

SPECTRAL AND PHOTODYNAMIC PROPERTIES OF A SILICON (TERT-BUTYL) PHTHALOCYANINE

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Abstract— Phthalocyanine derivatives are of increasing technological relevance due to their photophysical properties. Though silicon phthalocyanines bearing a different number of fused benzo-moieties are spectroscopically well investigated in solution, a complete spectroscopic characterization of their properties is not available, yet. To learn more about the influence of the silicon-metal in the benzo-annelated extended pi-system, we systematically investigated the spectroscopic and photodynamic properties of 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine dihydroxide (OH)₂Si-tBuPc). Since the centre of the phthalocyanine ligand is coordinated with silicon central metal ion, the electronic states are of both silicon and ligand origin. As a consequence the monomers of these compounds have a good absorbance than their metal-centered compounds. In addition, to mimic strong interaction between molecules, we investigated dimers/aggregates of the compound.

Keywords: silicon phthalocyanine, singlet oxygen, photodegradation, PDT

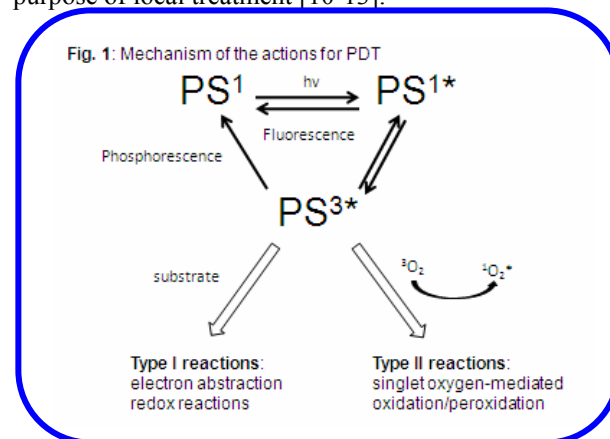
1. INTRODUCTION

Metallophthalocyanine complexes (MPc) represent an important class of coloring materials which present high thermal stability, light fastness, and inertness to acids and alkalis. Phthalocyanines are interesting and versatile compounds, which found many applications in industry, first of all as dyes and pigments, and later as photoconducting agents in photocopying machines [1]. They are also interesting for their electrochromism and electrocatalytic properties [2], for the ability to form liquid crystals [3-5] and Langmuir-Blodgett thin films [6], and for nonlinear optical properties [7].

The physicochemical, electrochemical, and spectroscopic properties, intramolecular interactions and performance associated to this application can be modulated by rational modification of the metal center and the substituents. As a consequence, various kinds of substituents such alkyl, alkoxy, and thioalkyl groups have been introduced onto the peripheral and/or nonperipheral positions of the phthalocyanine ligand.

Many substituted derivatives of phthalocyanines behave like active components in various redox processes, for example, in photoredox reactions and photooxidations in solution and for photodynamic cancer therapy [8]. Photodynamic therapy, PDT, is an evolving cancer

treatment method and implies three fundamental requirements: light, oxygen and a photosensitizer [9]. PDT consists in the systemic or topical application of a photosensitizer (PS) that, after a specific time interval for distribution, displays preferential accumulation in the neoplastic tissue. Subsequently, PS molecules are irradiated with laser light of a particular wavelength to induce photochemical and photophysical phenomena, marked by the occurrence of energy transfer to the nearby oxygen, generating reactive oxygen species as singlet oxygen, hydroxyl radical, and superoxide anions (Fig. 1). As a result of PDT-induced oxidative stress, cellular organelles and membranes become damaged, a process recognized as tumor photodamage. Singlet oxygen causes microvascular acute injury and blood vessel blockage in tumor and induces apoptosis of tumor cells, achieving the purpose of local treatment [10-13].



There is no single general drug for PDT, therefore, it is important to develop new improved PS for specific applications. The following characteristics should be maximized for PS in order to better fulfill the optimal profile to be used in PDT: concentration in tumor tissues, absorption of light in therapeutic window (600–800 nm), efficacy of energy transfer to oxygen, minimized time of elimination from organism and reduced dark toxicity.

2. EXPERIMENTAL SECTION

2.1. Materials and methods

Silicon 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine dihydroxide (Fig. 2) was purchased from Sigma-Aldrich and has been tested without further

purification. ZnPc and H₂Pc (Aldrich) have been used as reference for singlet oxygen determinations.

Uric acid (UA), a known singlet oxygen scavenger, used as a chemical dosimeter for the determination of photodynamic activity in PDT, was purchased from Merck.

The singlet oxygen trap, DPBF, obtained from Fluke (Porum grade) was used as received.

Absorption spectra were recorded using a SPECORD M400, Carl Zees Jena Spectrophotometer with double beam and equipped with a microprocessor. Background corrected UV-VIS absorption spectra were obtained on an SPECORD M42 UV/VIS spectrometer. Quartz cuvettes with 0.5-2 cm optical path lengths and containing 1 ml of cell suspension each were used. Molar extinction coefficients at a given wavelength, ϵ , were obtained using the Beer-Lambert law over the concentration range 10^{-4} - 10^{-7} mol dm⁻³. Fluorescence measurements were carried out in parallel with the absorption measurements, using a Jusco FP-6500 Spectrofluorimeter. A 2x2 mm cuvette, containing a 0.2 ml cell suspension was used. The excitation wavelength was 610 nm, the measurement range: 630-740 nm.

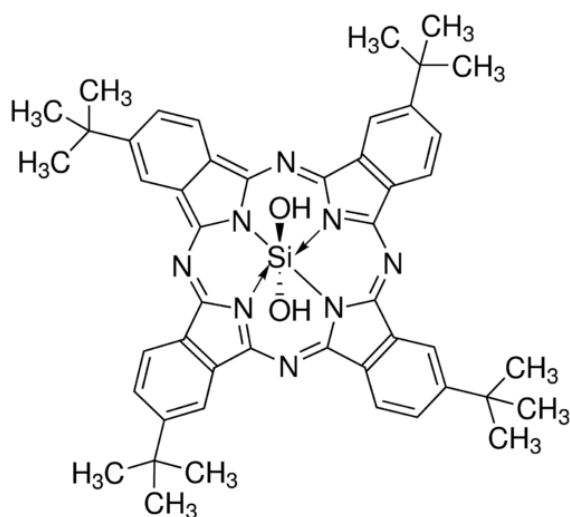


Fig. 2. The molecular structure of silicon 2,9,16,23-tetra-*tert*-butyl-29*H*,31*H*-phthalocyanine dihydroxide (Si-tBuPcDH)

2.2. Photochemical degradation

The photochemical experiments were carried out in a spectrophotometric cell of 1 cm pathlength. The experiments were carried out in air (i.e. without deoxygenating or bubbling of oxygen). Typically a 2 ml solution of (OH)₂Si-tBuPc ($0.5 - 1 \times 10^{-5}$ mol/l) was introduced to the cell and photolyzed in the Q-band region of the dye with a general electric quartz line lamp (300 W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off UV and far infrared radiation. An interference filter (670 nm) was placed in the light path before the sample. The light intensity was measured with a power meter (Lasermate/A) and was

found to be 5×10^{16} photons/s/cm². The wavelength of the interference filter was chosen such that it was close to the Q-band absorption of the Si-tBuPcDH. The quantum yields were determined using the following equation:

$$\phi = -[(C_t - C_0) \cdot V \cdot N_A] / I_{\text{abs}} \cdot S \cdot t \quad (1)$$

where:

C_t and C_0 in mol/l are the (OH)₂Si-tBuPc concentration after and prior to irradiation respectively;

V the reaction volume;

S the irradiated area of the cell (1.4 cm²);

t the irradiation time;

N_A the Avogadro's number = 6.023×10^{23} mol⁻¹

I_{abs} the overlap integral of the radiation source light intensity and the absorption of the (OH)₂Si-tBuPc (the action spectrum) in the region of the interference filter transmittance.

2.3. Singlet oxygen generation by photodegradation of DPBF

Measurements were carried out in a quartz cell (1cm x 1cm) at 25°C. Oxygen-saturated solutions ($V=0.2$ ml) containing sensitizer and 1,3-diphenylisobenzofuran (DPBF) ($c=0.858 \times 10^{-4}$ M) in DMSO were used. The photolysis cell was placed into the light beam of an UV-Vis spectrophotometer (Carl Zeiss Jena as described above), with DMSO as reference. The decreasing DPBF concentration was followed by a wave program measuring the absorbance at 420 nm ($\epsilon=23300$ M⁻¹.cm⁻¹) as a function of irradiation time (irradiation cycles, 20 x 20 sec) [14].

$$\phi_{\text{MPC}}^{\text{MPC}} = \phi_{\text{ZnPc}}^{\text{ZnPc}} \times \frac{\phi_{\text{DPBF}}^{\text{MPC}}}{\phi_{\text{DPBF}}^{\text{ZnPc}}} \times \frac{[\text{DPBF}]_{\text{MPC}}}{[\text{DPBF}]_{\text{ZnPc}}} \quad (2)$$

where:

-Pc is phthalocyanine rest;

-DPBF is 1,3-diphenylisobenzofuran;

- $\phi_{\text{MPC}}^{\text{MPC}}$ is the singlet oxygen quantum yield in presence of MPC;

- $\phi_{\text{ZnPc}}^{\text{ZnPc}}$ is the singlet oxygen quantum yield of ZnPc;

- $\phi_{\text{DPBF}}^{\text{MPC}}$ represents the quantum yield for DPBF in the presence of phthalocyanine (MPC);

- $\phi_{\text{DPBF}}^{\text{ZnPc}}$ is the quantum yield of DPBF in the presence of ZnPc;

- $[\text{DPBF}]_{\text{ZnPc}}$ is the concentration of DPBF in presence of ZnPc ;

- $[\text{DPBF}]_{\text{MPC}}$ is the concentration of DPBF in presence of MPC.

3. RESULTS AND DISCUSSIONS

The silicon phthalocyanines with axial substituents typically exhibit excellent photophysical properties, including higher quantum yields, longer fluorescence lifetimes and reduced aggregation with respect to zinc and aluminium species [15]. Reports of such compounds in the literature are extremely rare. Phthalocyanines exhibit an intense Q band about 400 cm^{-1} in the visible range at 650-700 nm with high molar extinction coefficients ($10^5 \text{ M}^{-1} \text{ cm}^{-2}$), Table 1. Their spectra is characterized by two main distinct absorption bands that appear as a result of $\pi\text{-}\pi^*$ transition within the delocalized 18π electron ring [16].

Table 1. Spectral parameters of $(\text{OH})_2\text{Si-tBuPc}$

λ (nm)	Absorption (DMSO)	
	$\epsilon \times 10^4$ ($\text{M}^{-1} \cdot \text{cm}^{-1}$)	
	monomer	aggregate
358	4.8398	
610	2.5784	
655	2.3254	
673	4.3224	3.1779
678	3.1493	6.3047
686	3.1208	4.8000

The spectral profile of monomeric $(\text{OH})_2\text{Si-tBuPc}$ has little variation from those of typical zinc phthalocyanine, showing Q band maxima at 693 nm. The Q band is generally extremely well resolved due to the prevention of ring interactions by the axial substituents [17].

The presence of axial ligands to the central coordinated metal ion is often favorable since it generates some degree of steric hindrance to intermolecular aggregation, without impairing the photophysical properties. The wavelength shift depends on the electron donating or electron withdrawing abilities of the axial ligand. The relationship between the axial substituent structure and Q-band absorption maximum show that a red-shift is preferred for a combination of electron withdrawing substituents of the axial ligand.

Aggregation in phthalocyanines generally occurs as a result of co-planar association of benzoporphyrine rings progressing from a monomer to a dimer and higher order aggregates. Aggregated species are distinguished in the UV-VIS absorption spectra by the appearance of extra peaks to the blue and/or red of the monomer peak. The $(\text{OH})_2\text{Si-tBuPc}$ shows aggregation in solution at concentrations up to $\sim 10^{-6} \text{ M}$. The sharp absorption bands in the Q-band region are assigned to monomer absorption, and the bands around 673 nm (which become stronger as the dye concentration increases) could be due to the characteristic face-to-face dimer or higher order aggregate (H-aggregate), as reported for structurally related compounds, **Figure 3**.

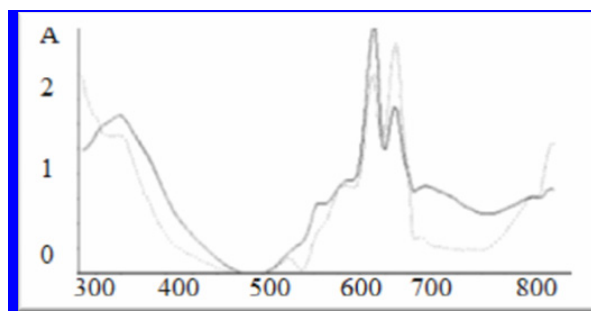


Fig. 3. The absorption spectra of $(\text{OH})_2\text{Si-tBuPc}$ monomer (—) and aggregates form (.....)

The presence of Si, a lighter atom, in the macrocycle, leads to low rates of inter-system crossing (ISC), efficient fluorescent emission and a fairly small non-radiative decay constant [18, 19]. For $(\text{OH})_2\text{Si-tBuPc}$ the sharp and intense well-defined Q-band centered at 673 nm indicates the lack of aggregation phenomena in solution, **Figure 4**. This behavior is quite important for an effective sensitization of the dye [20].

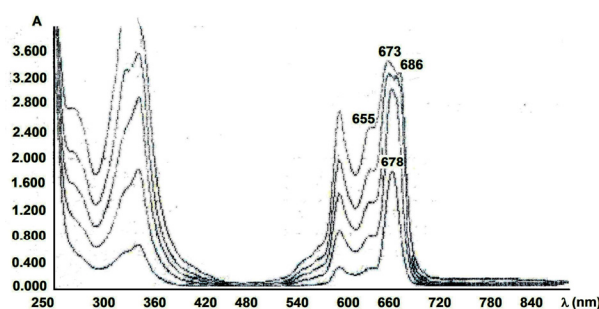


Fig. 4. The monomer and aggregated forms of $(\text{OH})_2\text{Si-tBuPc}$

Because there are quite similar UV-VIS spectra, this fact shows that axial substitution has a small or negligible influence. At low concentrations, the spectrum is dominated by the strong $\pi\text{-}\pi^*$ absorption of the monomer. As the concentration is increased, the apparent molar absorption coefficients of the monomer Q-band decrease with the appearance of a species with a broader, overlapping absorbance to the red. The band to the red of the monomer Q-band can be assigned to the dimer. The appearance of an isosbestic point at 783 nm is consistent with two-component equilibrium in the concentration range depicted in Figs. 3,4.

In order to determine the efficiency of some photochemical processes for the analyzed compounds, some basic photochemical was undertaken. Under Q-band excitation of complexes in the air, an initial relatively quick decrease in the Q-band occurs and the appearance of a new band at 678 nm was observed. This proves the photo transformation of the axial substituents upon photolysis. The presence of a diffuse isosbestic point indicates that photobleaching of the phthalocyanine

macrocycle is occurring to a small extent during the phototransformation of the axial substituents. The quantum yields for the phototransformation of the axial substituents are presented in Table 2.

Table 2. Quantum yield of singlet oxygen and photodegradation reaction

Compound	Quantum yield of singlet oxygen	Quantum yield of photodegradation
(OH) ₂ Si-tBuPc	0.99	0.127 x 10 ⁻⁴

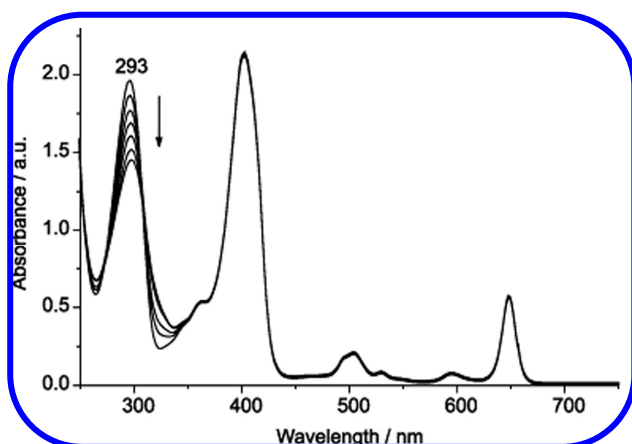


Fig. 5: Degradation of UA (293 nm) in ethanol solution containing (OH)₂Si-tBuPc. After laser irradiation at 683 nm for 1 s, 4 s, 240 s, 570 s, 840 s, 1320 s and 1470 s

For a high quantum yield of singlet oxygen generation, a higher stability has been observed, **Figure 5**. There is the possibility that photoinduced homolytic cleavage of Si-O bond is a key step of the phototransformation followed by a sequence for dark reactions of radicals with oxygen.

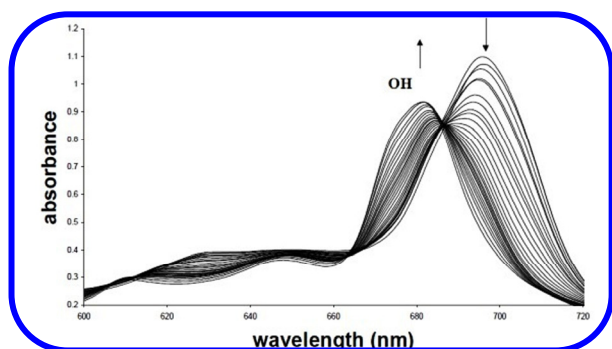


Fig. 6. The spectral changes of (OH)₂Si-tBuPc during the photodegradation reaction

The phthalocyanines and other photosensitizers are known to cause the degradation, **Figure 6**. Photobleaching, known also as a photodegradation, is a process whereby the dye molecule degrades in the presence of light [22]. After irradiation with intense light

the singlet oxygen is produced that is able to destroy the phthalocyanine molecule by a mechanism in agreement with literature (Fig.6).

The mechanism suggests singlet oxygen [4+2] cycloaddition to the pyrrole units in phthalocyanine macrocycle. As final reaction product phthalimide was found. The mechanism closely resembles that known for the reaction of 1,3-diphenylisobenzofuran (DPBF) and singlet oxygen [23].

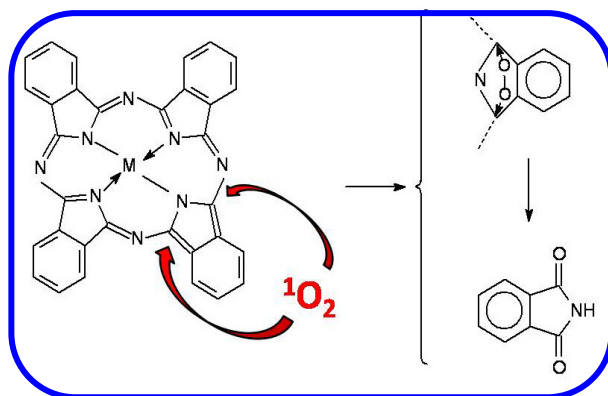


Fig. 7. The photodegradation mechanism of (OH)₂Si-tBuPc

4. CONCLUSIONS

The study has proved that the silicon-tetra(tert-butyl)-phthalocyanine dihydroxide has adequate spectral and promising photodynamic properties.

The spectral, photophysical properties have been evaluated and discussed, putting into evidence the aggregation equilibrium and the photodegradation processes, never treated in the literature for this phthalocyanine.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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