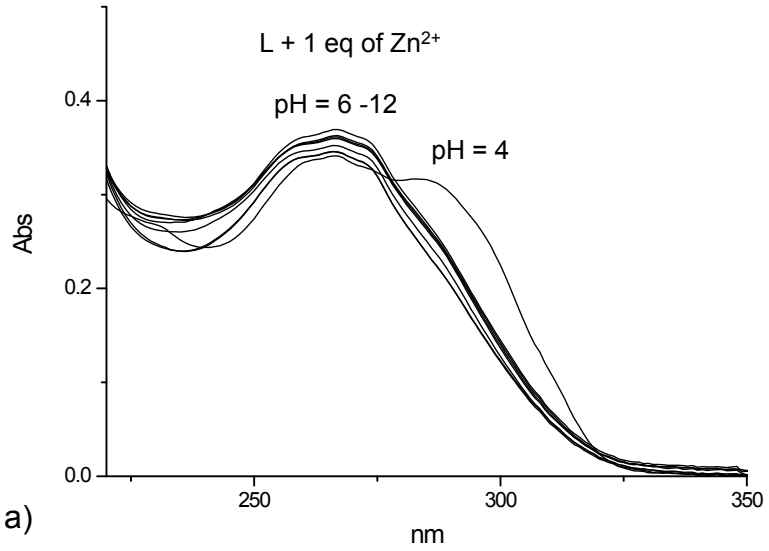

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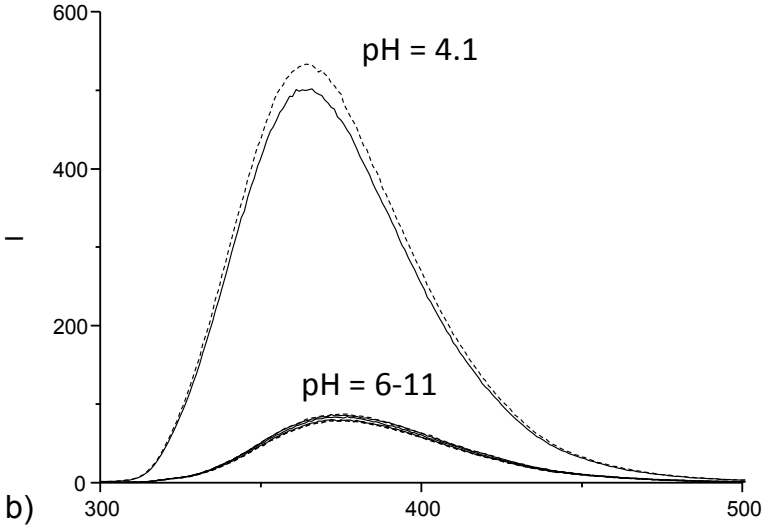

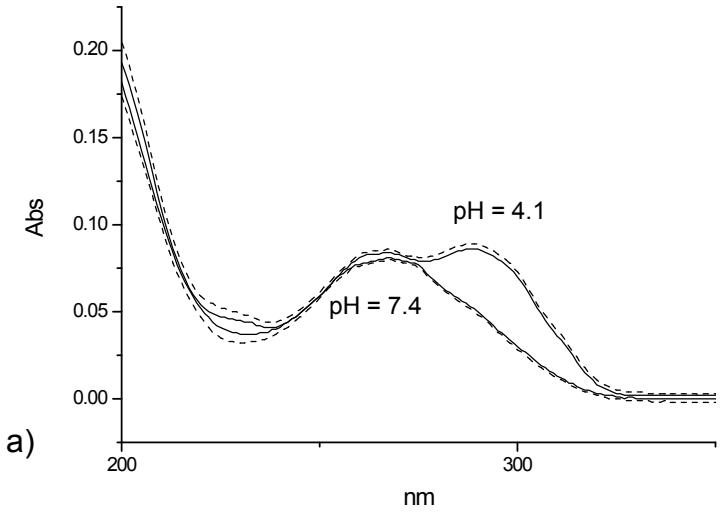

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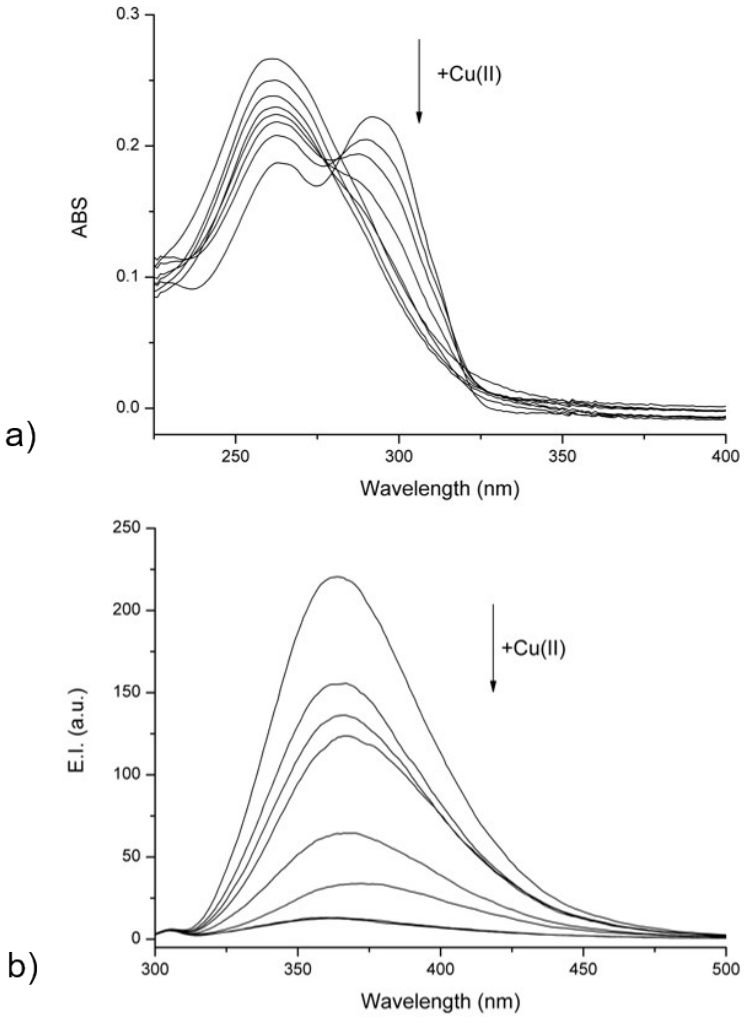

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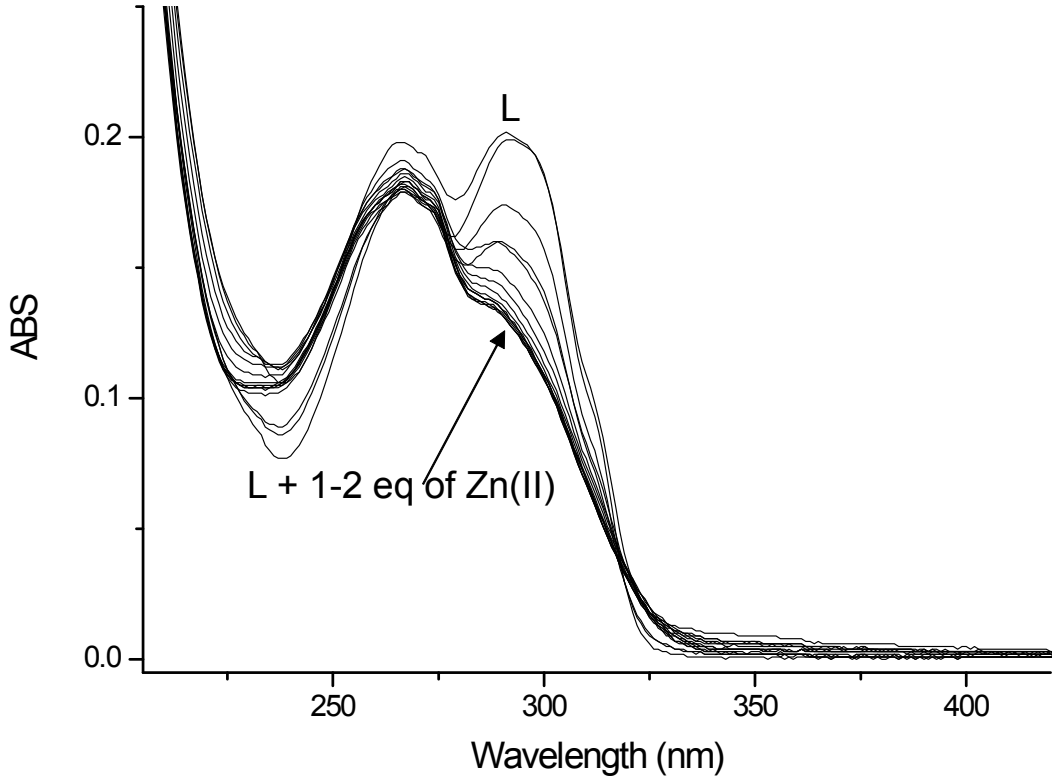

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