Supplementary Material

Experimental-theoretical approach for the chemical detection of glyphosate and its potential interferents using a copper complex fluorescent probe

Guilherme Martins[1], Karolyne V. Oliveira[1], Saddam Weheabby[2], Ammar Al-Hamry[2], Olfa Kanoun[2], Tobias Rüffer[3], Benedito J. C. Cabral[1,4] and Leonardo G. Paterno[1*]

[1]Laboratory of Research on Polymers and Nanomaterials, Institute of Chemistry, University of Brasilia, 70910-900, Brasília-DF, Brazil
[2]Chemnitz University of Technology, Professorship Measurement and Sensor Technology, 09126 Chemnitz, Germany
[3]Chemnitz University of Technology, Faculty of Natural Sciences, Institute of Chemistry, Inorganic Chemistry, 09107 Chemnitz, Germany
[4]BioISI-Biosystems and Integrative Sciences Institute and Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Lisboa, 1749-016, Portugal

*corresponding author: lpaterno@unb.br
ORCID id: 0000-0001-7716-0318

Summary

3.1. $[^nBu_4N]_2[Cu(opba)]$ structure

The synthesis of $[^nBu_4N]_2[Cu(opba)]$ was subject of previous contributions [1,2], where its structural features were discussed in detail. Herein, a set of spectroscopic methods with the addition of Raman and fluorescence spectra were employed. Figure S1 displays FT-IR, Raman, UV-Vis and fluorescence spectra of $[^nBu_4N]_2[Cu(opba)]$. Assignments of main bands presented in FT-IR (Figure S1a) and Raman (Figure S1b) spectra made in accordance with the literature [3] are collected in Table 1 and confirm the structure of $[^nBu_4N]_2[Cu(opba)]$. UV-Vis spectrum (Figure 2c) shows a main absorption peak centered at 322 nm, which is ascribed to a metal to ligand charge-transfer transition in accordance to ref. 4. As we shall see later, DFT calculations suggest this is a doublet-doublet ($^2P_1 \leftarrow {}^2P_0$) SOMO-LUMO transition, in which the charge is transferred from the Cu atom to the anionic ligand framework upon excitation. It is worth mentioning that GLY and AMPA show a single absorption at 205-206 nm, whereas NNG shows an addition band at 242 nm, due to the nitroso functional group. In Figure 2d, the emission spectra show two peaks at 375 nm and 400 nm, which are assigned to emissions from the ligand and from the ligand to metal ($^2P_0 \leftarrow {}^2P_1$) transitions, respectively.

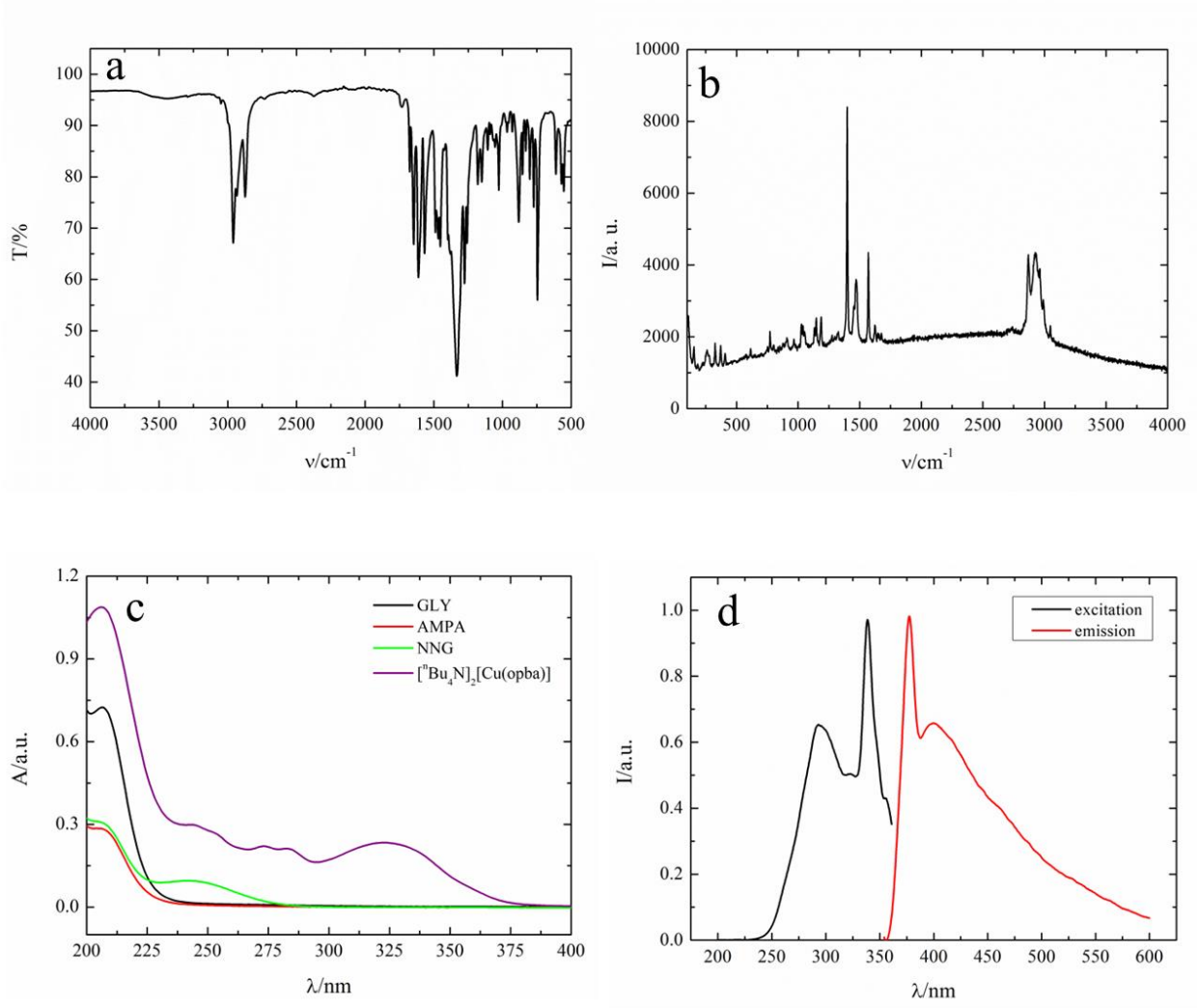

Figure S1. Spectroscopic characteristics of $[^nBu_4N]_2[Cu(opba)]$: (a) FTIR, (b) Raman, (c) UV-Vis, and (d) excitation/emission spectra (λ_{exc} = 340 nm). Absorption and emission spectra registered in acetonitrile. In part (c), spectra of GLY, AMPA and NNG (registered in ultrapure water) are also presented for comparison purposes.

Table S1. Assignment of FTIR and Raman bands for $[^{n}Bu_4N]_2[Cu(opba)]$.

IR bands (cm^{-1})	Raman bands (cm^{-1})	Assignment
1674	-	ν(C=O)
1646	1626	ν(C=O)
1612	1605	ν(C=O)
1566	1583	ν^{ϕ} (C-H) + γ^{ϕ} (C-H)
1489	1456	ν^{ϕ} (C-H) + γ^{ϕ} (C-H)
1452	-	ν^{ϕ} (C-H) + γ^{ϕ} (C-H)
1332	1398	ν^{ϕ} (C-H) + γ^{ϕ} (C-H) + ν(C-N)
1275	1198	ν(C-N) + ν(C-O) + β^{ϕ} (C-H)
1180	-	β^{ϕ} (C-H)
1151	-	β^{ϕ} (C-H)
1026	1019	β^{ϕ} (C-H)

ν: stretching; ν^{ϕ}: stretching in the benzene ring; γ^{ϕ} : torsion in the benzene ring; β^{ϕ} : bending in the benzene ring.

[1] Abdulmalic, M.A. et al. *Dalton Trans*. **2013**, *42*, 1798–1809.

[2] Weheabby, S. et al. *Electrochim. Acta* **2019**, *318*, 181-193.

[3] do Nascimento, G.M. et al.; *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc*. **2015**, *142*, 303–310.

[4] Cervera, B. et al. *J. Chem. Soc., Dalton Trans.* **1998**, 781–790.

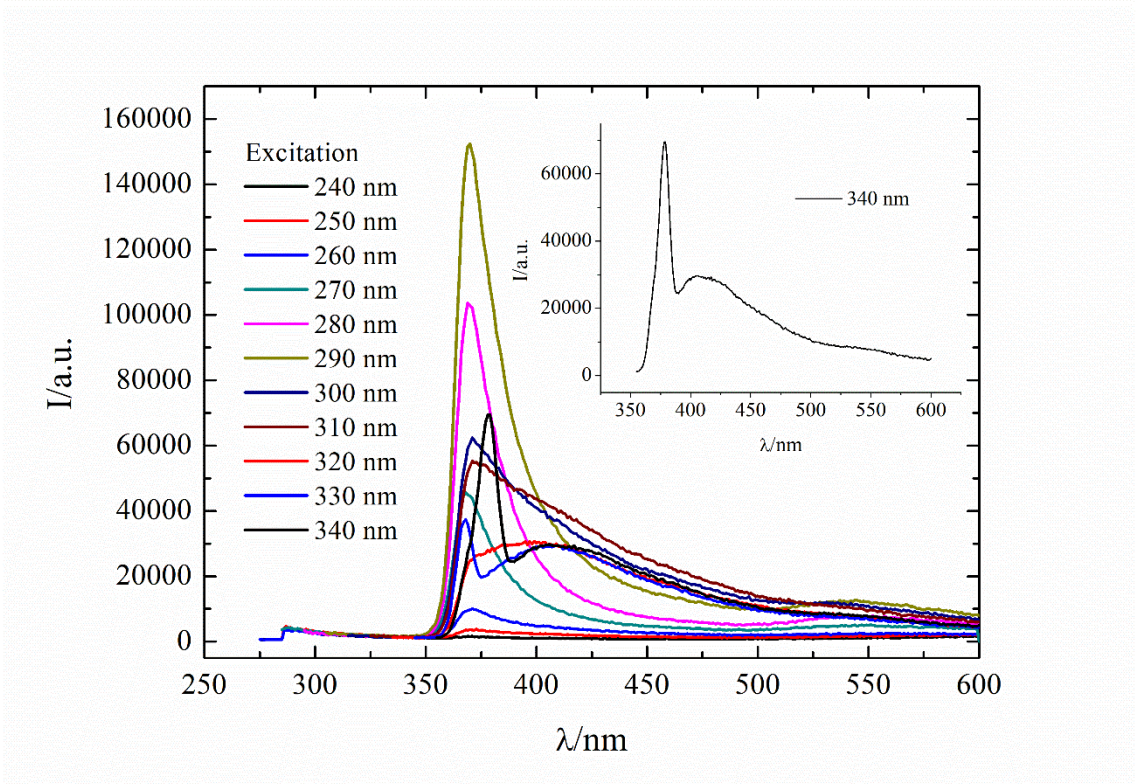

Figure S2. Emission spectra of $[Cu(opba)]^{2-}$ (0.2 mM) in acetonitrile as a function of the excitation wavelength, as indicated. The inset shows the spectrum registered at the excitation of 340 nm.

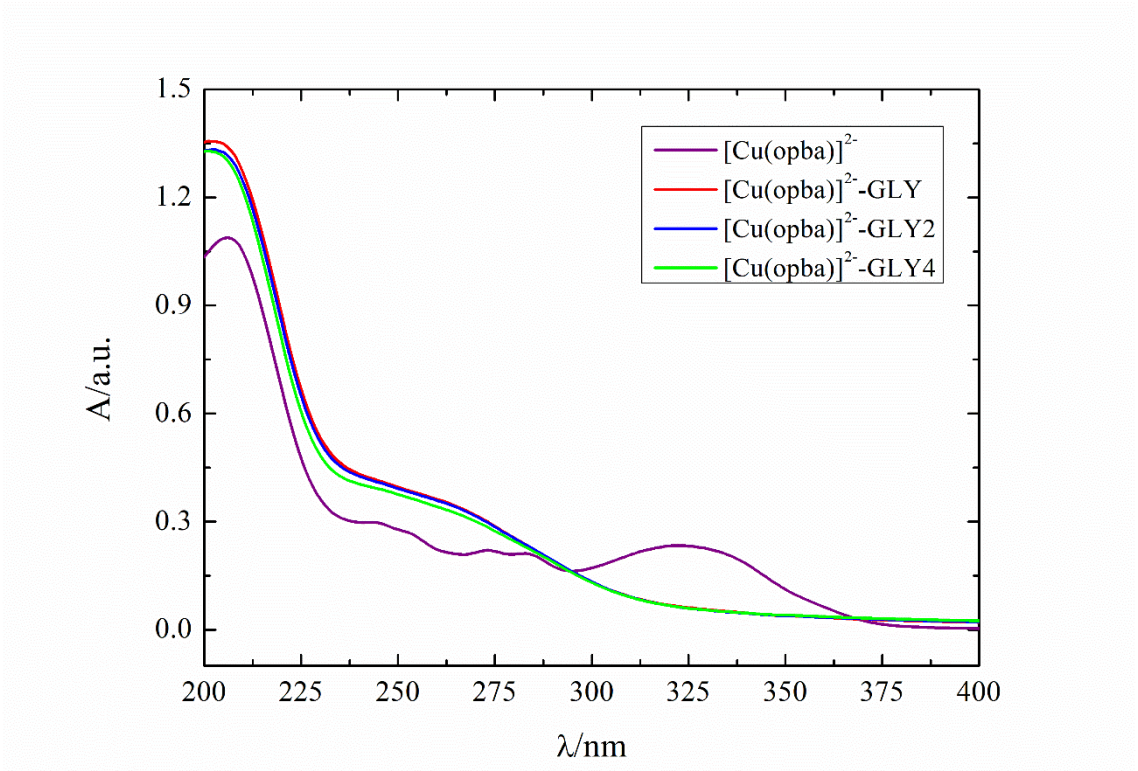

Figure S3. UV-Vis absorption spectra of $[Cu(opba)]^{2-}(GLY)_N$ (N = 1, 2, and 4) species. $[Cu(opba)]^{2-}$concentration = 0.2 mM; GLY concentrations = 0.2 mM, 0.4 mM, 0.8 mM. All in acetonitrile.

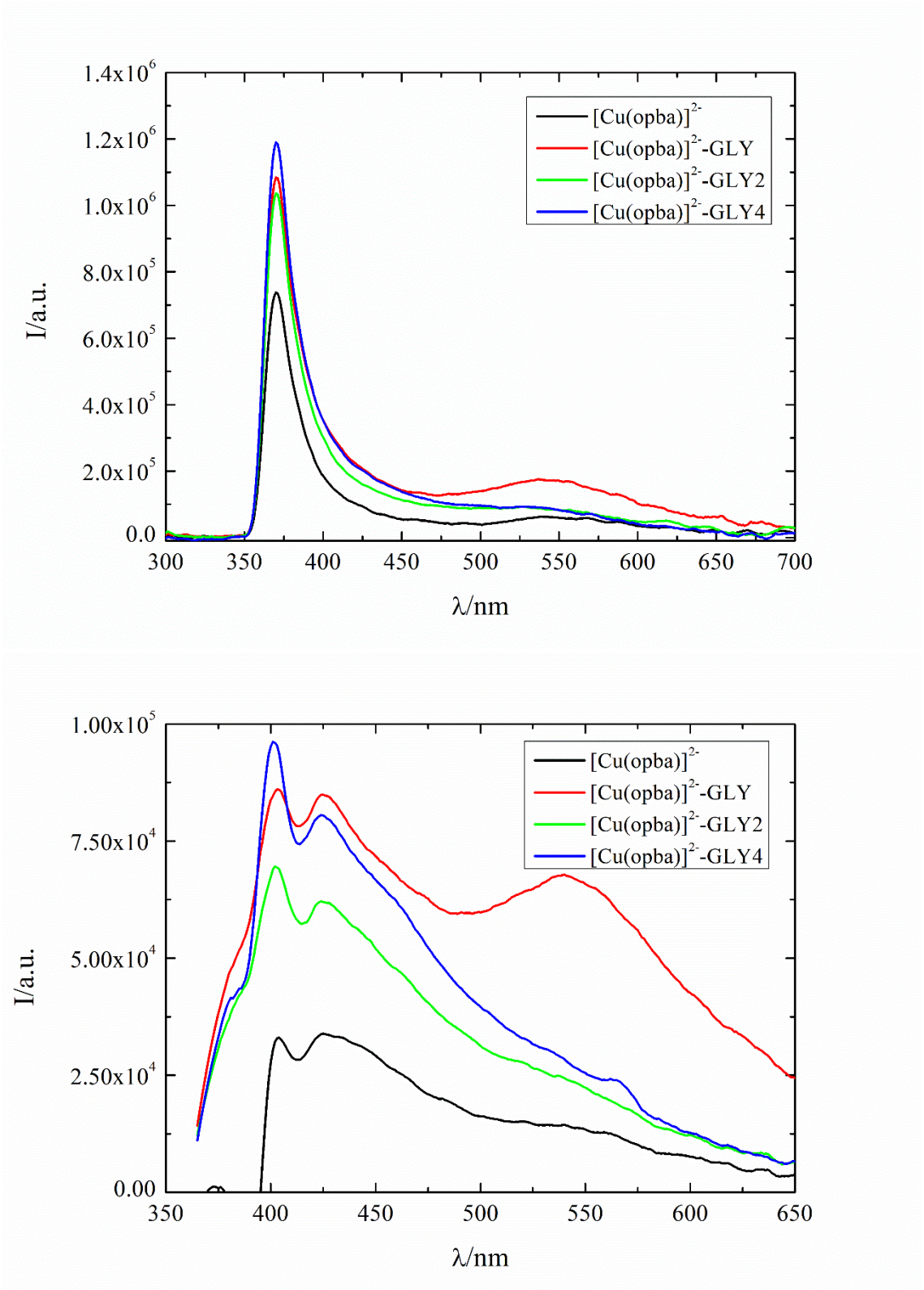

Figure S4. Emission spectra of $[Cu(opba)]^{2-}(GLY)_N$ (N = 1, 2, and 4) species registered under 270 nm (top) and 350 nm (bottom) excitation.