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Photochemical studies of tetra-2,3-pyridinoporphyrazines

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Abstract

Tetra-2,3-pyridinoporphyrazines and the corresponding water-soluble *N,N′,N′′,N′′′*-tetramethyl-tetra-2,3-pyridinoporphyrazine complexes, containing central metal atoms; M = Ge, Sn, Si and Zn, were synthesized and their photochemical properties were investigated. The reductive quenching of pyridinoporphyrazines excited states, enhanced relative to phthalocyanines, was considered as the first photochemical step of dyes phototransformation in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) solutions under irradiation with visible light. Efficiency of singlet oxygen photosensitization decreases significantly in the row phthalocyanines, unquaternized, quaternized tetra-2,3-pyridinoporphyrazine metallocomplexes.

Keywords: Pyridinoporphyrazine; Phthalocyanine; Sensitizer; Singlet oxygen; Photobleaching

1. Introduction

Since their initial use as dyes, phthalocyanines have found a wide variety of other applications based on their photochemical properties; including light harvesting coatings [1], photovoltaic devices [2,3] and non-linear optics [4]. Porphyrins and their analogs are interesting as sensitizers for the conversion of visible light into chemical energy [5,6]. Remarkable progress has been made in recent years in the use of phthalocyanine derivatives as sensitizers for photodynamic therapy of cancer [7,8]. Further progress in these and other branches of technology depends on synthesis and investigation of new photochemically active compounds.

Photochemically active water-soluble metallophthalocyanines (MPc) have found applications in many areas. The cationic, especially tetracationic phthalocyanine derivatives, possess enhanced oxidizing abilities and are particularly valuable for the photogeneration of molecular hydrogen from water in a sacrificial process [5]. Positively charged phthalocyanines possess promising photosensitizing properties for photodynamic therapy of cancer showing a higher photodynamic activity in vitro than commonly used haematoporphyrin [9]. It has been observed that the uptake and the killing of cells are higher for positively charged sensitizers than for neutral or negatively charged ones [10].

Tetrapyridinoporphyrazine (tppa, **I**) complexes are phthalocyanines in which the outer benzene rings are replaced with electron-withdrawing pyridine rings. The *N,N′,N′′,N′′′*-tetramethylated quaternized forms of tetrapyridinoporphyrazines (Tmtppa, **II**) are tetrapositively charged and hence water-soluble. According to the literature reports [11,12] these complexes do not form aggregates in aqueous solutions. The photochemistry and photosensitizing abilities of tetrapyridinoporphyrazines have received very little attention. In this work the complexes of tppa and Tmtppa with a series of non-transition metals (Ge, Si, Sn, Zn) have been synthesized, and their photochemical properties were investigated. Considering singlet oxygen to be responsible for photosensitized tumor cell inactivation in photodynamic therapy [13], the quantum yields of singlet oxygen photogeneration, Φ_Δ, of $(OH)_2$Getppa, $(OH)_2$Sitppa, $(OH)_2$Sntppa and Zntppa were estimated and compared with those of corresponding $(OH)_2$MPc (**III**) complexes and with those of the corresponding $[(OH)_2GeTmtppa]^{4+}$, $[(OH)_2SiTmtppa]^{4+}$, $[(OH)_2SnTmtppa]^{4+}$ and $[ZnTmtppa]^{4+}$ complexes. Photostability of these compounds in homogeneous solutions under Q-band excitation was also investigated.

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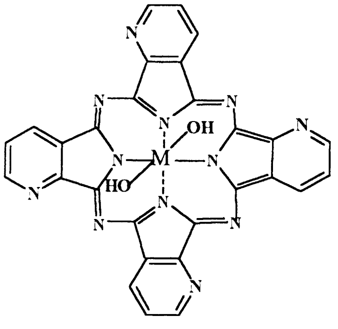
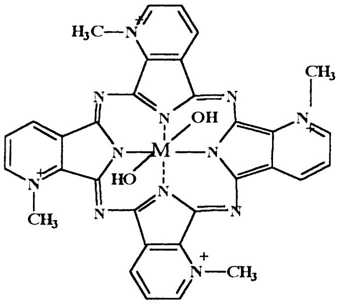


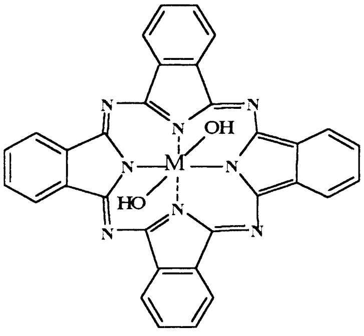
I

2,3-tetrapyridinoporphyrazine (tppa)



II

N, N′, N″, N‴-tetramethyl-2,3-tetrapyridinoporphyrazine (Tmtppa)



III

Metallophthalocyanine (MPc)

M = Ge(IV), Si(IV), Sn(IV) and Zn(II). No axial ligands for Zn complexes.

2. Experimental

2.1. Materials

Dichlorogermanium phthalocyanine (Cl_2GePc) was synthesized and purified according to literature procedures [14,15] and then hydrolyzed following literature methods [15], by refluxing with NaOH in pyridine to give the $(OH)_2GePc$. IR (KBr) shows the Ge–O asymmetric stretch at 644 cm^{-1} and the O–H stretch at 3496 cm^{-1} [15,16]. Anal. Calcd. for $C_{32}H_{18}GeN_8O_2\cdot 2H_2O$: C 61.95%; H 2.94% and N 18.06%. Found: C 61.09%; H 2.91% and N 17.49%.

Dihydroxytin ($(OH)_2SnPc$) and dihydroxysilicon ($(OH)_2SiPc$) phthalocyanine complexes were synthesized, purified and characterized according to reported methods [15]. Zinc phthalocyanine (ZnPc) was purchased from Sigma.

Germanium, silicon, tin and zinc tetra-2,3-pydidinoporphyrazine (tppa) complexes, Getppa, Sitppa, Sntppa and Zntppa, respectively, were synthesized and purified according to the method similar to that reported by Smith et al. [17] for the synthesis of the cobalt(II) pyridinoporphyrazine complex. The general procedure was as follows: urea (0.8 g, 13 mmol), ammonium molybdate (0.0315 g, 0.07 mol) and 2,3-pyridinedicarboxylic acid (0.35 g, 2 mmol) were ground together to form a homogenous mixture. The mixture was refluxed in 1,2,3-trichlorobenzene (40 ml) at 160°C for an hour. Then a second aliquot of urea (0.63 g) was added to the refluxing mixture followed by either $SiCl_4$ (3 ml) or $GeCl_4$ (4.5 ml) in accordance with the literature methods [17]. $ZnCl_2$ (0.25 g) or $SnCl_2$ (0.3 g) were ground together with the second aliquot of urea (0.63 g) before being added to the refluxing mixture. In each case the mixture was then refluxed for an additional 3.5 h at 210°C. The resulting solids were purified according to literature methods [17]. The synthesis and characterization of Zntppa has been reported [11], and it gave satisfactory characterization in accordance with the literature. The rest of the Mtppa complexes are reported for the first time here and their characterization is given below. The purification method of the Mtppa complexes incorporates washing with 5% NaOH, which brought about the hydrolysis of the complexes, giving $(OH)_2$Mtppa.

2.1.1. *$(OH)_2$Getppa*

Yield 42%. IR (KBr): $\nu_{\text{Ge–O}} = 646\,cm^{-1}$ and a strong O–H stretch at 3489 cm^{-1}, confirm hydrolysis. Anal. Calcd. for $C_{28}H_{14}GeN_{12}O_2\cdot 6H_2O$: C 45.99%; N 22.30%; H 3.56%. Found: C 45.47%; N 23.83%; H 2.75%.

2.1.2. *$(OH)_2$Sitppa*

Yield 37%. IR(KBr): $\nu_{\text{Si–O}} = 830\,cm^{-1}$. Anal. Calcd. for $C_{28}H_{14}SiN_{12}O_2\cdot 5H_2O$: C 50.29%; N 25.15%; H 3.59%. Found: C 51.14%; N 25.78%; H 2.49%.

2.1.3. *$(OH)_2$Sntppa*

Yield 28%. IR(KBr): $\nu_{\text{Sn–O}} = 556\,cm^{-1}$. Anal. Calcd. for $C_{28}H_{14}SnN_{12}O_2\cdot 5H_2O$: C 44.29%; N 22.14%; H 3.16%. Found: C 43.2%; N 22.8%; H 2.10%.

N,N′,N′′, N′′′ -tetramethyl-2,3-tetrapyridinoporphyrazine (Tmtppa) complexes of tin ($[(OH)_2SnTmtppa]^{4+}$), germanium ($[(OH)_2GeTmtppa]^{4+}$), zinc ($[ZnTmtppa]^{4+}$) and silicon ($[(OH)_2SiTmtppa]^{4+}$) were obtained by methylation of the corresponding Mtppa using freshly distilled dimethyl sulfate (Aldrich) following a procedure reported before [17]. The conversion yields from the corresponding Mtppa to the MTmtppa were as follows: $[(OH)_2SnTmtppa]^{4+}$ (∼10%, highly hygroscopic complex); $[(OH)_2GeTmtppa]^{4+}$ (60%); $[ZnTmtppa]^{4+}$ (71%); and $[(OH)_2SiTmtppa]^{4+}$ (70%). All the MTmtppa complexes were readily soluble in aqueous solutions.

Dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were freshly distilled before use. Triply distilled deionized water was employed for studies in aqueous solutions. 1,3-Diphenylisobenzofuran (DPBF, Aldrich) was used as a singlet oxygen quencher in non-aqueous solutions.

2.2. Photodegradation studies

The kinetic and quantum yields for the photodegradation of the Mtppa derivatives were studied in a spectrophotometric cell of 1 cm pathlength. Experiments were performed in air. Typically a 2 ml solution of the complex (about 1×10^{-5} mol l^{-1}) was introduced to the cell and photolyzed in the Q-band region with a General Electric Quartz line lamp (300 W). For kinetic studies a 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and far infrared radiation. An interference filter (Intor, 670 or 650 nm with bandwidths of 20 nm) was placed additionally in the light path before the sample, for the determination of quantum yields. The wavelength of the interference filter was chosen such that it was close to the Q-band absorption of the porphyrazine under investigation. The light intensity was measured with a power meter (Lasermate) and was found to be 5×10^{16} photons s^{-1} cm^{-2}.

The quantum yields of the photobleaching of $(OH)_2$Getppa was determined using the following equation

$$\Phi = -\frac{(C_t - C_0)VN_A}{I_{abs}St}$$

where C_t and C_0 in mol l^{-1} are the dye concentrations after and prior to irradiation, respectively, the change in concentration of the dyes was about 15% for these studies. Values of C_t and C_0 were obtained in DMF using the Q-band extinction coefficient for $(OH)_2$Getppa ($\varepsilon = 52{,}000\,dm^3\,mol^{-1}\,cm^{-1}$). V is the reaction volume, S the irradiated area of the cell, t the irradiation time, N_A is the Avogadro's number and I_{abs} the overlap integral of the radiation source light intensity and the absorption of the $(OH)_2$Getppa (the action spectrum) in the region of the interference filter transmittance and is defined as

$$I_{abs} = \int (1 - 10^{A_\lambda}) I_\lambda \, d\lambda$$

where I_λ is the intensity of light and A_λ the absorbance of the porphyrazine at wavelength λ.

Experiments were performed also whereby the solutions were deaerated with N_2 gas or saturated with O_2 in order to study the role of oxygen in the photodegradation process.

2.3. Singlet oxygen quantum yields determination

Quantum yields of singlet oxygen photogeneration were determined in DMSO or DMF solutions (in air, without bubbled oxygen) using the relative method with zinc phthalocyanine (ZnPc) as reference and DPBF as chemical quencher for singlet oxygen. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [18] the concentration of DPBF was lowered to $\sim 3 \times 10^{-5}$ mol l^{-1}. Solutions of sensitizer (absorbance below 1 at the irradiation wavelength) containing DPBF were prepared in the dark and irradiated in the Q-band region using the setup described in Section 2.2. DPBF absorption decay at 417 nm was monitored. The light intensity and amount of absorbed photons were obtained as explained in Section 2.2, with the wavelength of the interference filter being chosen such that it was close to the Q-band absorption of the porphyrazine or of the ZnPc standard.

The values of Φ_Δ were calculated with the following relationship

$$\Phi_\Delta = \Phi_\Delta^{PcZn} \frac{W I_{abs}^{PcZn}}{W^{PcZn} I_{abs}}$$

where Φ_Δ^{PcZn} is the singlet oxygen quantum yield for ZnPc. For ZnPc in DMF, the Φ_Δ^{PcZn} of 0.56 [18] and in DMSO $\Phi_\Delta = 0.67$ [19] were employed. W and W^{ZnPc} are the DPBF photobleaching rates in the presence of Mtppa derivatives under investigation and ZnPc, respectively. I_{abs} and I_{abs}^{ZnPc} are the rates of light absorption by the tppa derivative and ZnPc, respectively. The initial DPBF concentrations are kept the same for both the ZnPc reference and the samples. Changes in porphyrazine absorption, if they occurred during these experiments, did not exceed 10%.

The quantum yields were determined with an accuracy of ∼15%. All the experiments were carried out at room temperature. UV–VIS spectra were recorded on a Varian 500 UV–VIS/NIR spectrophotometer. IR spectra (KBr pellets) were recorded on a Perkin-Elmer Spectrum 2000 FTIR spectrometer.

3. Results and discussion

3.1. Tetra-2,3-pyridinoporphyrazines

The solubility of unsubstituted Mtppa complexes is extremely low. Only in DMSO or DMF we could obtain solutions suitable for spectroscopic and photochemical studies, with concentrations of about 10^{-6} to 10^{-5} mol l^{-1}. $(OH)_2$Sitppa and $(OH)_2$Sntppa complexes were found to be

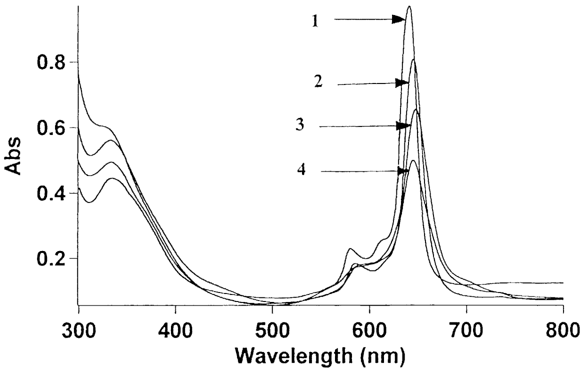


Fig. 1. Electronic absorption spectra in DMSO of (1) (OH)$_2$Getppa; (2) Zntppa; (3) (OH)$_2$Sitppa; (4) (OH)$_2$Sntppa.

less soluble than (OH)$_2$Getppa and Zntppa. Despite the low solubility, pyridinoporphyrazines under investigation show monomeric behavior in solution. The visible absorption spectra of the Mtppa complexes in DMSO are presented in Fig. 1 and show a sharp Q-bands in the 641–648 nm region (see Table 1 for Q-band absorption maxima) and vibration satellites at 580–590 nm. This band structure is typical for phthalocyanine derivatives and the blue shift of the Q-band relative to phthalocyanines is characteristic of the pyridinoporphyrazines complexes [11]. Lambert–Beer law was obeyed in DMSO or DMF solutions at low concentrations in which the dyes show solubility.

3.1.1. Phototransformation

Photostability of Mtppa metallocomplexes was studied in DMF and DMSO solutions. Due to low and slow solubility of Mtppa complexes, preparation of solutions needs time (hours). Within this period absorption of dye increases until a constant value is obtained. After the complexes were completely dissolved, the photochemical properties of the complexes were then investigated.

Table 1
Spectral data and singlet oxygen quantum yields of metalloporphyrazine metallophthalocyanine complexes^{a}

Compound	Q-band absorption, λ_{max} (nm) $(\log\varepsilon)^{b}$	Φ_Δ
(OH)$_2$GePc	676	0.25 (0.34)^{c}
(OH)$_2$Getppa	641 (4.71)	0.17 (0.22)^{c}
[(OH)$_2$GeTmtppa(−2)]$^{4+}$	687	<0.01
(OH)$_2$SiPc	672	0.28
(OH)$_2$Sitppa	645	0.21
[(OH)$_2$SiTmtppa(−2)]$^{4+}$	653, 640	0.01
(OH)$_2$SnPc	697	0.26
(OH)$_2$Sntppa	648	0.15
[(OH)$_2$SnTmtppa(−2)]$^{4+}$	642	0.02
ZnPc	672	0.67 [19]^{d}
Zntppa	647	0.16
[ZnTmtppa(−2)]$^{4+}$	641, 655	0.06

[a] Solvent: DMSO.
[b] $\log\varepsilon$ given in parentheses.
[c] Φ_Δ values in DMF given in parentheses.
[d] Reference given in square bracket.

Fig. 2 shows the absorption spectra changes observed on photolysis of Zntppa in the Q-band region and in DMSO. There is a gradual decrease in the Q-band absorption intensity without formation of new peaks. This kind of photoprocesses is termed photobleaching and reflects the deterioration of conjugated chromophore structure of the dye.

The complexes (OH)$_2$Getppa, (OH)$_2$Sntppa and (OH)$_2$ Sitppa display slightly different behavior from that shown in Fig. 2 for Zntppa, under light excitation. As demonstrated on Fig. 3 with (OH)$_2$Getppa as an example, photobleaching and photoinduced change in the Q-band absorption may be divided on two parts. The first part consists of up to 25% fast decrease in the Q-band intensity with simultaneous increase

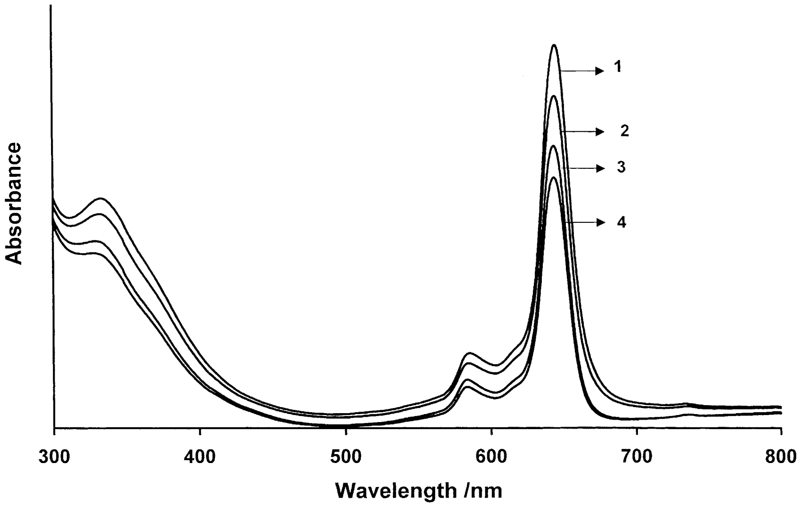


Fig. 2. Electronic absorption spectral changes observed during photolysis of Zntppa in DMSO. Photolysis times: (1) 0 min; (2) 2 min; (3) 6 min; (4) 20 min. Excitation wavelength >600 nm.

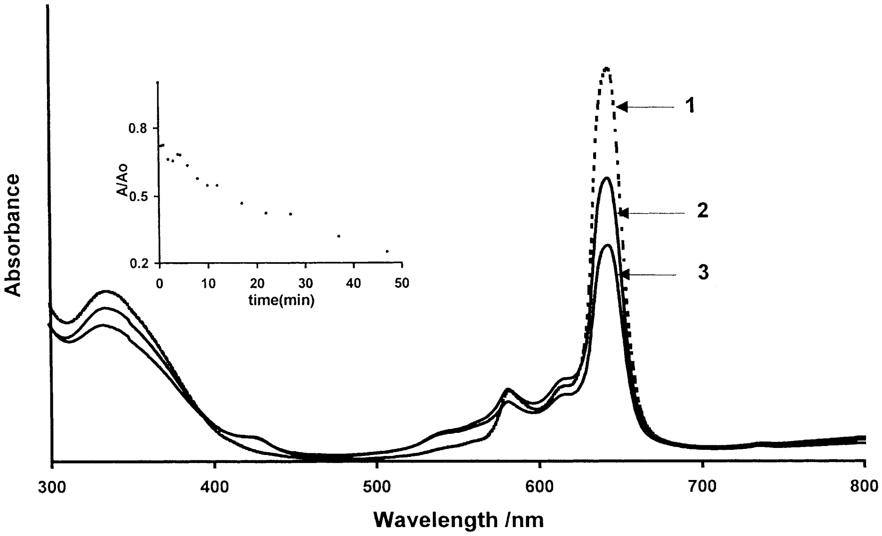


Fig. 3. Electronic absorption spectral changes observed during photolysis of $(OH)_2$Getppa in DMSO. Photolysis times: (1) 0 min; (2) 30 s; (3) 12 min. Excitation wavelength >600 nm.

of absorption in the short-wavelength region, around 540 and 620 nm. These spectral changes are typical of ring reduction in phthalocyanine [20] and porphyrazine [11] complexes. The new peak observed near 420 nm has been observed for ring reduced phthalocyanines [20]. Chemical reduction (using sodium borohydride) of $(OH)_2$Getppa resulted in the formation of these bands, hence confirming that the photobleaching is accompanied by the photoreduction of the complexes. The reduction peaks at 540 and 620 nm were only obtained within 30 s of photolysis, then decreased in intensity as photolysis progressed. Clear photobleaching process was observed after this time. The insert shows the kinetic curve for the photobleaching process in Fig. 3. The relative kinetic curves for the decrease in the Q-band absorption, obtained under identical conditions with $\lambda > 600$ nm excitation (without the use of an interference filter) of Mtppa complexes in DMSO, are presented on Fig. 4. The plots of Fig. 4 show first, a fast drop in the Q-band absorption during the first 30 s due to the photoreduction process, followed by photobleaching kinetics. Photobleaching rates of compounds under investigation do not differ significantly with the lowest rate being for Zntppa and the highest rate for the $(OH)_2$Getppa complex.

Kinetic curves for the photobleaching $(OH)_2$Getppa in DMF, saturated with O_2, air or N_2 are shown on Fig. 5. The curves shown in Fig. 5 represent only the photobleaching component, excluding the first step due to the initial formation of the reduced species. The quantum yields were calculated to be $(7.5\pm0.5)\times10^{-5}$, $(5.0\pm0.5)\times10^{-4}$ and $(1.2\pm0.2)\times10^{-3}$, respectively, for O_2, air or N_2 saturated solutions of $(OH)_2$Getppa. The results obtained demonstrate that photobleaching rates and quantum yields of $(OH)_2$Getppa in DMF decrease with increase in oxygen concentration. The increase of photobleaching rate under nitrogen when compared to oxygen and air saturated solutions was observed

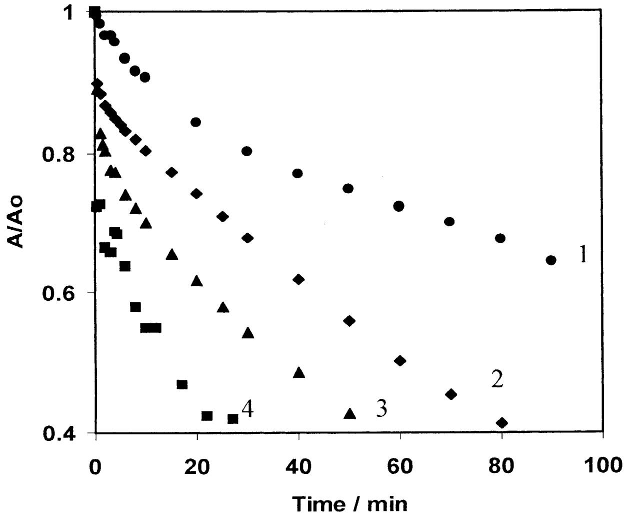


Fig. 4. Kinetic curves for the photobleaching in DMSO and in the presence of air of (1) Zntppa; (2) $(OH)_2$Sitppa; (3) $(OH)_2$Sntppa; (4) $(OH)_2$Getppa. Excitation wavelength >600 nm.

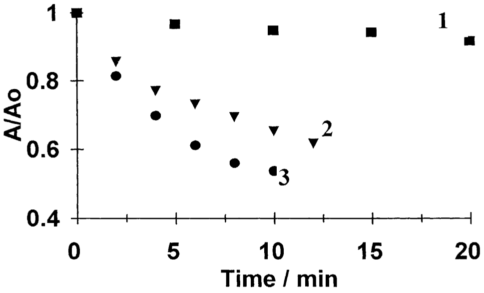


Fig. 5. Kinetic curves for the photobleaching in DMF of Getppa for (1) oxygen; (2) air; (3) nitrogen saturated solutions. The curves exclude the first part due to the initial formation of the reduced species (see text). Excitation wavelength >600 nm.

for $(OH)_2$Getppa, in DMSO solutions as well. The fact that photobleaching is more pronounced in the nitrogen saturated solutions indicates that photoreduction is responsible for the degradation of $(OH)_2$Getppa in DMF and DMSO solutions. In their study on the phototransformation of Zntppa in the presence of electron donors, Wohrle et al. [11] found that the electron-withdrawing effect of the annelated pyridine rings resulted in reductive quenching of the excited states of the Zntppa species. Thus, electron or hydrogen atom transfer from the solvent (S–H in the Scheme below) to the excited porphyrazine molecule (Pz*) may be assumed as the first step in the photobleaching process.

$$\mathrm{Pz}^{*} + \mathrm{S{-}H} \rightarrow \mathrm{Pz}^{\bullet -}(\mathrm{PzH}^{\bullet}) + \mathrm{S{-}H}^{\bullet +}(\mathrm{S}^{\bullet}) \tag{1}$$

$$\mathrm{Pz}^{\bullet -}(\mathrm{PzH}^{\bullet}) + \mathrm{O_2} \rightarrow \mathrm{Pz} + \mathrm{O_2}^{\bullet -}(\mathrm{HO_2}^{\bullet}) \tag{2}$$

$$\mathrm{S{-}H}^{\bullet +}(\mathrm{S}^{\bullet}) \overset{\mathrm{O_2}}{\rightarrow} \text{peroxides} \tag{3}$$

$$\mathrm{O_2}^{\bullet -}(\mathrm{HO_2}^{\bullet}) \overset{\mathrm{S{-}H}}{\rightarrow} \mathrm{H_2O_2} \tag{4}$$

$$\mathrm{Pz}^{\bullet -}(\mathrm{PzH}^{\bullet}) \overset{\mathrm{O_2}}{\rightarrow} \text{oxidized products} \tag{5}$$

$$\mathrm{Pz} \overset{\mathrm{H_2O_2},\ \text{peroxides}}{\rightarrow} \text{oxidized products} \tag{6}$$

Free radicals, formed during the primary photoreduction process are very reactive chemically and react mainly with residual oxygen. Interaction of semi-reduced dye radicals with oxygen results in the recovery of the dye according to step 2 of the Scheme. We examined the recovery of $(OH)_2$Getppa after photolysis under N_2 conditions, and we found that bubbling dioxygen through solution with 30–40% of photobleaching leads to about 50% recovery of the Q-band absorption of the dye, this observation may be considered as confirmation of step 2 of the above Scheme. Reactions of primary radicals with oxygen may give oxidized products shown in reactions 3–6, the relative efficiency of which depending on the dye structure. Thus, primary photoreduction of the dye in the presence of oxygen leads ultimately to the degradation of the dye through oxidative process given by steps 3–6 of the Scheme. This mechanism is known as photooxidation with chemical sensitization.

The relationship between photobleaching rates and electronic structure of dye molecules is consistent with key role of dye photoreduction in over-all photobleaching. Thus, the kinetic curves, presented on Fig. 6 show that $(OH)_2$Getppa with electron-withdrawing pyridine rings in macrocycle structure, hence more easily reduced ring, has a significantly higher photobleaching rate, than $(OH)_2$GePc.

3.1.2. Singlet oxygen quantum yields

Singlet oxygen quantum yields (Φ_Δ) for $(OH)_2$Getppa, $(OH)_2$Sitppa, $(OH)_2$Sntppa and Zntppa are summarized in Table 1. The results obtained show that values of Φ_Δ range from 0.15 to 0.21, hence Φ_Δ is only slightly affected by the nature of central metal atom in the series of complexes studied. For comparison, literature or experimental data of Φ_Δ values for the corresponding MPc complexes are also presented. Quantum efficiency of singlet oxygen production was generally measured in DMSO solutions; for $(OH)_2$GePc and $(OH)_2$Getppa the experiments were performed in DMF as well. The other $(OH)_2$Mtppa complexes showed a low solubility in DMF. Values of Φ_Δ are higher in DMF (Table 1), and for $(OH)_2$GePc in DMF, the Φ_Δ value is close to one reported in [21] for GePc complexes containing bulky axial substituents. The results shown in Table 1 give evidence for lower singlet oxygen quantum yields for the porphyrazine complexes when compared with the phthalocyanines. The low efficiency of singlet oxygen photogeneration by pyridinoporphyrazines may be explained in terms of their short triplet state lifetimes. The triplet state lifetimes for some metallocomplexes of tppa were found to be only ca. 10^{-7} s [11], shorter compared to phthalocyanines containing a similar central metal. Since singlet oxygen is generated by energy transfer from excited triplet state of the photosensitizer to ground state oxygen, the high triplet state lifetime is an important prerequisite for efficient singlet oxygen photogeneration.

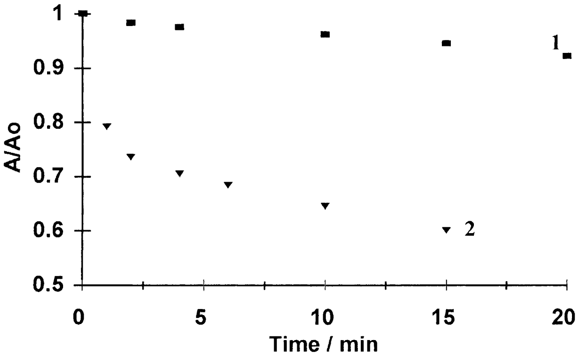


Fig. 6. Kinetic curves for the photobleaching in DMF and in the presence of air for (1) $(OH)_2$GePc; (2) $(OH)_2$Getppa. Excitation wavelength >600 nm.

3.2. N,N′,N″,N‴-tetramethyl-2,3-tetrapyridinoporphyrazines

The complexes $[\mathrm{MTmtppa}]^{4+}$ are synthesized as methyl sulfate salts, prepared by quaternization of the pyridine nitrogen atoms in Mtppa complexes with dimethyl sulfate. The $[\mathrm{MTmtppa}]^{4+}$ are water-soluble and display a behavior different from that reported above for the Mtppa complexes. In DMSO solutions only the $(OH)_2$SnTmtppa complex gave a blue solution of $[(OH)_2\mathrm{SnTmtppa}(-2)]^{4+}$ (where pa(−2) is the porphyrazine dianion) with a sharp Q-band at $\lambda_{max} = 642$ nm, characteristic for monomeric phthalocyanine species. The solutions of the $(OH)_2$GeTmtppa, $(OH)_2$SiTmtppa and ZnTmtppa complexes in DMSO gave purple–violet color with broad absorption bands in the 500–600 nm region indicative of the presence of ring reduced products. For the ZnTmtppa complex the product of the first reduction $[ZnTmtppa(-3)]^{3+}$, is known to absorb in water at 570 nm, the second reduction product $[ZnTmtppa(-4)]^{2+}$ absorbs at 500 nm [11]. It should be noted, that the extent of ring reduction in MTmtppa complexes may be affected by the nature of the solvent, pH, light, temperature, etc. On addition of chemical oxidants (e.g. bromine), the purplish–violet solutions of $(OH)_2GeTmtppa$, $(OH)_2SiTmtppa$ and ZnTmtppa species in DMSO turned blue with spectra typical of $[MTmtppa(-2)]^{4+}$ species. The purplish–violet solutions of the ring reduced MTmtppa complexes were found to turn blue if left for a prolonged period in DMSO (overnight) resulting in mainly the $[(OH)_2GeTmtppa(-2)]^{4+}$, $[(OH)_2SiTmtppa(-2)]^{4+}$ and $[ZnTmtppa(-2)]^{4+}$ species. The visible spectra of the resulting blue solutions in DMSO are presented in Fig. 7. High absorption at the short-wavelength slope of Q-band in the spectra of $[(OH)_2GeTmtppa(-2)]^{4+}$ and $[(OH)_2SiTmtppa(-2)]^{4+}$ (Fig. 7) is not affected by oxidants and was thus, attributed to the formation of aggregates. Beer's law was not obeyed for these complexes. The corresponding spectra in Fig. 7 for $[(OH)_2SnTmtppa(-2)]^{4+}$, $[ZnTmtppa(-2)]^{4+}$ are characteristic of the monomeric species in phthalocyanine and porphyrazine [11] complexes. The Q-band spectra for $[ZnTmtppa(-2)]^{4+}$ and $[(OH)_2SiTmtppa(-2)]^{4+}$ in Fig. 7 show splitting, due to the presence of symmetrical and unsymmetrical constitutional isomers. For the $[ZnTmtppa(-2)]^{4+}$ species in water, the absorption maxima were observed at 637 and 648 nm, which coincides with those reported in [11]. It worth noting that the corresponding less polar unquaternized Mtppa complexes, do not show Q-band splitting (Fig. 1), though they are expected to have the same isomeric components as the MTmtppa complexes. Since aggregation prevents photoactivity due to the fast dissipation of excitation energy in radiativeless processes, phototransformation of the complexes were studied only for the monomeric $[(OH)_2SnTmtppa(-2)]^{4+}$, $[ZnTmtppa(-2)]^{4+}$ complexes in DMSO.

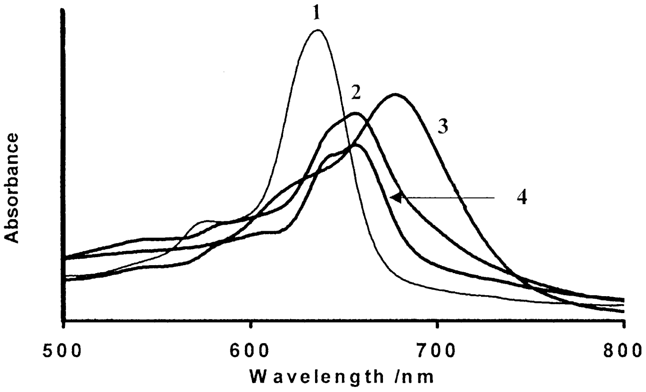


Fig. 7. Electronic absorption spectra in DMSO of (1) $[(OH)_2SnTmtppa(-2)]^{4+}$; (2) $[(OH)_2SiTmtppa(-2)]^{4+}$; (3) $[(OH)_2GeTmtppa(-2)]^{4+}$; (4) $[ZnTmtppa(-2)]^{4+}$.

3.2.1. Phototransformation

The spectral changes, induced by Q-band excitation of $(OH)_2SnTmtppa$ in DMSO in the presence of air, are shown on Fig. 8. A decrease of Q-band absorption intensity and relative increase of short-wavelength absorption provide evidence for the formation of one-electron reduction

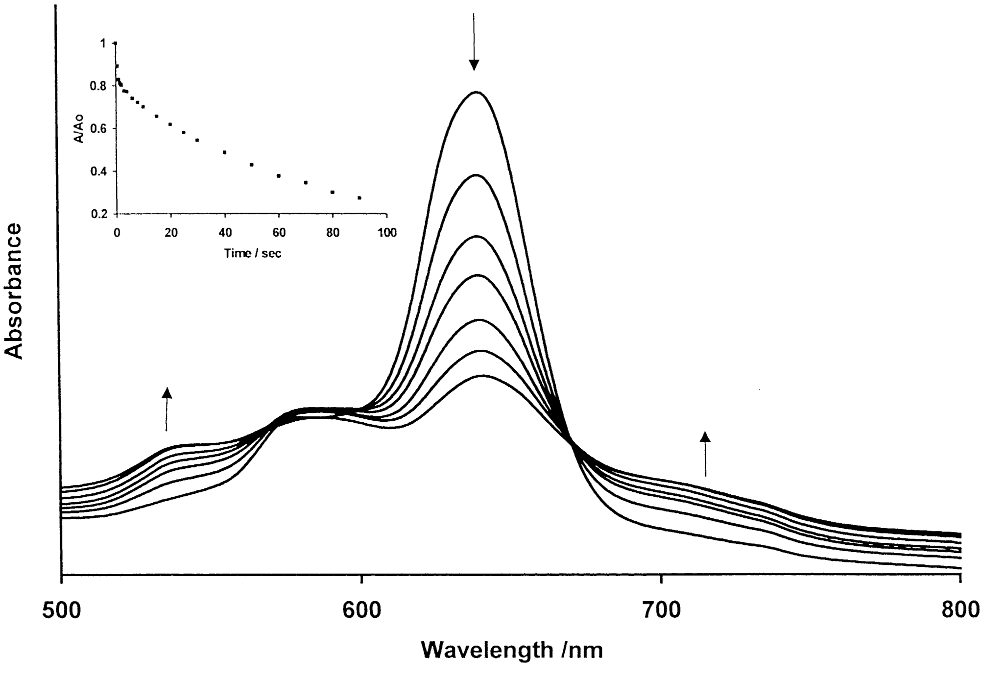


Fig. 8. Electronic absorption spectral changes observed during photolysis of $[(OH)_2SnTmtppa(-2)]^{4+}$, in DMSO. (a) Before photolysis; (b) 20 min after photolysis. Photolysis at $\lambda > 600$ nm. Insert the dependence of absorbance on time for the spectroscopic changes.

product (absorption about 560 nm). This band then decreases in intensity with time with the formation of a new band at 520 nm, due to the second one-electron reduction of the ring. The insert on Fig. 8 presents the kinetics for the photoreduction of $[(OH)_2SnTmtppa(-2)]^{4+}$, the decrease in the Q-band intensity obeying pseudo first-order rate law. The product of photoreduction reacts in a slow dark process with dioxygen resulting in recovery of the tetracation $[(OH)_2SnTmtppa(-2)]^{4+}$ with a Q-band maxima at 642 nm. Addition of bromine increases the rate of the regeneration of the $[(OH)_2SnTmtppa(-2)]^{4+}$ species. The $[ZnTmtppa(-2)]^{4+}$ species in DMSO, displays a similar photoreduction behavior to that shown in Fig. 8 for $[(OH)_2SnTmtppa(-2)]^{4+}$. The results obtained confirm the conclusion of other researchers [11], that alkylated tetramethyl-2,3-tetrapyridinoporphyrazines show a strong tendency towards reductive quenching of excited states.

Unlike in the behavior reported above for DMSO and DMF, no light induced photoreduction of the $[MTmtppa(-2)]^{4+}$ complexes was observed in water solutions, in the absence of added electron donors. Only gradual photobleaching was observed in water as evidenced by the decrease in the spectra without formation of new peaks.

3.2.2. Singlet oxygen quantum yields

Singlet oxygen quantum yields of $[MTmtppa(-2)]^{4+}$ complexes in DMSO solution are summarized in Table 1. The Φ_Δ values, reflecting the aggregation state of compounds under investigation in solution, are negligible ($\Phi_\Delta \leq 0.01$) for $[(OH)_2GeTmtppa(-2)]^{4+}$ and $[(OH)_2SiTmtppa(-2)]^{4+}$ complexes. The monomeric complexes $[ZnTmtppa(-2)]^{4+}$ and $[(OH)_2SnTmtppa(-2)]^{4+}$ show slightly higher Φ_Δ values when compared to the aggregated Ge and Si complexes, but show low efficiencies of singlet oxygen photosensitization when compared to the corresponding MPc complexes (Table 1). The decrease of singlet oxygen formation may be caused by low excited state lifetimes due to their enhanced degradation in competitive reductive quenching.

4. Conclusion

It is well known, that complexes of phthalocyanines with non-transition metals have long lived excited states, high triplet state quantum yields and therefore, sensitize singlet oxygen efficiently. Thus, phthalocyanines and their derivatives are promising sensitizers for different applications including PDT. In the present study the efficiency of phthalocyanine pyridine analogs, tetra-2,3-pyridinoporphyrazine complexes with diamagnetic metals, such as Zn, Si, Sn and Ge in sensitization of singlet oxygen were examined for the first time. It was found, that the increase in electron-withdrawing character of phthalocyanine macrocycle periphery leads to decrease in singlet oxygen quantum yields probably due to enhanced excited states reductive quenching. The most outstanding property of tetra-2,3-pyridinoporphyrazines is their enhanced ability to act as oxidizing agents. These compounds under visible light excitation and in organic media sensitize the formation of radicals in electron transfer process, through a type I mechanism. Since type I mechanism is also important for PDT, tetra-2,3-pyridinoporphyrazines and their water-soluble quaternized forms cannot be ruled out as promising sensitizers for this application and need further investigations. Due to enhanced oxidizing ability pyridinoporphyrazines may be interesting also as photoredox sensitizers for functional materials.

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