SPECTRAL CHARACTERIZATION
OF MACRO-HETEROCYCLIC COMPOUND RhTMPyP / ZnTSPc

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ABSTRACT

Macro-heterocyclic compounds, such as porphyrins and phthalocyanines, are being studied extensively for their important physical and chemical properties. Their ability to absorb light throughout the spectrum and self-organization being adequate for the realization of several applications. Investigations of the spectral properties of the supramolecular assembly RhTMPyP/ ZnTSPc- 5,10,15,20 rhodium tetramethyl-pyridyl porphyrin / 2,9,16,23 zinc tetrasulfonated-phthalocyanine are registered by UV-Vis, FT-IR and Raman spectroscopic techniques.

KEYWORDS: porphyrins, phtalocyanines, macro-heterocyclic compound, UV-Vis, FT-IR, Raman

1. Introduction

Tetrapyrrole macrocycle based π-conjugated systems, such as porphyrin and phthalocyanine derivatives, are very famous rigid and aromatic molecular building blocks with special electronic structures [1]. Both porphyrin and phthalocyanine derivatives have distinctive photophysical, photochemical and electrochemical properties and the application of these systems have been developed in the field of photochemistry and electrochemistry [2].

As very chemically versatile compounds, both of these chemical compounds could insert different central metals, a wide range of photophysical, photochemical properties and also interesting applications could be obtained [3]. By coupling porphyrins with phthalocyanines, heterocomplexes useful for photodynamic applications could be obtained. Their association is based on „electrostatic"mixed dimers by pairing porphyrin and phtalocyanine bearing substituents with opposite charges, and have higher efficiency and stability [4].

Porphyrins are a class of macro-heterocyclic organic compounds, composed of four modified pyrrole subunits interconnected at their α carbon atoms via methine bridges [5]. In metallo-porphyrins, different metals (with bi-, tri- or tetra-valence) could be inserted into the macrocycle and for their spatial stability, halogen atoms could be attached as axially ligand, as is the case of Rh(III)TMPyP (Figure 1), where a single chlorine atom is necessary for this metallo-porphyrin stability [6].

Because Rh has a large atomic radius (1.4 Å), it cannot be included in the plane structure of porphyrin, where the macrocycle has the size of the cavity 1.3 Å and, in this sense, it can adopt a position above the porphyrin plane, with chlorine as axial ligand.

Phthalocyanines are azaporphyrins consisting of four benzoindole nuclei connected by nitrogen bridges in a 16-membered ring of alternating carbon and nitrogen atoms around a central metal atom which form stable chelates with metal cations (die or paramagnetic ion).

The molecule consists of the central metal atom, which is surrounded by four nitrogen atoms-pyrrole; four other nitrogen atoms-bridging aza; 32 carbon atoms-the pyrrole and the benzene ones (Figure 2) [7, 8].
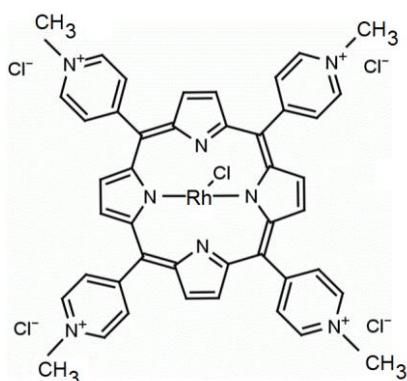
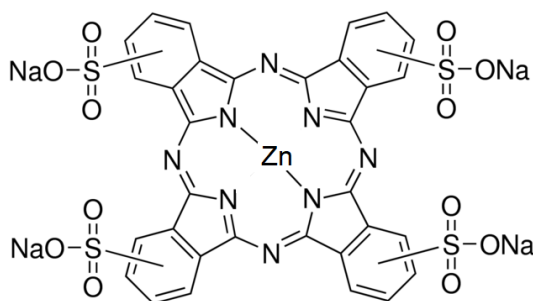*Fig. 1. Chemical structure of RhTMPyP*

Fig. 2. Chemical structures of ZnTSPc

One of the most important properties of the porphyrin and phthalocyanine molecules is their ability to coordinate to metal ions, yielding to stable systems.

Stable complexes of metallo-porphyrins and metallo-phthalocyanines results from formation of four equivalent σ bonds N→M. Both of them contain a 18π electron system that contributes to their remarkable thermal and chemical stability [9, 10].

In this work, the spectral properties of the macro-heterocyclic compound: rhodium-tetramethyl-pyridyl porphyrin (RhTMPyP) with zinc-tetra-sulphonated phthalocyanine (ZnTSPc) has been studied through UV-Vis, FT-IR and Raman analysis.

2. Materials and Methods

2.1. Materials

Rh (III)TMPyP and ZnTSPc have been used as pure materials, without any supplementary procedures from Aldrich company, while their heteroaggregate has been prepared in the laboratory after the following method: Rh (III)TMPyP has been converted into their chloride salts by passing them through the VIONIT AS-14 ion-exchange column in the chloride form. Then, the phthalocyanine was transformed into its sodium salt. A 0.088 g sample of

ZnTSPc was dissolved on a stoichiometric amount (1:4) of NaOH (3.9 mL, 0.1 M). The solution was filtrated, and the filtrate was dried under a stream of air overnight. A 0.05 g amount of this product was dissolved in 30 mL of water.

In another beaker, an equimolar mass of Rh (III)TMPyP (0.05 g) was dissolved in the same amount of water and the two solutions were mixed.

The final solutions were left for three weeks to ensure complete precipitation and then filtered by gravity [11].

2.2. Methods

The UV–VIS spectra were recorded with a SPECORD M 400 Carl Zeiss Jean spectrophotometer with microprocessor and double beam.

Infrared spectra were measured using an 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. ATR spectroscopy usually requires little to no sample preparation.

Raman spectra were recorded with a portable Xantus-2 TM Raman analyzer (Rigaku, Boston, United States of America) equipped with two laser sources (i.e., 785 nm and 1064 nm) and two detectors (i.e., TE cooled CCD and TE cooled InGaAs).

3. Results and discussions

Porphyrins and phthalocyanines, are compounds with great potential for serving as components of molecular materials that possess unique electronic, magnetic and photophysical properties, due to a large number of these chromophores, and for this reason it is of importance to construct arrays in which the molecules are organized in well-defined geometries with respect to their neighbours.

The phthalocyanine exhibit UV–Vis absorption spectra with an intense π-π transitions, usually referred to as Q-bands, in the range 660–799 nm with associated higher energy vibrational components in the range 600-660 nm [12].

Also, the phthalocyanines have a B Soret band in the range 420-320 nm, an N-band around 330-285 nm and an L-band at 270-230 nm. The UV-Vis spectra of the phthalocyanines are highly solvent and concentration-dependent. At high concentration in liquid protic solvent in water, for example, phthalocyanines could form aggregates [11].

During this study the spectra of phthalocyanine and porphyrin were carried out in DMSO solutions because DMSO prevents aggregation of each entity.

In general, the UV–VIS spectra of phthalocyanine free base shows a Q absorption band at 718 nm with a shoulder at 689 nm. As metallic complex with Zn, and with sulphonated substituents, the phthalocyanine shows blue shifts [13].

In the porphyrin free base spectra, could be registered a Soret band (around 414 nm) and four Q bands from 500 to 700 nm.

By metallation, the Soret band support a red shift, while the Q bands are reduced to only two bands (around 560 and 650 nm).

The existence of heterodimers and heterotrimers between the porphyrin and the phthalocyanine has been demonstrated by titration using spectrophotometric methods, such as absorption spectroscopy.

The heteroaggregate between Rh(III)TMPyP and ZnTSPc can adopt a close-contact, face-to-face mutual configuration, in order to optimize the π-π interactions between aromatic cores. The spectral evolution of a solution of Rh(III)TMPyP in DMSO upon addition of ZnTSPc is shown in Figure 3.
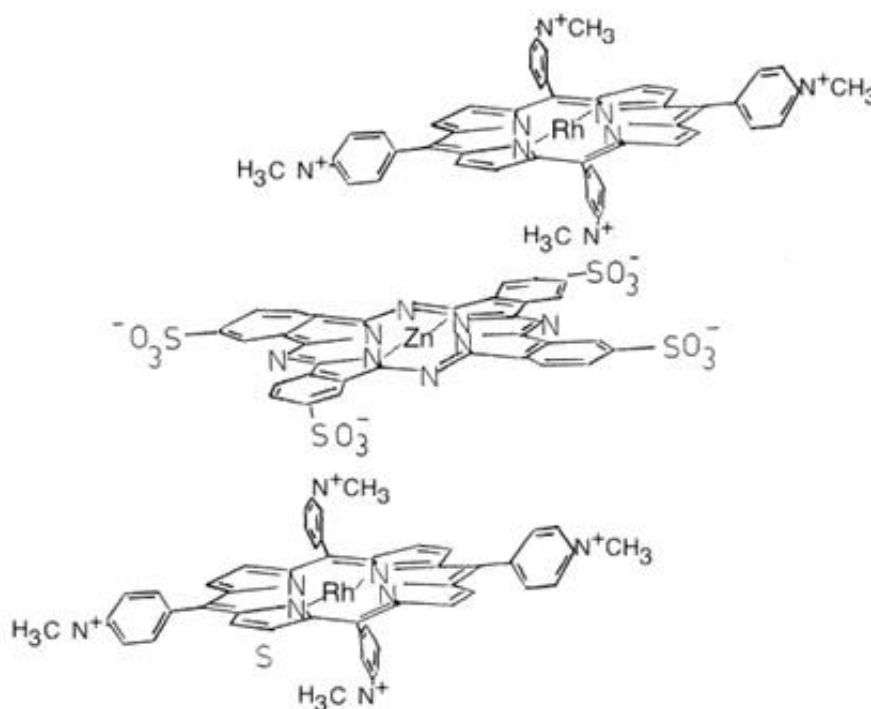

Fig. 3. *The structure of the heteroaggregate Rh(III)TMPyP/ZnTSPc*
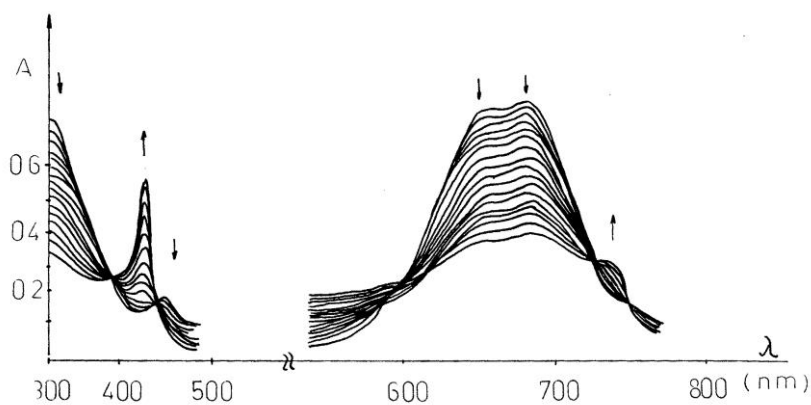

Fig. 4. *The spectral changes of UV-Vis for Rh(III)TMPyP/ZnTSPc*

During the titration, the Q-band of the phthalocyanine from 717 nm will become less intense and broader until its disappearance. A heteroaggregate with shorter distances between the components exhibits a larger shift of the porphyrinic Q 0,0 -band.

The heteroaggregation will occur only between N+ substituents from the porphyrine and the sulfonated phtalocyanine from the meso-positions (Figure 4).

Infrared (IR) spectroscopy is the most suitable method for identifying the presence of polar functional groups in the molecule structure of organic compounds.

To determine the structure of organic compounds, only the middle IR domain is used, and the characterization is achieved by using wavenumbers in the range 400-4000 cm^{-1}.
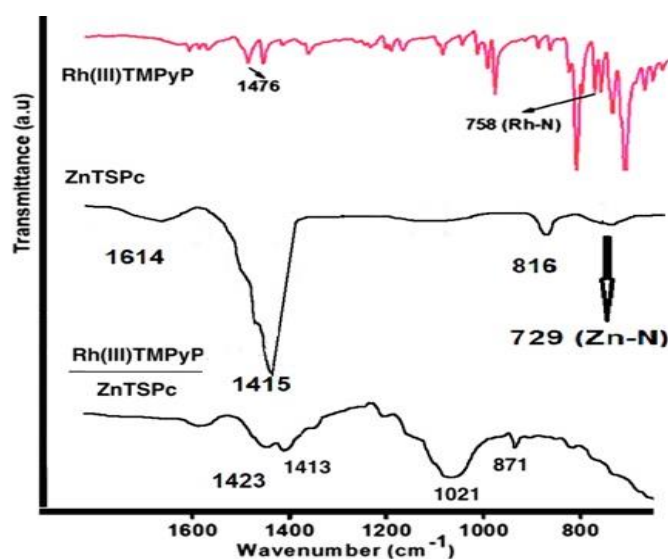

Fig. 5. IR spectra of RhTMPyP / ZnTSPc and individual components

The IR spectra of aromatic condensed benzene rings of metal phthalocyanines and porphyrins include the most extensive set of stretching and bending vibration bands: stretching vibrations of C-H bonds (3046-3060 cm^{-1}).

Relatively low intensity and skeletal C-C vibrations (1580-1610 cm^{-1}) with intensities are varying from moderate to very low. The frequency of 1580 cm^{-1} is caused by stretching vibrations of the C-C bond condensed with the pyrrole cycle.

Intense vibrations in the region of 947 cm^{-1} are totally symmetric stretching vibrations of C-C bonds of the aromatic ring. Plane bending vibrations of C-H are in the ranges of 1283–1289, 1158–1167, 1091–1096, and 1033–1060 cm^{-1}. Out-of-plane bending vibrations of C–metal bonds of metal phthalocyanines and porphyrins appear in the range of 720–780 cm^{-1}.

The complexity of the metallo-porphyrin molecule and the strong interaction of the ligand and metal ion could be responsible for the coupling of the ligand and metal-ligand vibrations [14, 15]. The high stability of the metallo-porphyrins suggests a somewhat higher frequency for the metal-nitrogen stretching mode. The far-infrared spectra of the metallo-porphyrins show a series of metal-dependent ligand absorption bands. The broad, medium intensity porphyrin deformation band at 500 cm^{-1} is shifted to a higher frequency in the metallo-porphyrins.

The most intense band in the far-infrared spectra of the metalloporphyrins appears at 350 cm^{-1}, and the adjacent weaker band at 380 cm^{-1}, can be attributed to the metal-free ligands and metal-nitrogen bond.

Vibrations of the –C=C–N= group (pyrrole fragment and nitrogen meso-atoms) appear as a low intensity band at 1396–1407 cm^{-1} and a very strong (characteristic of all phthalocyanines) band at 1320–1365 cm^{-1} [16].

At porphyrins, a high-intensity band at 1500–1530 cm^{-1} corresponds to vibrations of nitrogen bridging atoms (meso-atoms –N=). Stretching vibrations including vibrations of the pyrrole and benzene residues are in the range of 1420–1480 cm^{-1}; the band intensity varies from low to very high. The bands at 1594-1608 cm^{-1} and 1573-1582 cm^{-1} can be assign to C-N stretching vibrations, see Figure 5.

Different from the IR spectroscopic method which only depends on the chemical composition and phase of the samples, the resonance Raman spectral features also depend on the excitation wavelengths.
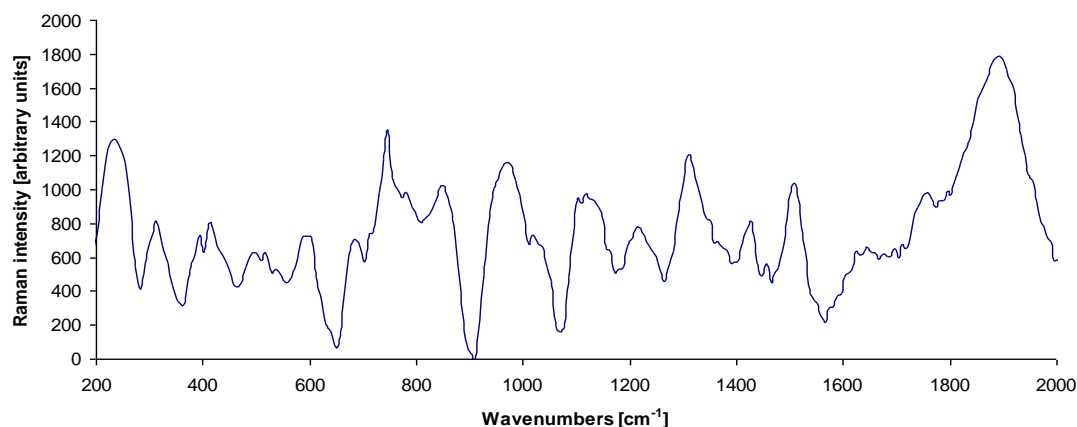
Fig. 6. *Raman spectra of RhTMPyP / ZnTSPc*

The obtained Raman spectrum shows prominent peaks whose Raman displacements are characteristic of the vibrational frequencies of the atoms in the molecules in which they are found, see Figure 6. The Raman spectra of analysed macro-heterocyclic compound shows some specific bands for these compounds at 1527 and 1538 cm^{-1}. They have been collected using laser excitation sources emitting at 632.8 and 785 nm. Under excitation at 632.8 nm, the most intense Raman band appears at 1598 cm^{-1} which is assigned to the isoindole stretching.

Typical Raman marker bands of the monoanion radical Pc.- were observed at 1499–1512 cm^{-1} as a medium band and at 1521−1538 cm^{-1} as a band whose intensity increases with the aggregation, resulting from the coupling of N^+ with SO_3^{-2} respectively.

In the context of surface chemistry, porphyrins, phthalocyanines and their metal complexes stand out from other organic molecules because of their, in relation to size and complexity, remarkable stability, their specific ligand-functionality and reactivity towards metals, as well as the planar structures of their parent macrocyles [17].

4. Conclusions

To develop new sensitizers based on macro-heterocyclic compounds, in this paper were studied the RhTMPyP/ ZnTSPc compound. Spectral properties of the studied materials indicated that these could be perspective for many applications, due to their versatility to change their central metal valence and to attach new substituents.

Under this context, RhTMPyP/ ZnTSPc is a special compound with proper properties. Their capacity of association has been identified by UV-Vis, FT-IR and Raman spectral 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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