

Synthesis, Characterization and Photophysical Studies of a New Complex of Ruthenium Coordinated to a New Red PDI.

Edjane R. dos Santos^{1,2}(PQ), João M. F. P. B. Pina³(PQ), Carlos Balezão²(PQ), Rose M. Carlos^{*1}(PQ), José M. G. Martinho^{*2}(PQ).

¹ Department of Chemistry, Universidade Federal de São Carlos, CP 676, 13565-905 São Carlos, SP, Brazil.

² Centro de Química-Física Molecular and IN- Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, 1049-001 Lisboa, Portugal.

³ Department of Chemistry, Universidade de Coimbra, 3004-535 Coimbra, Portugal.

Keywords: Ru(II) complex, Red PDI, Photochemistry and Photophysics

Introduction

A dyad of a red emitting perylene-3,4-dicarboxylic diimide (PDI) dye covalently linked to Ru(II) diimine complex was prepared. Perylenediimides (PDIs) are very photostable compounds with high absorption in the visible, high fluorescence quantum yield and short lifetime, while Ru(II) complexes display broad singlet absorption in the UV-vis and long-lived emission in the visible region from the ³MLCT state. The combination of these two dyes in dyads can bring new properties resulting from the synergies between the two moieties that can be useful for diverse applications such as singlet oxygen (¹O₂) generation from the PDI triplet excited state (³PDI) generated upon electronic excitation of the Ru(II) complex^{1,2}. The key features are intense absorption and emission in the visible to near IR region and long luminescence lifetime in CH₃CN aerated solutions (500 ns) originated from the PDI excited triplet state.

Results and Discussion

By excitation at 450 nm both the Ru(II) complex and the PDI were electronically excited. The emission is a broad band centered at ~773 nm due to PDI fluorescence and phosphorescence (Fig.1). The fluorescence lifetime of the complex by excitation in the PDI absorption region (670 nm) is complex with a long lifetime of 1.8 ns identical to the lifetime of PDI. However, by excitation at 450nm where both the PDI and the Ru(II) complex moieties absorb a very long decay component of ~500 ns with low amplitude, attributed to the PDI phosphorescence decay, was also observed. The transient absorption spectra at several times upon excitation at 400 nm, show transient absorption spectra centered at 950, 1250 and 1500 nm. The decay with lifetime similar to the lifetime of PDI suggests that at both 950 nm and 1250 exist a transient absorption from the singlet excited state of PDI.

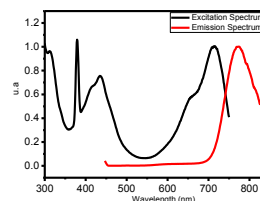


Fig. 1 Emission and Excitation spectra of Complex 1 in CH₃CN at 25°C.

The fast component of ~2 ps is probably due to a fast conformation relaxation process. The other rise and decay components are probably related to the evolution of the ³MLCT state of Ru(II) complex to end-up in the triplet excited state of ³PDI, whose phosphorescence has a lifetime of ~500 ns (aerated solutions in CH₃CN) observed in the fluorescence decays by excitation at 450 nm.

Tabela 1. Decay times and associated pre-exponential factors obtained from the femtosecond transient absorption experiments for the Complex in CH₃CN at 293 K.

λ_{exc} (nm)	λ_{em} (nm)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	a_1	a_2	a_3
400	949	2.0	44.8	1630	0.071	-	0.929
						0.501	
730	949	1.6	190	1610	0.222	0.118	0.660

Conclusions

The new dyads show photochemical stability, intense absorption and emission in the NIR region. The formation of the triplet state of PDI by excitation at 450 nm suggests that the complex can be a good ¹O₂ sensitizer.

Aknowledgments

FAPESP for financial support. E.R.dos S. Pos-doc fellowship (Grant number 2013/23943-8).

¹ Yukruk, F.; Dogan, A. L.; Canpinar, H.; Guc, D.; Akkaya, E. U. *Org. Lett.* **2005**, *7*, 2885.

² Cardoso, C. R.; Lima, M. V. S., *J. Med. Chem.* **2014**, *57*, 4906.