NEW METALLO-PORPHYRINS FOR SOLAR ENERGY CONVERSION

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Abstract: *Tetrapyrrole macrocycles play important roles that serve nature in various ways to energy conversion. Under such context, the tetra-aryl porphyrins derivatives are known as one of the most efficient sensitizers in solar energy conversion. The investigations of spectral properties of the metallic complexes (rhodium and ruthenium) of 5,10,15,20-p-tetra-aryl porphyrins, are achieved by UV-Vis and FT-IR analysis. The surface morphology of the samples was probed by scanning electron microscopy (SEM, SEM+EDS). The investigation results of the studied porphyrins revealed the perspective for potential photochemical applications of such materials.*

Key words: *porphyrins, photochemical potential, FTIR, SEM, EDS.*

1. Introduction

The porphyrins have been, for decades, widely studied due its very interesting photophysical and photochemical properties [17]. In fact, the porphyrins as an important class of molecules are present in many biological processes, such as oxygen, electrons transport and energy transfer in photosynthesis [7].

Furthermore, porphyrins have been highlighted as efficient sensitizers and catalysts in chemical and photochemical processes, such as in photodynamic therapy (PDT) applied in cancer treatment [5]. In addition, porphyrins have shown great capability to be employed in photonic devices. At the 90's, porphyrins were by Kay and Grätzel as light-harvesting material in dye sensitized solar cells (DSSC), being today a major focus of research [11].

The function of the dye sensitized solar cells is based on the electron injection from the photoexcited state of the dye molecule into the conduction band of the TiO_2, followed by regeneration of the dye by an iodide/triiodide redox couple [2].

The efficiency of DSSC device using porphyrin as sensitizer having anchoring group at -meso position had not crossed 4% till 2003, even though a variety of substitutions have been introduced on the porphyrin macrocycle [4], [6], [10], [14].

The porphyrins have widely-varied properties strongly linked to the central metal and axial ligand, proper for solar energy applications [3]. Because they have high visible light

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absorption and stable physical properties, the tetra-aryl porphyrin derivatives are recognized as p-type semiconductors [19].

This paper presents the main results, which have been obtained by studying the spectroscopic (UV-Vis, FT-IR) behaviour of some metallic complexes of tetra-aryl porphyrins derivatives - tetraphenyl pophyrin (TPP) and tetramethoxyphenyl pophyrin (TMPP), as free bases or metallic complexes (Ru, Rh) together with the surface morphology of the samples by scanning electron microscopy (SEM, SEM+EDS).

2. Material and Methods

2.1. Materials

The structure of free bases: 5,10,15,20-p-tetra-phenyl porphyrin (TPP) and 5,10,15,20-p-tetramethoxy phenyl porphyrin (TMPP) with their metallo-complexes, as rhodium 5,10,15,20-p-phenyl porphyrin (Rh-TPP); rhodium 5,10,15,20-p-tetramethoxy phenyl porphyrin (Rh-TMPP), ruthenium 5,10,15,20-p-phenyl porphyrin (Ru-TPP) and ruthenium 5,10,15,20-p-tetramethoxy phenyl porphyrin (Ru-TMPP) are shown in Figure 1.
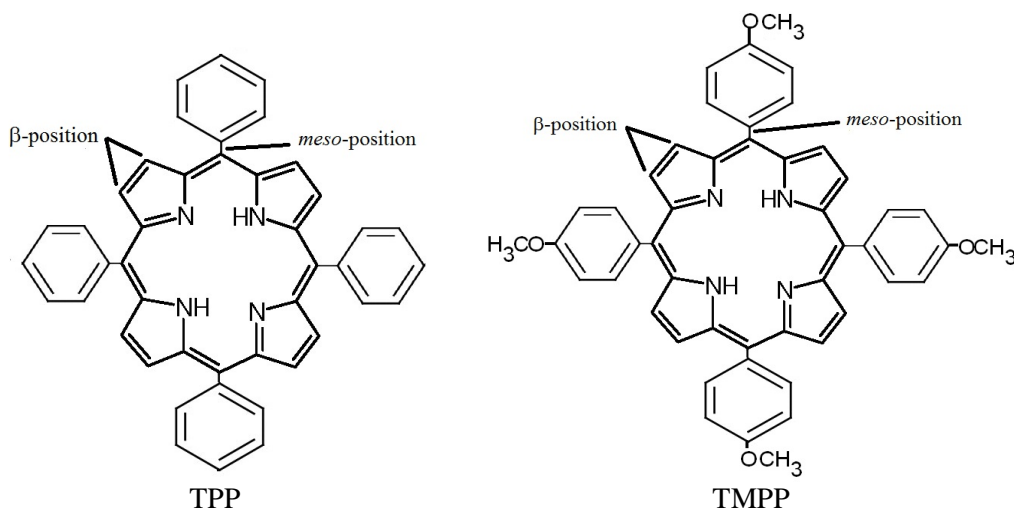

Fig. 1. *The structure of free base porphyrins (TPP at the left and TMPP at the right)*

All of them have been prepared and purified after literature receipts [9].

2.2. Methods

The absorption spectra were recorded on a UV/VIS spectrophotometer Carl Zeiss Jena, with double-beam and monochromator in a quartz cuvette with optical path of 1 cm. The spectra have been recorded in solution in benzene (Sigma Aldrich), used as pure solvent which has been used without any purification.

The FT-IR spectra have been recorded with a FT-IR spectrometer (VERTEX 80), in the following conditions: range 4000 cm^{-1} to 580 cm^{-1}, 32 scan, resolution 4 cm^{-1}. FT-IR spectra were achieved using Attenuated Total Reflectance (ATR) accessory with diamond crystal. The samples were investigated directly on ATR without special preparation.

Scanning electron microscope (SEM) has been recorded with SU-70 microscope coupled with Energy Dispersive Spectrometer (EDS). SEM magnification range is 30 X-800.000 X and the resolution at 15 kV acceleration voltages is 1 nm. EDS spectrometer attached allows qualitative and quantitative analysis (from Be (Z = 4) to Pu (Z = 94)) on the point, rectangle, circle or the free choice and multiple choice line analysis, X-ray mapping, solutions to overlapping peaks.

3. Results and Discussions

The molecules exhibit strong absorption in the visible and near-infrared spectral regions as well as interesting photophysical properties suggesting possible applications in light harvesting.

The porphyrin skeleton (Figure 1) is formed when four pyrrole units joint as a planar ring by single carbon atom bridges, at the α-position of the pyrrole rings. In the porphyrin macrocycle a fully conjugated π-orbital is formed. The nitrogen atoms constitute a central cavity which is able to bind variety of metal cations. Non-metallated porphyrins are called free base porphyrins. The addition and substitution reactions on porphyrins can take place at the β- or at the *meso*-position [15-18].

In the UV-Vis spectrum at the wavelength range 400-440 nm there are Soret band corresponding to the transition from the ground state (S_0) to the second excited singlet state (S_2). Four weaker absorption bands in the spectral region of 450-700 nm arise from the transition from the S_0 state to the first singlet state (S_1). These bands remain non-modified at different concentrations of the porphyrins, but in non-polar solvents, as is benzene. An example is given for TPP, where it is presented the absorption spectra at different concentrations in benzene used as solvent (Figure 2).
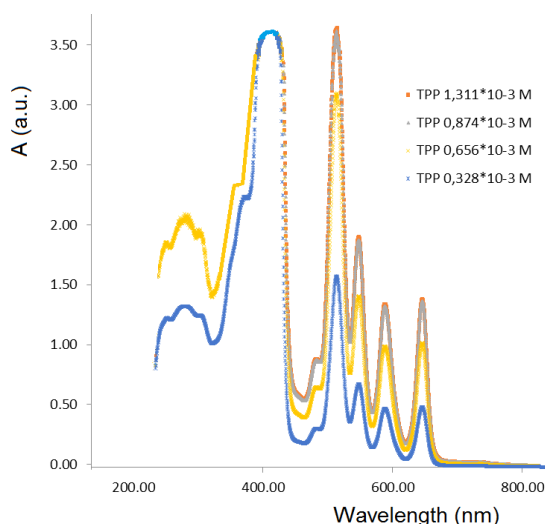

Fig. 2. *The absorption spectra of TPPs at different concentrations in benzene*

In the case of metallo-porphyrins, especially of those with Ru or Rh, the visible absorption bands are radical changed, as it is visible in Table 1.

The absorption maxima of free base porphyrins in benzene and DMF   Table 1

Compound	Solvent	Absorbance/ ε_{Soret} (10^{-3}) λ_{abs} (nm) / (M^{-1} × cm^{-1})
ClRu(III)TPP	Benzene	417/214; 541/98.3; 580/56.7; 637/64.5
ClRu(III)TMPP		422/532; 553/20.5; 593/9.51; 653/16.4
ClRh(III)TPP		419/207; 536/82; 594/42.7; 648/46.8
ClRh(III)TMPP		424/492; 535/76.5; 595/42.1; 653/41
ClRu(III)TPP	Dimethylformamide (DMF)	411/214.7; 541/98.3; 580/56.7; 637/64.5
ClRu(III)TMPP		420/532.6; 553/20.5; 592/9.5; 650/16.5
ClRh(III)TPP		424/265.7; 532/20.4; 567/5.9; 648/1.7
ClRh(III)TMPP		428/193.7; 535/13.7; 572/6.9; 604/3.4

In the case of rhodium complexes, the absorption maxima progressively shifted to longer wavelengths as the donor capacity of the solvent increased, most probably due to the molecular complexes. Rhodium porphyrins react more easily with ligands and the spectral changes associated with the addition of a ligand on the sixth position are larger for the ruthenium complexes (Figure 3).
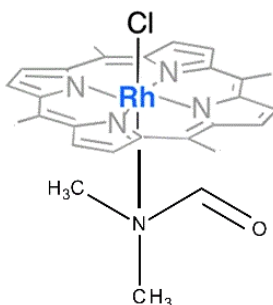

Fig. 3. *The rhodium porphyrins with the addition of DMF on the sixth position*
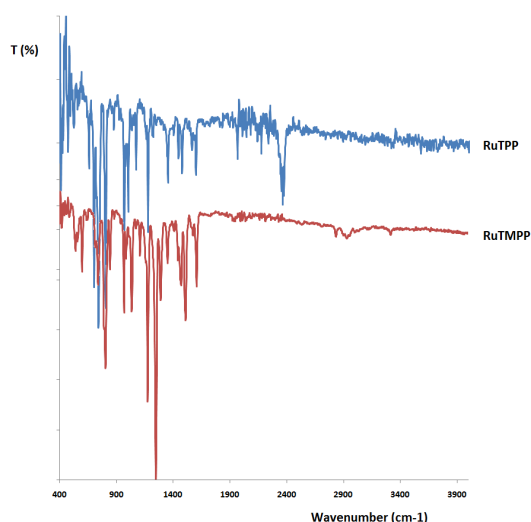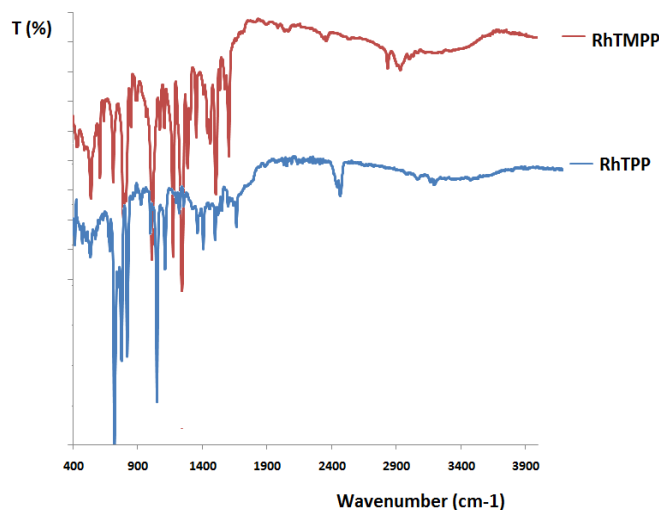

Fig. 4. *FT-IR spectra for RuTPP and RuTMPP*

Fig. 5. *FT-IR spectra for RhTPP and RhTMPP*

By analyzing the FT-IR spectra, could be observed the following aspects (Figures 4 and 5): specific spectra for porphyrins, with strong transmittance bands in the region 1800 - 400 cm^{-1}; strong bands in the regions 700-400 cm^{-1} due to the bands Ru(Rh)-Cl bonds; for TMPP porphyrins, the spectra are more complex, most probably due to an association process that happens at such porphyrins, in good agreement with literature data [12].
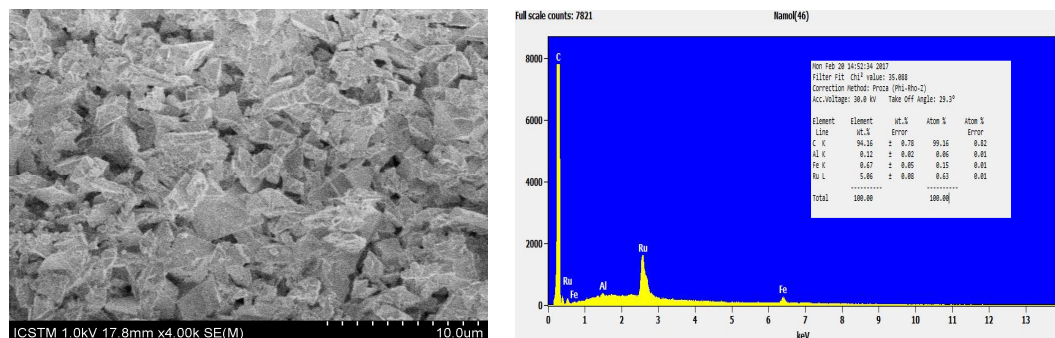

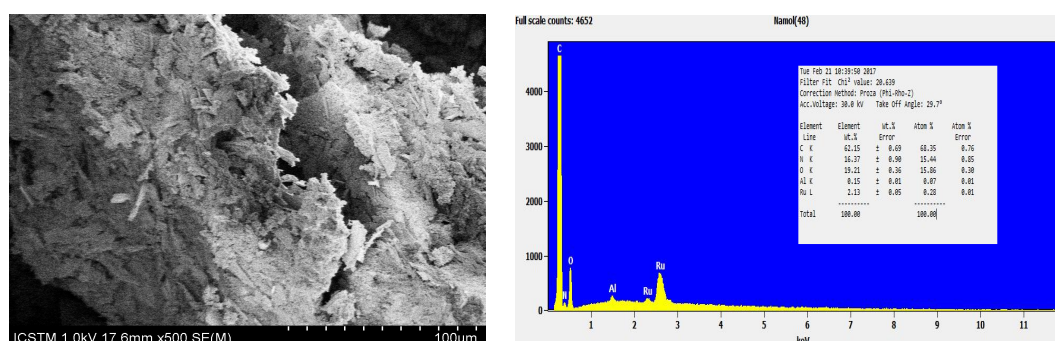Fig. 6. *SEM Image and EDS Spectrum for RuTPP*

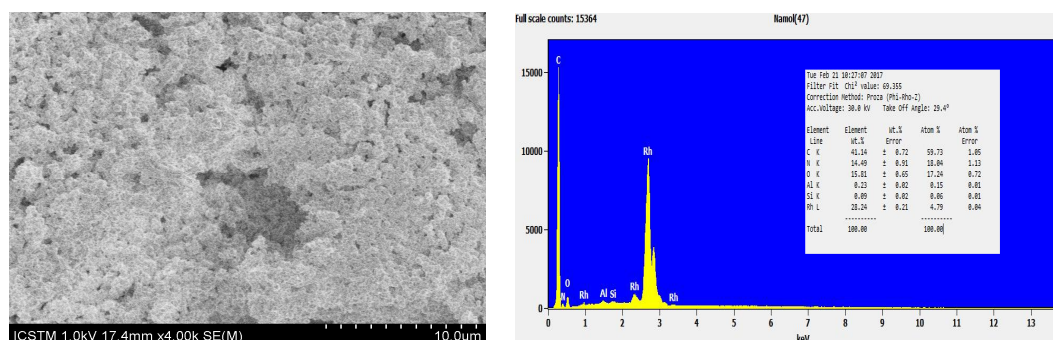Fig. 7. *SEM Image and EDS Spectrum for RuTMPP*

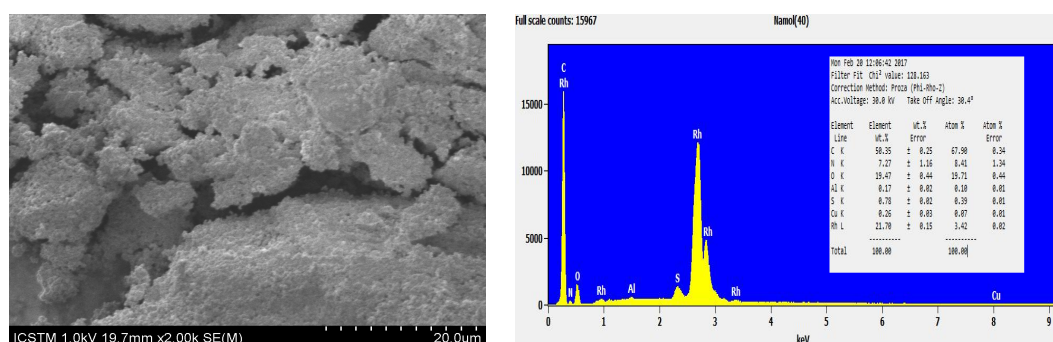Fig. 8. *SEM Image and EDS Spectrum for RhTPP*

Fig. 9. *SEM Image and EDS Spectrum for RhTMPP*

By analyzing the SEM+EDS spectra, could be observed the following aspects (Figures 6 to 9): the metallo-porphyrin TPP derivates shown acicular cristals (RuTPP) or rod aspects (RhTPP), which is in agreement with their smaller size and planar spatial distribution [8]; the other metallo-complexes RuTMPP and RhTMPP are bigger, they show larger crystals, with a plaquettes aspect, most probably due to TMPP bigger size and their capacity to electrostatic associate through methoxy substituents and chlorine axial ligand [13].

These aspects could be correlated with the spatial structure of the porphyrins, whose bonds Me-Cl have been identified in FTIR spectra in the region 700-400 cm^{-1}. These could create some hindered spatial configurations, responsible for larger size of these porphyrins and for the aspects visible in SEM images. These statements are in good agreement with other literature reposrts, even the literature reports are not very reach [1].

4. Conclusions

To develop new sensitizers based on ruthenium complexes of porphyrins, in this paper were studied new Ru and Rh complexes, which could be used as efficient sensitizers for DSSCs (with power conversion efficiencies of more than 10%).

Spectral properties of the studied porphyrins indicated that these materials could be perspective for solar energy conversion applications, due to their versatility to change their central metal valence, to add new axial ligands and to attach new substituents. Under this context, rhodium and ruthenium porphyrins are special compounds with proper properties.

Their capacity of association has been identified by FT-IR and SEM-EDS spectral/microscopic techniques, which identified their internal bonds, their capacity to add new axial ligand and to create larger and versatile spatial structures.

Acknowledgements

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