

**Supporting information: Indirect consequences of exciplex states
on the phosphorescence lifetime of phenazine-based 1,2,3-triazole
luminescent probes**

Bárbara B. A. Costa¹, Guilherme A. M. Jardim², Paloma L. Santos³, Hállen D. R. Calado²,
Andrew P. Monkman³, Fernando B. Dias³, Eufrânio N. da Silva Júnior², Luiz A. Cury^{1†}

¹*Instituto de Ciências Exatas, Departamento de Física,
Universidade Federal de Minas Gerais,
31270-901, Belo Horizonte, Minas Gerais, Brazil*

²*Instituto de Ciências Exatas, Departamento de Química,
Universidade Federal de Minas Gerais,
31270-901, Belo Horizonte, Minas Gerais, Brazil*

³*Department of Physics, University of Durham,
South Road DH1 3LE, Durham, United Kingdom*

[†] Corresponding author. E-mail address: cury@fisica.ufmg.br

Related results about the exciplex formation in our probe+ Cd^{2+} solution with the addition of different equivalents of Cd^{2+} ions were published in an earlier article.¹ The **Figure 1** shows practically the same absorption spectra for the probe and the probe+ Cd^{2+} solutions, just confirming that exciplexes are entities existing only at excited states.

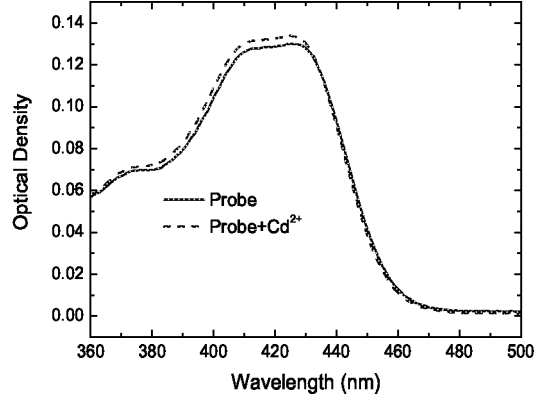


FIG. 1: (Color online) Absorption spectra for the probe (full line) and the probe+ Cd^{2+} (dashed line) solutions in water/acetonitrile (8.5:1.5) at room temperature.

Two steady-state photoluminescence (PL) emission spectra corresponding to the addition of 1.0 and 2.5 equivalents of Cd^{2+} ions to the probe solution are shown in **Figure 2a**. For the case of 2.5 equivalents (dashed curve) the probe+ Cd^{2+} solution is in excess of Cd^{2+} ions. The corresponding PL emission presents practically only the exciplex peak emission, centered at 504 nm, while for the probe+ Cd^{2+} solution with 1.0 equivalent of Cd^{2+} ions (full curve) the contributions of the probe (smaller PL peak at 458 nm) and of the exciplex (PL peak at 518 nm) are observed. Only the prompt fluorescence (PF) time-resolved PL emission is detected for the probe+ Cd^{2+} solution with 2.5 equivalents of Cd^{2+} ions. Some representative PF spectra at different delay times and the decay curve for this probe+ Cd^{2+} solution are shown in **Figures 2b** and **2c**, respectively.

The lack of delayed fluorescence (DF) and phosphorescence emissions for this probe+ Cd^{2+} solution in excess of Cd^{2+} ions is assigned to the predominant formation of exciplex states, with not enough remaining singlet probe states left to undergo intersystem crossing to triplet manifold states. The decay curve in **Figures 2c** is fitted just by a monoexponential, corroborating the preponderance of the exciplex emission. The corresponding lifetime of

$\tau_1 = (9.0 \pm 0.4) \text{ ns}$ for the exciplex emission is in agreement with the exciplex time component [$\tau_2 = (9 \pm 1) \text{ ns}$] observed in the biexponential decay curve (**Figures 5a** shown in the paper) of the probe+ Cd^{2+} solution with 1.0 equivalent of Cd^{2+} ions.

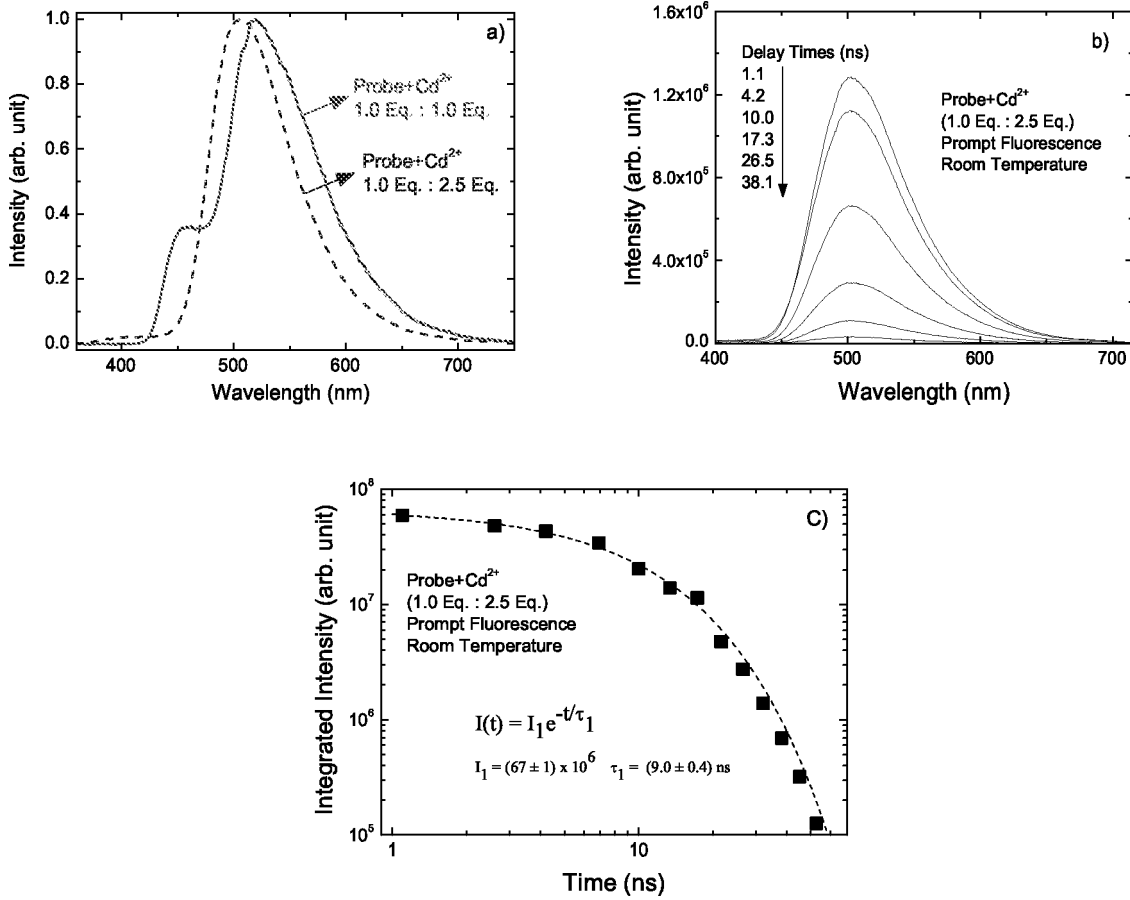


FIG. 2: (Color online) (a) Steady-state Photoluminescence emission spectra at room temperature with addition of 1.0 (full line) and 2.5 (dashed line) equivalents of Cd^{2+} ions to the probe solution in water/acetonitrile (8.5:1.5). The excitation was made at $\lambda_{Exc} = 355 \text{ nm}$. (b) Prompt fluorescence representative spectra at different delay times for the probe+ Cd^{2+} solution with 2.5 equivalent of Cd^{2+} ions at room temperature. (c) Prompt fluorescence integration intensity for the probe+ Cd^{2+} solution with 2.5 equivalent of Cd^{2+} ions at room temperature as a function of delay time. The fitting curve (dashed line), the corresponding expression, lifetime and intensity parameters are included in the figure.

In **Figure 3** is presented a proposed form of interaction between the + Cd^{2+} ions and the

probe molecule, which was considered in our discussion of conformational changes of the probe molecule, leading to modified spin-orbit interactions and faster ISC rate.

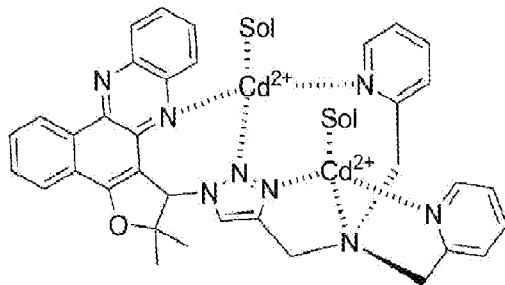


FIG. 3: (Color online) Proposed form of interaction between the $+Cd^{2+}$ ions and the probe molecule.

Acknowledgments

B. B. A. Costa, L. A. Cury, G. A. M. Jardim, H. D. R. Calado, E. N. da Silva Júnior thank FAPEMIG, CAPES, CNPq, the Instituto Nacional de Ciência e Tecnologia em Dispositivos Semicondutores (INCT-DISSE) from Brazil for the financial support. P. L. Santos thanks CAPES - Science Without Borders, for the Doctorate studentship, Proc. 12027/13-8. L. A. Cury and F. B. Dias also thank CAPES - Science Without Borders, for the PVE Program, Proc. 88881.030369/2013-01.

¹ G. A. M. Jardim, H. D. R. Calado, L. A. Cury, E. N. da Silva Júnior, Eur. J. Org. Chem. 2015(4) (2015), 703.