



## FLUORESCENCE QUENCHING STUDY OF AN OXAZOLE DERIVATIVE BY METAL IONS

Cristina TABLET,<sup>a,\*</sup> Alexandru T. BALABAN<sup>b</sup> and Mihaela HILLEBRAND<sup>c</sup>

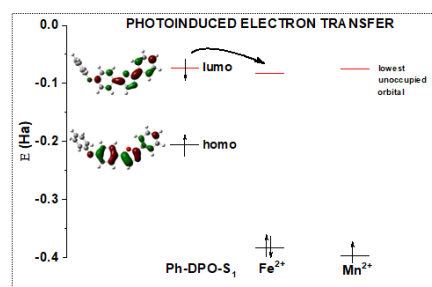
<sup>a</sup> Faculty of Pharmacy, “Titu Maiorescu” University, Bd. Gh. Sincai 16, Bucharest, Roumania

<sup>b</sup> Texas A&M University, Galveston, USA

<sup>c</sup> Department of Physical Chemistry, University of Bucharest, Bd. Regina Elisabeta 4-12, 030018, Bucharest, Roumania

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The effect of various metal ions on the fluorescence of an oxazole derivative, 5-(4-phenoxyphenyl)-2-phenyl-1,3-oxazole (Ph-DPO), was investigated. All metal ions quenched the fluorescence of Ph-DPO without altering the shape of the fluorescence band, and resulted in linear Stern–Volmer plots. The quenching mechanism was elucidated corroborating spectral data with cyclic voltammetry measurements and DFT calculations on the fluorophore and the quenchers. We found that metal ions quench the fluorescence of Ph-DPO through photoinduced electron transfer from the excited Ph-DPO to the metal ions.



### INTRODUCTION

Chemical compounds with good scintillator properties are largely used due to their ability to detect metal ions. Among the different spectral methods, fluorescence spectroscopy is very convenient for the prediction of their scintillator or/and laser emission, the most important properties of scintillators being the large emission quantum yield and the position of the fluorescence maximum in the visible range of the spectrum. Abiding by these characteristics, oxazole derivatives are largely used as scintillators.<sup>1–5</sup> As the fluorescence quenching process by metal ions can represent a source of errors in such measurements, it is important to

identify the mechanism of this process. Continuing our works on the fluorescence and deactivation pathways of various oxazole derivatives,<sup>6–9</sup> we were also interested in their behaviour in the presence of metal ions. The quenching behaviour of a related compound, 2,5-phenyl-1,3-oxazole, was previously studied<sup>10</sup> and explained by an electron transfer mechanism from the excited state of the fluorophore donor to the acceptor *lumo* orbital of the metal ion. It is the aim of this paper to report the study of the quenching effect exerted by several bivalent metal ions on the fluorescence emission of a more structurally complex compound in the oxazole class, 5-(4-phenoxyphenyl)-2-phenyl-1,3-oxazole (Ph-DPO), shown in Fig. 1.

\* Corresponding author: [cristinatablet@yahoo.com](mailto:cristinatablet@yahoo.com)

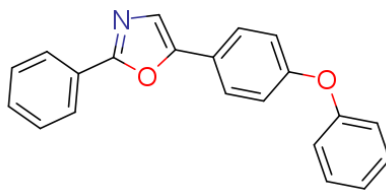


Fig.1 – Structure of 5-(4-phenoxyphenyl)-2-phenyl-1,3-oxazole (Ph-DPO).

This study will consider the following steps: (1) recording of the fluorescence spectra of Ph-DPO with increasing metal ion concentration; (2) calculation of the Stern-Volmer quenching constants; (3) elucidation of the quenching mechanism. Some of these steps will be sustained by theoretical DFT calculations.

## RESULTS AND DISCUSSION

### Fluorescence measurements

The fluorescence data show that the increase of the metal ion concentration determines a decrease of the fluorescence intensity of Ph-DPO, with no change in the position or shape of the emission

band, the effect independent on the metal type. As an example, the behaviour of Ph-DPO in the presence of  $\text{Fe}^{2+}$  ions is presented in Fig. 2A.

Considering  $I_0$  the fluorescence intensity in the absence of the quencher and  $I$  the fluorescence intensity in the presence of the metal ion, the Stern-Volmer constants ( $K_{SV}$ ) were obtained using equation 1 by plotting  $(I_0/I)-1$  versus the molar concentration of the metal ion,  $[Q]$ .

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \quad (1)$$

The plots for  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  are presented in Fig. 2 (B) and the resulted Ksv values are given in Table 1. It can be seen that there are strong quenchers ( $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ), medium quenchers ( $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ) and practically inefficient quenchers ( $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$ ).

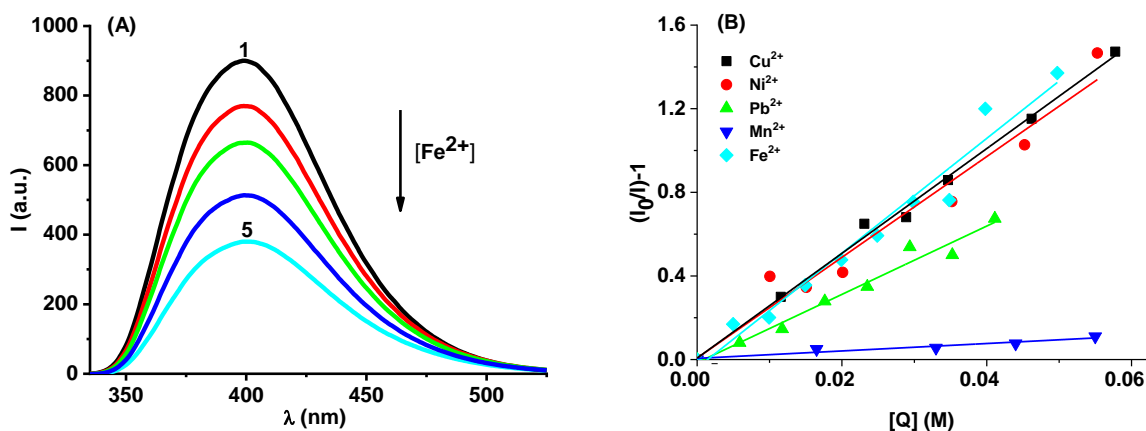


Fig. 2 – A) Fluorescence spectra of Ph-DPO in the presence of increasing concentrations of  $\text{Fe}^{2+}$  ions; B) Stern-Volmer plots associated with the Ph-DPO fluorescence quenching by several metal ions.

Table 1

Values of the Stern-Volmer constants obtained from Ph-DPO fluorescence quenching by different bivalent metal ions in a 2:3 methanol-water mixture.  $r$  is de correlation coefficient for the linear Stern-Volmer plot

Quencher	$K_{sv} (\text{M}^{-1})$	$r$
$\text{Fe}^{2+}$	$27.44 \pm 1.79$	0.983
$\text{Cu}^{2+}$	$25.06 \pm 0.79$	0.998
$\text{Ni}^{2+}$	$24.47 \pm 0.61$	0.992
$\text{Hg}^{2+}$	$19.15 \pm 1.39$	0.980
$\text{Pb}^{2+}$	$17.76 \pm 1.68$	0.978
$\text{Co}^{2+}$	$8.15 \pm 0.11$	0.995
$\text{Zn}^{2+}$	$3.37 \pm 0.28$	0.993
$\text{Mn}^{2+}$	$1.78 \pm 0.27$	0.967
$\text{Cd}^{2+}$	$0.96 \pm 0.07$	0.978

### Mechanism of quenching

To distinguish between static and dynamic quenching, the fluorescence spectra were recorded at two different temperatures, namely at room temperature and at 70°C. In the case of static quenching, the increase of temperature would determine a decrease of  $K_{SV}$ , while for a dynamic

quenching mechanism, the temperature increase would determine an increase of  $K_{SV}$ . The effect of temperature on the fluorescence quenching is presented in Fig. 3 for the system Ph–DPO–Pb<sup>2+</sup>. A slight increase of  $K_{SV}$  can be seen. Furthermore, no positive deviation from the linearity of the Stern–Volmer plot was encountered, these two observations attesting that the quenching mechanism is not static.

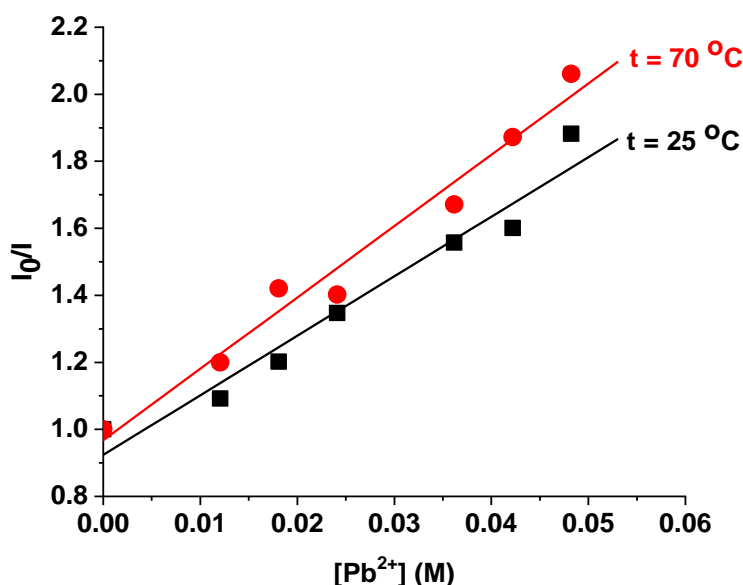


Fig. 3 – Temperature influence on the Stern–Volmer plots for the Ph–DPO–Pb<sup>2+</sup> system.

In order to establish if the quenching process originates in an electron transfer mechanism, we have calculated the variation of the Gibbs free energy,  $\Delta G^0$ , using the Rehm–Weller (Eq. 2),

$$\Delta G^0 = E_{D^+/D}^0 - E_{A/A^-}^0 - E_{00} - \frac{e^2}{4\pi\epsilon r_{DA}} \quad (2)$$

in which  $E(D^+/D)$  represents the oxidation potential of

the donor,  $E(A/A^-)$  the reduction potential of the acceptor,  $E_{00}$  the excitation energy,  $e$  the electron charge,  $\epsilon$  the dielectric constant of the medium and  $r_{DA}$  the donor–acceptor distance in the collision moment.

The reduction potentials of the metal ions were taken from literature data.<sup>10</sup> Their values are listed in Table 2.

Table 2

Parameters describing the quenching of the Ph–DPO fluorescence by metal ions via photoinduced electron transfer

Metal ions	R (Å)	E1/2 (V/SCE)	C (eV)	$\Delta G_0$ (eV)
Fe <sup>2+</sup>	0.76	0.44	– 0.0314	– 2.67
Ni <sup>2+</sup>	0.69	0.40	– 0.0361	– 2.64
Co <sup>2+</sup>	0.72	0.12	– 0.0318	– 2.36
Hg <sup>2+</sup>	1.10	0.50	– 0.0319	– 2.74
Zn <sup>2+</sup>	0.74	0.10	– 0.0318	– 2.34
Mn <sup>2+</sup>	0.80	0.34	– 0.0317	– 2.58
Pb <sup>2+</sup>	1.20	0.60	– 0.0307	– 2.84
Cu <sup>2+</sup>	0.72	0.43	– 0.0302	– 2.73
Cd <sup>2+</sup>	0.97	0.46	– 0.0298	– 2.70

In the case of the fluorophore, the oxidation potential was obtained by a cyclic voltammetry measurement (Fig. 4). The cyclic voltammogram of Ph–DPO reveals two successive irreversible

electron transfer processes in both the oxidation and reduction waves. As there are no reverse peaks, the oxidation potential of Ph–DPO was estimated from the peak value (1.276 V).

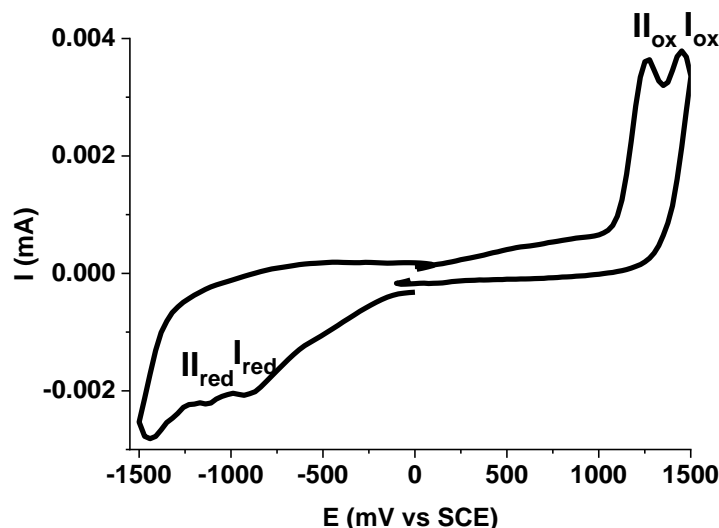


Fig. 4 – Cyclic voltammogram of Ph-PPO in 2:3 methanol-water mixture.

The  $E_{00}$  value, *i.e.* the energy difference  $S_1(n_v=0) - S_0(n_v=0)$ , was calculated from the intersection of the absorption and fluorescence spectra. The intersection of the two spectra was found at  $\lambda = 350.4$  nm and corresponds to 3.54 eV. Using the ionic radius of the metal ions taken from literature<sup>10</sup> and considering the fluorophore radius of 6.69 Å (*i.e.* 40% of the longest diameter of the optimized geometry<sup>11</sup>), we have calculated the Coulombic term  $C$ .

The values of the calculated Gibbs free energy are listed in Table 2. Their negative signs show that the process is spontaneous and suggest an electron transfer from the excited Ph-DPO fluorophore to the metal ion. The same mechanism was found for

a related compound already mentioned, 2,5-diphenyl-1,3-oxazole.<sup>10</sup>

## DFT CALCULATIONS

In order to have more data on the fluorescence quenching mechanism, DFT calculations were performed on the donor compound, Ph-DPO, in ground state,  $S_0$ , and in first excited singlet state,  $S_1$ . The energies of these two states are listed in Table 3 together with predicted absorption and emission wavelengths ( $\lambda_{\text{calc}}$ ) and oscillatory strengths of the respective transitions ( $f$ ).

Table 3

Calculated spectral data on the absorption and fluorescence of Ph-DPO

State	E (Ha)	$\lambda_{\text{exp}}$ (nm)	$\lambda_{\text{calc}}$ (nm)	$f$	Assignment
$S_0$	-1013.5311704	320	333	1.0866	<i>homo</i> → <i>lumo</i>
$S_1$	-1013.5192854	399	426	1.3601	<i>homo</i> → <i>lumo</i>

The computed absorption and fluorescence spectra agree in acceptable manner with the experimental ones. Both the absorption and fluorescence bands correspond to a *homo* → *lumo* transition, mainly implying the planar DPO moiety of the system (Fig. 5).

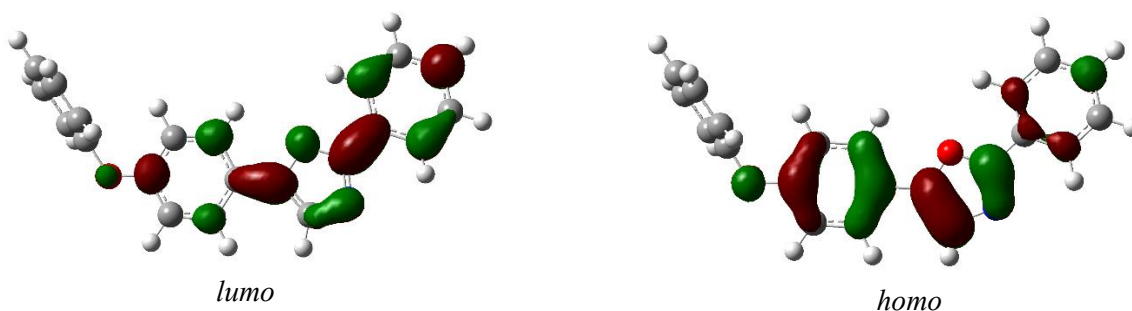


Fig. 5 Frontier molecular orbitals of Ph-DPO in  $S_0$  state.

Although  $\Delta G^0$  contains several terms, the electron transfer process is possible only if the metal ion has a vacant orbital lower in energy than the excited electron in the  $S_1$  state (the *lumo* orbital of Ph–DPO). The calculation of the orbitals of the metal ions used

in the experiment, excepting  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  for which the atomic numbers were out of the range of the atomic base used in our work, attests the presence of such a vacant orbital. An example is given in Fig. 6 for the  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions.

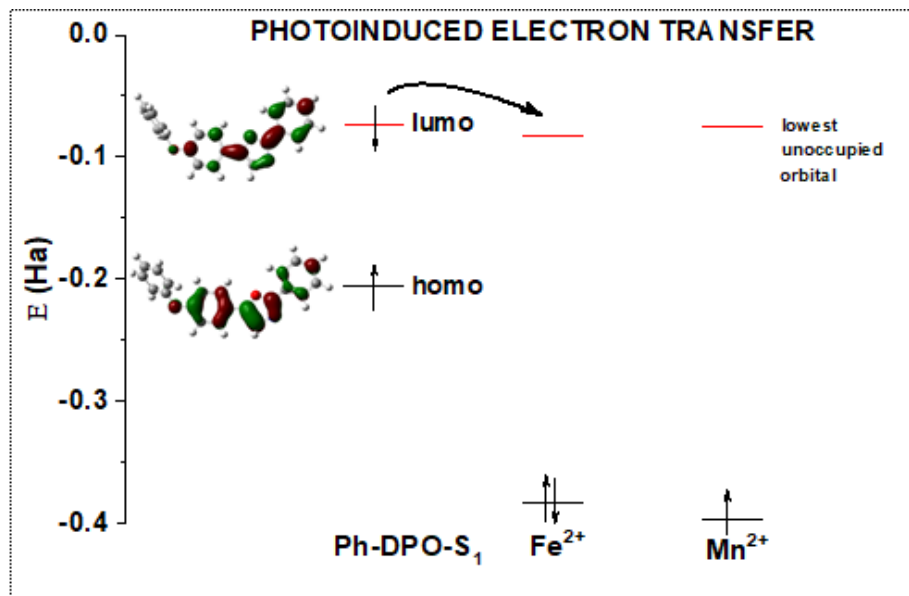


Fig. 6 – Energy diagram that supports the photoinduced electron transfer from excited Ph–DPO to  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions, respectively.

## EXPERIMENTAL

### Fluorescence spectroscopy and cyclic voltammetry

The absorption and fluorescence spectra were recorded on a Jasco spectrophotometer (V-560) and a Jasco spectrofluorometer (FP-6300), respectively. The spectrofluorimeter was equipped with a Lauda thermostatic bath.

The cyclic voltammetry experiments were performed with the VOLTALAB-32 system using a three electrodes cell: the working electrode – a platinum disk with 2 mm diameter, an auxiliary platinum electrode and as reference electrode a saturated calomel electrode. As supporting electrolyte, we have used a tetrabutylammonium tetrafluoroborate solution (0.1 M).

The Ph–DPO fluorophore was synthesized using the method described previously<sup>12,13</sup> and solved in methanol (Aldrich). The metal ion solutions ( $10^{-2}$  M) were prepared in distilled water. The working solutions were prepared from these two initial solutions in order to have in each one a 2:3 methanol-water ratio and different metal ion concentrations. The metal salts used were  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{CdCl}_2$ ,  $\text{HgCl}_2$ ,  $\text{PbSO}_4$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ . The spectra were firstly recorded for

the free Ph–DPO solution and after for the solutions containing different concentrations of metal ions.

### Theoretical calculation

DFT calculations were performed with the Gaussian09 program<sup>14</sup> for the states involved in the absorption and fluorescence spectra of Ph–DPO, the ground state ( $S_0$ ) and the first excited state ( $S_1$ ). We have used the PBE0 functional<sup>15</sup> and the 6-311(d,p) basis set. The compound was optimized considering the PCM solvation model<sup>16</sup> and a dielectric constant corresponding to the 2:3 methanol-water mixture used in the experiments ( $\epsilon=57$ ).

## CONCLUSIONS

Considering the different possible quenching mechanisms, both the experimental and theoretical data attest that the main cause of the quenching consists in the electron transfer from the excited state of Ph–DPO to the metal ions. Our conclusion is proved by the negative  $\Delta G^0$  values calculated with the Rehm–Weller relationship and supported by the relative position of the molecular orbitals involved in electron transfer, namely the highest singly occupied molecular orbital of the Ph–DPO donor and the first vacant orbital of the metal ions, the acceptors.

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