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Silicon octaphenoxyphthalocyanines: photostability and singlet oxygen quantum yields

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Abstract

Photochemical properties of series of axially substituted silicon octaphenoxyphthalocyanines with aryloxy, siloxy, aminoalkoxy, esters of carboxylic acids and sulphonic acid esters residues as axial ligands were studied in dimethylsulfoxide (DMSO) solution. It was found, that under Q-band excitation axial ligands in compounds studied have the propensity to be changed by hydroxyl groups with quantum yields in the range 10^{-5} to 10^{-2} depending on the nature of the axial ligand. Axial substituent phototransformation was followed by slow photobleaching of dihydroxysilicon octaphenoxyphthalocyanine (photoproduct) in self-sensitized singlet oxygen mediated oxidation of the macrocycle. Singlet oxygen quantum yields were found to be in the range 0.15–0.20 for majority of the phthalocyanines (Pc) studied.

Keywords: Silicon phthalocyanine; Phototransformation; Singlet oxygen; Quantum yields

1. Introduction

There is considerable interest in phthalocyanines (Pc) containing non-transition metals for use as photosensitizers in the relatively new method of cancer treatment called photodynamic therapy (PDT) [1–3]. The mode of operation in PDT is based on visible light excitation of a tumor-localized photosensitizer. After excitation, energy is transferred from the photosensitizer (in its triplet excited state) to ground state oxygen ($^3O_2$), forming singlet oxygen ($^1O_2$). This process is the dominating initial elementary step of PDT, and it is followed by oxidation of cellular targets (sub) by $^1O_2$; the so-called type II mechanism [3–5]

$$\mathrm{Pc} \xrightarrow{h\nu} {}^1\mathrm{Pc}^* \xrightarrow{\mathrm{ISC}} {}^3\mathrm{Pc}^*$$

$$^3\mathrm{Pc}^* + {}^3\mathrm{O}_2 \rightarrow \mathrm{Pc} + {}^1\mathrm{O}_2$$

$$^1\mathrm{O}_2 + \mathrm{sub} \rightarrow \text{oxidized sub}$$

where ISC is intersystem crossing from the singlet to the triplet excited state.

In addition to the singlet oxygen pathway, the formation of radicals by photoinduced electron transfer and radical oxidation of biological substrates can occur through the so-called type I mechanism [4,5]

$$^3\mathrm{Pc}^* + \mathrm{O}_2 \rightarrow \mathrm{Pc}^{\bullet +} + \mathrm{O}_2{}^{\bullet -}$$

$$^3\mathrm{Pc}^* + \mathrm{sub} \rightarrow \mathrm{Pc}^{\bullet -} + \mathrm{sub}^{\bullet +}$$

$$\mathrm{Pc}^{\bullet -} + \mathrm{O}_2 \rightarrow \mathrm{Pc} + \mathrm{O}_2{}^{\bullet -}$$

$$\mathrm{O}_2{}^{\bullet -} \xrightarrow{\mathrm{H}^+} \mathrm{HO}_2{}^{\bullet}$$

$$\mathrm{HO}_2{}^{\bullet} + \text{sub-H} \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{sub}^{\bullet}$$

$$\mathrm{sub}^{\bullet +};\ \mathrm{sub}^{\bullet};\ \mathrm{H}_2\mathrm{O}_2 \rightarrow \text{further reactions, oxidized sub}$$

The route via singlet oxygen is considered to be the main process in photosensitized tumor cell inactivation.

The study of the photochemical properties of Pc complexes is of importance for their use in PDT and other applications based on their photosensitizing abilities, such as in photovoltaic devices [6,7], light harvesting coatings [8] and non-linear optics [9]. To date, several reports can be found in the literature on the influence of the central metal and the structure of the macrocycle on the photostability and efficiency of singlet oxygen photogeneration by Pc and their analogs [10–13]. However, some Pc complexes such as SiPc possess covalently bound axial substituents, which further influence the molecule's physico-chemical properties. Furthermore, axially ligated SiPc exist as single isomers if both the available axial positions are substituted [14].

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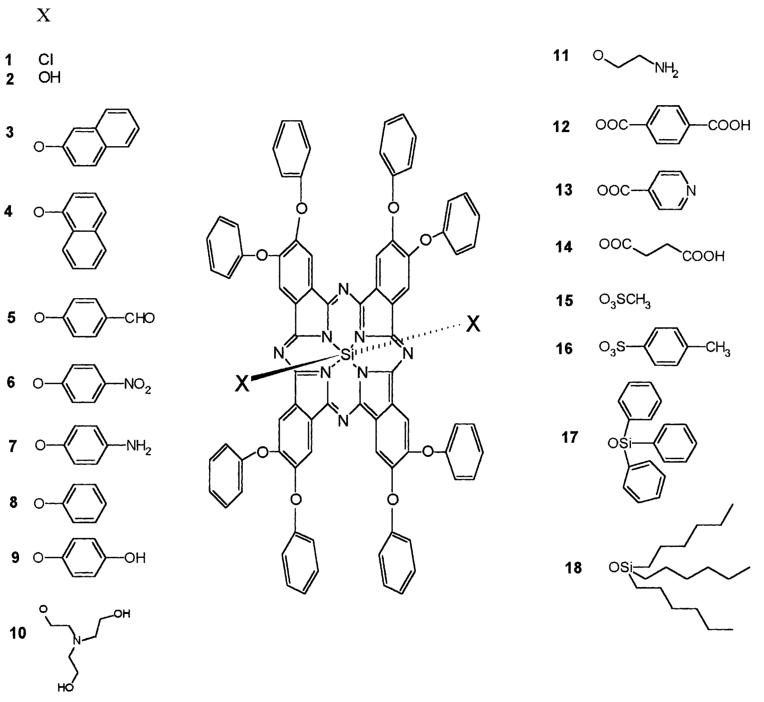

Scheme 1. Schematic of compounds **1–18** used in this study.

Several axially ligated SiPc have been prepared and studied as photodynamic agents. The results obtained have shown that SiPc and their annelated analogs are promising dyes for PDT of cancer [15–17] as well as for the inactivation of viruses in blood [18].

The effect of axial ligand substitution of Pc complexes on their photochemical properties has not received much attention and this work was carried out in order to evaluate the photostability and singlet oxygen quantum yields of various axially substituted silicon Pc. As a model we used organic solvent soluble silicon octaphenoxyphthalocyanine containing a variety of substituents (*X*) in the axial position ($((X)_2$SiOPPc, Scheme 1).

2. Experimental

2.1. Materials and synthesis

Dimethylsulfoxide (DMSO), 1,3-diphenylisobenzofuran (DPBF), diazabicyclooctane (DABCO), benzaldehyde, 1-naphtol, 2-naphtol, triphenylsilanol, trihexylsilanol, triethanolamine, methylsulphonic acid, succinic anhydride, 4-nitrophenol, 4-aminophenol, *p*-toluene sulphonic acid, terephthalic acid, isonicotinic acid and aminoethanol were used as supplied (Sigma–Aldrich). Zinc phthalocyanine (ZnPc) was a gift from Dr. V. Derkacheva, from the Organic Intermediates and Dyes Institute in Moscow.

Compound **1** (see Scheme 1 for structure and Table 1 for naming) was synthesized from 4,5-diphenoxy-diiminoisoindoline as follows: 4,5-diphenoxy-dicyanobenzene (0.75 g, 2.40 mmol) [19] was added to a mixture of dry methanol (7 ml) and sodium methoxide (0.013 g). Anhydrous ammonia gas was bubbled through the stirred suspension for 1 h. The suspension was then refluxed for 6 h with continued addition of ammonia gas. The mixture was filtered and the green product precipitated from methanol with water (20 ml), filtered and dried at 60°C in vacuo (0.61 g, 72%). The mixture was filtered and the green product precipitated from methanol with water (20 ml), filtered and dried at 60°C in vacuo (0.61 g, 72%). To the crude diphenoxy-diiminoisoindoline (0.60 g) was added $SiCl_4$ (0.2 ml) and dry quinoline (2 ml). This mixture was then refluxed for 120 min under nitrogen and allowed to cool, filtration of the precipitate and Soxhlet extraction with methanol yielded the pure compound **1** (0.45 g, 67%). Compound **2** was synthesized by hydrolysis of **1** with a 1:1 pyridine:25% NH_4OH solution.

The formation of the various axial ligated complexes, shown in Scheme 1, was achieved by the following general procedure. To a solution of compound **1** or **2** in DMF (1 ml per 0.1 g) was added a 6 M excess of the appropriate ligands for the synthesis of compounds **3–18**. The solution was refluxed for 30 min and the reaction mixture quenched by addition of water (until complete precipitation). The precipitates were worked up in three different ways as follows: (1) excess ligands present following the synthesis of **3–9**, **12**, and **13** were removed by dissolving the precipitate in chloroform and extracting with a 10% NaOH solution (3 × 20 ml). Compound **7** was additionally washed with a

Table 1
^{1}H NMR (number of protons in brackets) and elemental analytical data for the $(X)_2$SiOPPc compounds

Compound	^{1}H NMR data of Pc ring	^{1}H NMR data for axial substituents	Elemental analysis
Bis(chloro) silicon octaphenoxyphthalocyanine (**1**)	9.21 (8), 7.50 (16), 7.30 (24)	–	$C_{80}H_{48}Cl_2N_8O_8Si$: Calc. C, 71.27; H, 3.59; N, 8.31. Found: C, 68.91; H, 3.24; N, 7.71
Bis(hydroxy) silicon octaphenoxyphthalocyanine (**2**)	–	–	$C_{80}H_{50}N_8O_{10}Si$: Calc. C, 73.27; H, 3.85; N, 8.55. Found: C, 69.10; H, 3.44; N, 7.90
Bis(2-naphthyl) silicon octaphenoxyphthalocyanine (**3**)	9.00 (8), 7.51 (16), 7.29 (24)	7.05 (2, d), 6.93 (4, m), 6.43 (2, d), 6.21 (2, d), 2.79 (2, s)	$C_{100}H_{62}N_8O_{10}Si$: Calc. C, 76.81; H, 4.05; N, 7.24. Found: C, 76.22; H, 3.77; N, 7.01
Bis(1-naphthyl) silicon octaphenoxyphthalocyanine (**4**)	8.98 (8), 7.47 (16), 7.30 (24)	7.04 (4, t), 6.92 (4, m), 6.44 (2, d), 6.18 (2, d)	$C_{100}H_{62}N_8O_{10}Si$: Calc. C, 76.78; H, 4.01; N, 7.19. Found: C, 76.94; H, 4.33; N, 6.89
Bis(*p*-formyl phenoxy) silicon octaphenoxyphthalocyanine (**5**)	8.96 (8), 7.50 (16), 7.32 (24)	9.14 (2, s), 6.26 (4, d) 2.54 (4, d)	$C_{92}H_{56}N_8O_{12}Si$: Calc. C, 74.08; H, 3.76; N, 7.54. Found: C, 74.12; H, 3.49; N, 7.88
Bis(*p*-nitrophenoxy) silicon octaphenoxyphthalocyanine (**6**)	8.94 (8), 7.53 (16), 7.32 (24)	6.59 (4), 2.44 (4)	$C_{92}H_{56}N_{10}O_{14}Si$: Calc. C, 71.13; H, 3.63; N, 9.02. Found: C, 71.82; H, 4.06; N, 9.04
Bis(*p*-amino phenoxy) silicon octaphenoxyphthalocyanine (**7**)	9.02 (8), 7.51 (16), 7.32 (24)	5.04 (4, d), 3.22 (4, s), 2.26 (4, d)	$C_{92}H_{60}N_{10}O_{10}Si$: Calc. C, 74.04; H, 3.97; N, 9.38. Found: C, 73.58; H, 3.48; N, 9.49
Bis(phenoxy) silicon octaphenoxyphthalocyanine (**8**)	8.98 (8), 7.49 (16), 7.28 (24)	5.76 (4, t), 5.65 (4, t), 2.41 (2, d)	$C_{92}H_{58}N_8O_{10}Si$: Calc. C, 75.47; H, 4.04; N, 7.73. Found: C, 74.87; H, 4.15; N, 7.66
Bis(*p*-hydroxy phenoxy) silicon octaphenoxyphthalocyanine (**9**)	8.97 (8), 7.49 (16), 7.29 (24)	5.12 (4, d) 3.48 (2, s), 2.27 (4, d)	$C_{92}H_{58}N_8O_{12}Si$: Calc. C, 73.88; H, 3.93; N, 7.48. Found: C, 74.21; H, 3.48; N, 7.88
Bis(diethanolamino-2-ethoxy) silicon octaphenoxyphthalocyanine (**10**)	9.04 (8), 7.53 (16), 7.30 (24)	0.95 (8, t), 0.5 (8, s), −1.21 (4, t), −2.20 (4, t)	$C_{92}H_{76}N_{10}O_{14}Si$: Calc. C, 70.17; H, 4.86; N, 8.92. Found: C, 69.94; H, 4.55; N, 8.78
Bis(2-aminoethoxy) silicon octaphenoxyphthalocyanine (**11**)	8.95 (8), 7.49 (16), 7.35 (24)	1.23 (2, s), −1.28 (4, t), −2.47 (4, t)	$C_{84}H_{60}N_{10}O_{10}Si$: Calc. C, 72.21; H, 4.30; N, 10.04. Found: C, 72.44; H, 4.10; N, 9.86
Bis(terephthaloyl) silicon octaphenoxyphthalocyanine (**12**)	8.96 (8), 7.50 (16), 7.31 (24)	6.95 (4), 5.18 (4)	$C_{96}H_{58}N_8O_{16}Si$: Calc. C, 71.72; H, 3.64; N, 6.97. Found: C, 70.75; H, 3.21; N, 6.71
Bis(isonicotinoyl) silicon octaphenoxyphthalocyanine (**13**)	8.98 (8), 7.51 (16), 7.33 (24)	7.61 (4), 4.97 (4)	$C_{92}H_{56}N_{10}O_{12}Si$: Calc. C, 72.62; H, 3.71; N, 9.21. Found: C, 72.18; H, 3.81; N, 8.74
Bis(succinoyl) silicon octaphenoxyphthalocyanine (**14**)	9.05 (8), 7.51 (16), 7.32 (24)	−0.91 (4, t), −2.10 (4, t)	$C_{88}H_{58}N_8O_{16}Si$: Calc. C, 69.86; H, 3.91; N, 7.37. Found: C, 70.11; H, 3.58; N, 7.15
Bis(methane sulfonoyl) silicon octaphenoxyphthalocyanine (**15**)	8.98 (8), 7.57 (16), 7.34 (24)	0.28 (3, s)	$C_{82}H_{54}N_8O_{14}S_2Si$: Calc. C, 67.14; H, 3.68; N, 7.59. Found: C, 66.78; H, 3.77; N, 7.77
Bis(*p*-toluene sulphonoyl) silicon octaphenoxyphthalocyanine (**16**)	8.49 (8), 7.48 (40)	7.21 (8, m), 2.95 (6, s)	$C_{94}H_{62}N_8O_{14}S_2Si$: Calc. C, 69.69; H, 3.89; N, 6.92. Found: C, 69.41; H, 3.47; N, 6.75
Bis(triphenylsiloxy) silicon octaphenoxyphthalocyanine (**17**)	8.92 (8), 7.54 (16), 7.30 (24)	6.81 (6), 6.53 (12), 4.88 (12)	$C_{116}H_{78}N_8O_{10}Si_3$: Calc. C, 76.18; H, 4.31; N, 6.12. Found: C, 76.10; H, 4.25; N, 6.01
Bis(tri-*n*-hexylsiloxy) silicon octaphenoxyphthalocyanine (**18**)	9.02 (8), 7.49 (16), 7.29 (24)	0.91 (12), 0.73 (18), 0.51 (12), −1.20 (12), −2.41 (12)	$C_{116}H_{126}N_8O_{10}Si_3$: Calc. C, 74.21; H, 6.78; N, 6.02. Found: C, 74.78, H, 6.49; N, 5.85

Table 2
Absorption spectra data for DMSO solutions, quantum yields of axial substituent phototransformation ϕ_P and singlet oxygen photosensitization ϕ_Δ of compounds **1–18**

Compound	Q-band maxima, nm (log ε)	ϕ_P	ϕ_Δ
1	678 (5.16)	$\sim 1 \times 10^{-5}$	0.14
2	678 (5.30)	–	0.07
3	684 (5.11)	1.7×10^{-3}	0.20
4	684 (5.12)	1.7×10^{-3}	0.21
5	690 (5.11)	2.0×10^{-3}	0.21
6	693 (5.06)	1.0×10^{-3}	0.19
7	688 (5.07)	3.3×10^{-5}	0.03
8	688 (5.13)	1.6×10^{-3}	0.21
9	690 (5.14)	4.0×10^{-3}	0.18
10	679 (5.17)	1.9×10^{-5}	0.11
11	684 (5.39)	1.7×10^{-5}	0.14
12	689 (5.32)	1.8×10^{-5}	0.21
13	696 (5.09)	7.0×10^{-5}	0.14
14	686 (5.17)	1.4×10^{-5}	0.17
15	682 (5.34)	1.5×10^{-2}	0.16
16	714 (5.31)	0.8×10^{-2}	0.15
17	687 (5.21)	3.0×10^{-5}	0.20
18	681 (5.24)	4.1×10^{-5}	0.41

1 mol/l HCl solution (2 × 15 ml). The chloroform layer was then evaporated off to yield compounds **3–9**, **12**, and **13** all in quantitative yields (excess of 95%); (2) excess ligands from the synthesis of **10**, **11**, **15**, and **16** were removed by dissolving the respective precipitates in chloroform and washing with water (3 × 20 ml), the chloroform was again evaporated off to give **10**, **11**, **15**, and **16** in quantitative yields (greater than 95%); (3) compounds **14**, **17** and **18** were isolated from their respective precipitates by thin layer chromatography (TLC) using chloroform as an eluent to give the following yields for **14** (82%), **17** (57%) and **18** (60%).

The complexes were characterized by ^{1}H nuclear magnetic resonance (^{1}H NMR, 400 MHz), UV–VIS spectroscopies, and by elemental analysis. UV–VIS spectra were recorded on a Varian 500 UV–VIS/NIR spectrophotometer. ^{1}H NMR spectra were recorded in $CDCl_3$ using the Bruker EMX 400 NMR spectrometer. Spectral and elemental analysis data for the complexes are listed in Tables 1 and 2.

2.2. Photochemical studies

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 $(X)_2$SiOPPc complex ($0.5–1 \times 10^{-5}$ 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 (Intor, 670 nm with a bandwidth of 20 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/cm^2. The wavelength of the interference filter was chosen such that it was close to the Q-band absorption of the phthalocyanine.The quantum yields were 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 are the Pc concentration after and prior to irradiation respectively, V the reaction volume, S the irradiated area of the cell (1.4 cm^2), t the irradiation time, N_A the Avogadro's number and I_{abs} the overlap integral of the radiation source light intensity and the absorption of the Pc (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 Pc at wavelength λ. Values of C_0 were obtained from using the extinction coefficients of the Q-band dye absorbance maxima (Table 2). Concentrations after irradiation, C_t, were calculated by using the difference between molar extinction coefficients for the substrate and the photoproduct at the wavelength of the substrate Q-band absorption maxima. Experiments were also performed whereby the solutions were deaerated with N_2 gas or saturated with O_2 in order to study the role of oxygen in the mechanism for photobleaching and photoassisted axial ligand exchange in $(X)_2$SiOPPc complexes. 2,4-Di-*tert*-butylphenol (1×10^{-2} mol/l) and DABCO (2×10^{-3} mol/l) were used as radical and singlet oxygen scavengers, respectively.

2.3. Singlet oxygen quantum yields determination

To determine singlet oxygen quantum yields the relative method using ZnPc as reference and DPBF as scavenger of singlet oxygen were used. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [12], the concentration of DPBF was lowered to $\sim 3 \times 10^{-5}$ mol/l. These conditions resulted in first order kinetics being observed.

The typical procedure was as follows: DMSO solutions containing the $(X)_2$SiOPPc derivative (absorbance below 1 at the irradiation wavelength) and DPBF (3×10^{-5} mol/l) were prepared in the dark. Experiments were carried out in air without bubbling oxygen using a 2.0 ml sample of solution and this was irradiated in the Q-band region using the set-up described in Section 2.3. DPBF absorption decay at 417 nm was then followed. The light intensity and amount of absorbed photons were also obtained as mentioned above. The values of ϕ_Δ were calculated using 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 in DMSO (0.67 [13]), W and W^{ZnPc} are the DPBF photobleaching rates in the presence of SiPc derivatives under investigation and ZnPc, respectively. I_{abs} and $I_{\mathrm{abs}}^{\mathrm{PcZn}}$ are the rates of light absorption by the SiPc derivative and ZnPc correspondingly. The initial DPBF concentrations are kept the same for the ZnPc reference and the samples. The quantum yields presented in Table 2 were determined with an accuracy of ~10%. All the experiments were carried out at room temperature (23–25°C).

3. Results

3.1. Synthesis

All the reagents used in the syntheses for axial substitution in compounds **1** or **2** are commercially available and relatively inexpensive. The strategies employed in this work result in the formation of high yields of spectroscopically pure products by convenient synthetic and workup procedures. All compounds **3–18** are soluble in chloroform and thus, ^{1}H NMR could be used to verify their structures. The yields of compounds **14**, **17** and **18** are lower due to the necessary chromatographic step and especially compounds **17** and **18** had only 60% yields which may be attributed to the decreased acidity of the silanol hydroxyl groups.

3.2. Spectral characterization

All the compounds with the exception of **2** (chloroform insoluble) were analyzed by ^{1}H NMR spectroscopy. The compounds displayed the same ^{1}H NMR behavior with slight differences for the phthalocyanine ring protons (Table 1). The deshielded protons responsible for the singlet near 9 ppm were due to the non-peripheral protons of the phthalocyanine ring and integrated for eight protons for all complexes. The phenyl ring protons nearest the ether bond were more deshielded than their neighboring phenyl protons and integrated as a triplet for 16 protons at ~7.5 ppm. What appears to be a doublet at 7.3 ppm for all compounds is in fact a combination of a doublet and a triplet integrating for 24 protons and the remaining protons on the phenyl ring are responsible for these resonances. The multiplicities for the ring protons are thus, not given in Table 1. The ^{1}H NMR data for the axial ligands on each of the compounds **3–18** are summarized in Table 1 with their respective multiplicities.

Compounds **1–18** are lipophilic and all except **2** have good solubility in organic solvents (DMSO, DMF, $CHCl_3$). Their UV–VIS absorption spectra are typical of Pc and consist of two main bands: Q and Soret at about 690 and 350 nm, respectively. Absorption spectra for complexes **1**, **12** and **14** in DMSO are shown in Fig. 1. The wavelengths of absorption maxima and molar extinction coefficients for Q-bands are summarized in Table 2. A shift of the Q-band on changing the axial substituent is observed in Table 1 for example, a 25 nm shift from 678 nm for complexes **1** and **2** to 714 nm for complex **16** is observed. The relationship between axial substituent structure and Q-band absorption maxima point to a red-shift being preferred for a combination of electron withdrawing substituents and aromatic functions on the axial ligand. Photochemical processes are known to occur more readily when photosensitizers are in the monomeric state [1,20]. All the $(X)_2$SiOPPc molecules **3–18** show monomeric behavior (sharp Q-bands and Beers law is obeyed) in the concentrations required for photochemical studies.

3.3. Phototransformation involving axial substituents

Under Q-band excitation of complexes **3–18** in air and in DMSO solutions two changes, indicating two different photoprocesses in the Q-band region were observed. The first process was the phototransformation of the axial substituents, this process was evidenced by the decrease of the Q-band and the appearance of a new band at 678 nm, upon

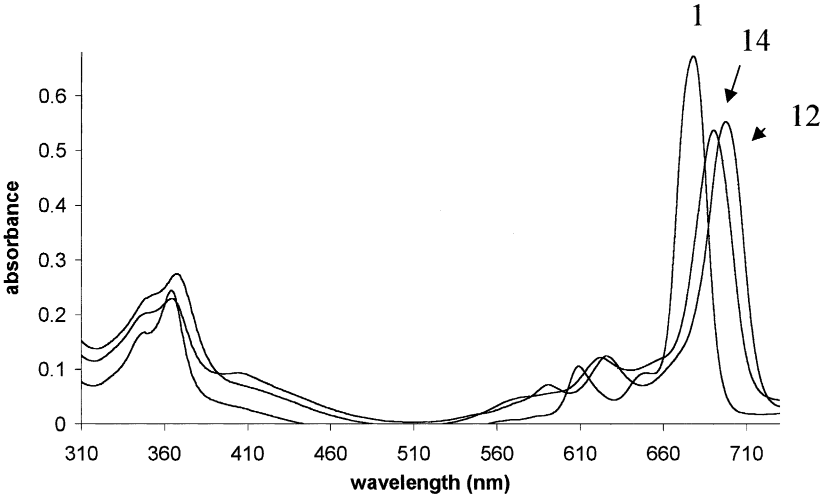

Fig. 1. UV–VIS spectra of compounds **1**, **12** and **14** in DMSO.

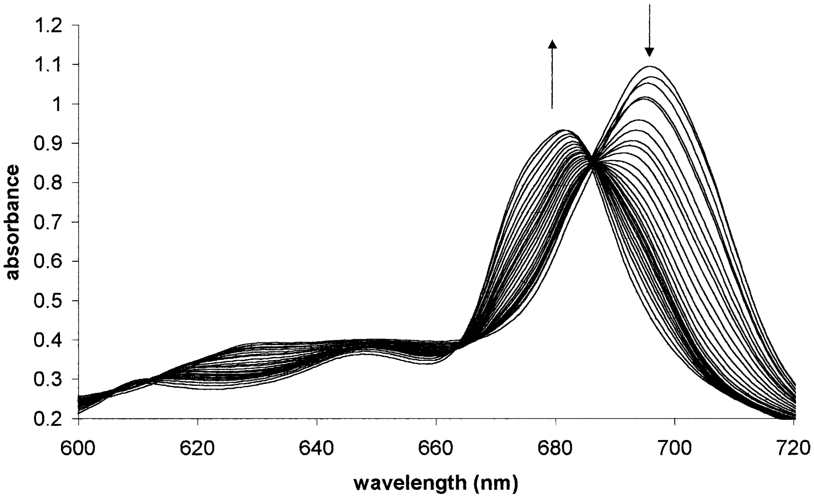

Fig. 2. Visible spectral changes observed during axial ligand phototransformation of compound **13** in DMSO, in the presence of air and under excitation with light of wavelength 670 ± 10 nm.

photolysis (Fig. 2). This phototransformation followed first order kinetics. The presence of a diffuse isosbestic point indicates that other processes are occurring in addition to axial substituent phototransformation. There is a possibility of photobleaching of the $(X)_2$SiOPPc occurring to a small extent during the phototransformation of the axial substituents.

The overlapping of the absorption spectra of products formed for compounds **3–18** following the axial substituent phototransformation. Fig. 2, proves that the same product is formed for all these compounds. Complexes **1** and **2** have the same absorption maxima as the product of phototransformation of complexes **3–18**. TLC (eluent, chloroform) indicates that **1** is also phototransformed into the dihydroxy derivative **2**. Using TLC transformation times, we have estimated the quantum yield for axial substituent phototransformation of complex **1–2** to be approximately equal to 1×10^{-5}.

Axial ligands in complexes **1** and **3–18** have a propensity to be substituted by hydroxyl groups to form compound **2**. The quantum yields for the phototransformation (ϕ_P) of the axial substituents for complexes **1** and **3–18** are summarized in Table 2. It was found that the axial ligands have an influence on the ϕ_P as large as three orders of magnitude from 1.4×10^{-5} for complex **14** to 1.5×10^{-2} for complex **15**. Thus, we conclude that ligand substitution in silicon octaphenoxyphthalocyanine from any covalently bound axial group to the hydroxyl one occurs for all of the complexes under discussion.

The following types of axial ligands were used in this study: aryloxy, siloxy, aminoalkoxy, esters of carboxylic acids and sulphonic acid ester residues. It was found that although members of each group have very similar values of ϕ_P, groups differ in ϕ_P by orders of magnitude from each other (with the exception of **7** in the aryloxy row). No relationship between electronic structure and reactivity in phototransformation of axial substituents was observed. Therefore, it may be concluded that geometry rather than electronic properties is responsible for the reactivity of silicon octaphenoxyphthalocyanine derivatives during the axial substituent phototransformation.

The effects of oxygen concentration, a singlet oxygen inhibitor, a radical scavenger and deuterated solvent on the rate of phototransformation of axial substituents were studied with **6** as an example. It was found that ϕ_P in saturated nitrogen or oxygen solutions were equal to 2.0×10^{-3} and 4.5×10^{-3}, respectively in comparison with 1.1×10^{-3} observed in the presence of air. The singlet oxygen quencher (DABCO) and the radical scavenger (2,4-di-*tert*-butylphenol) do not inhibit the axial substituent phototransformation process. The most pronounced effect on phototransformation efficiency is the deuterium effect of the solvent. The value of ϕ_P for compound **6** in deuterated DMSO in air decreases to 1.0×10^{-4} indicating that hydrogen atom abstraction from the solvent is involved in the process.

3.4. Photobleaching studies

Photobleaching (the degradation of the phthalocyanine macrocycle) of complex **2** was observed as the second photochemical process following the axial substituent phototransformation discussed above for compounds **1**, **3–18**. Irradiation of compound **2** in the Q-band region resulted in its photobleaching with a quantum yield $\sim 5 \times 10^{-6}$. Fig. 3 compares the effect of solvent, oxygen and singlet oxygen quencher on the photobleaching process. The increase of the photobleaching rate with increase in oxygen concentration, indicates that oxygen is involved in the process, as seen by comparing the kinetic curves for nitrogen, air and oxygen saturated solutions (Fig. 3). Inhibition of the photobleaching process in the presence of the singlet oxygen quencher, DABCO, and the increase in the photobleaching rate in D^6-DMSO solution (Fig. 3) are in agreement with the

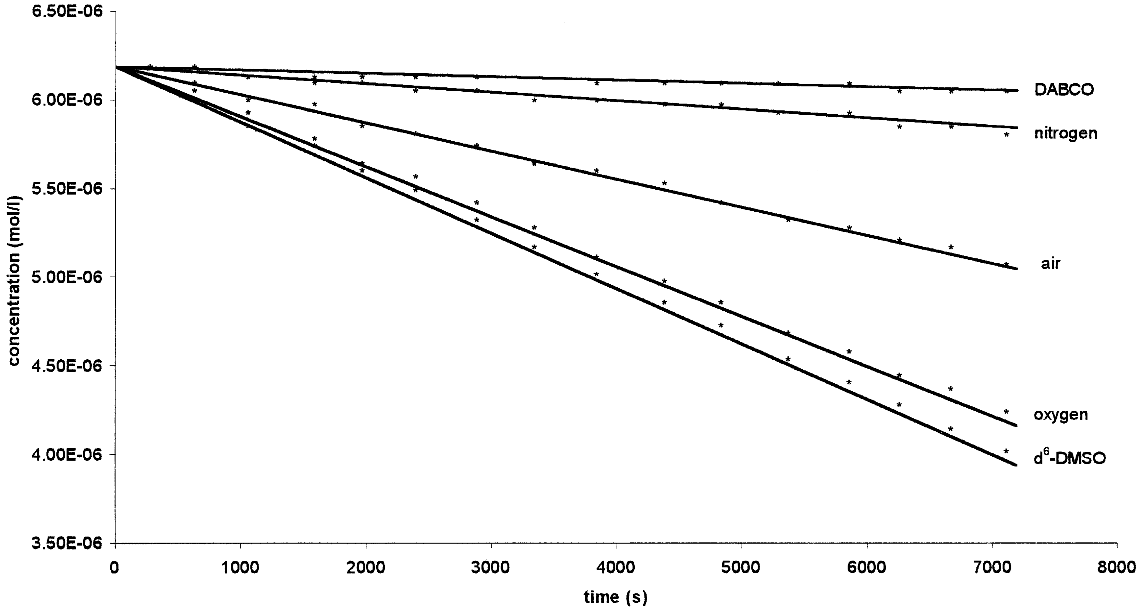

Fig. 3. Photobleaching kinetic curves for compound **2** in DMSO saturated with air, nitrogen or oxygen and in aerated DMSO in the presence of 0.02 mol/l DABCO.

involvement of singlet oxygen in the photoxidation of the phthalocyanine macrocycle in compound **2**. We have found that dihydroxyl derivative **2** in DMSO sensitizes formation of singlet oxygen with a quantum yield of 0.07 (Table 2). Thus, the photobleaching of compound **2** in DMSO solution most likely proceeds mainly through a self-sensitized photooxidation by singlet oxygen. There has been some speculation in the literature about the singlet oxygen interaction with the phthalocyanine macrocycle. Wöhrle suggests singlet oxygen cycloaddition to phthalocyanine pyrrole units resulting in the macrocycle destruction and formation of phthalimide [11].

3.5. Singlet oxygen quantum yields

Quantum yields of singlet oxygen photogeneration (ϕ_Δ) of compounds **1–18** are presented in Table 2. No photobleaching or phototransformation of the $(X)_2$SiOPPc complexes was observed during the determination of singlet oxygen quantum yields, since these processes occur much slower than singlet oxygen production. The majority of the values in Table 2 are in the range 0.1–0.20 with a few compounds having lower values ($\phi_\Delta = 0.07$ for **1** and $\phi_\Delta = 0.03$ for **7**) or a higher value ($\phi_\Delta = 0.41$ for **18**), ϕ_Δ for compound **2** deviates from the other compounds due to its low solubility, possibly caused by hydrogen bond attraction between the axial hydroxyl groups. It is well known that intermolecular interactions between phthalocyanine rings result in decreased photochemical activity due to enhanced probability of radiationless decay of excited states. On the other hand, bulky hexyl substituents in the axial position of the silicon phthalocyanine **18** prevents association or aggregation of the rings, resulting in higher singlet oxygen quantum yields. Compound **7** has an extremely low value of $\phi_\Delta = 0.03$, although it has good solubility and exists in monomeric form in DMSO. Amine-substituted compounds are known to be singlet oxygen quenchers. Indeed, amines **10** and **11** also have low ϕ_Δ values of 0.11 and 0.14, respectively, which may be explained by partial singlet oxygen quenching by the axial substituents. Compound **7**, however, exhibits a lower ϕ_Δ value when compared to the rest of the amine-containing axial substituents. Compound **7** does not deviate only in singlet oxygen quantum yields, but as noted above, also in axial substituent phototransformation efficiency as well. Such behavior from our point of view indicates enhanced competitive degradation of compound **7** excited states, decreasing photochemical activity. Generally, $(X)_2$SiOPPc complexes in DMSO have decreased singlet oxygen quantum yields compared to their unsubstituted silicon phthalocyanine $(X)_2$SiPc counterparts by a factor of approximately 2. The singlet oxygen quantum yield of Cl_2SiPc using the relative method was found to be $\phi_\Delta = 0.38$ which is in good agreement with that in the literature [15]. Compound **1** has a substantially decreased value of $\phi_\Delta = 0.14$. Since **1** is more soluble than Cl_2SiPc a difference in solubility cannot explain the higher ϕ_Δ values of Cl_2SiPc. Obviously this is the effect of the ring structure, which will be studied further with an expanded row of silicon phthalocyanine derivatives.

4. Discussion

This work shows that axially substituted silicon octaphenoxyphthalocyanines undergo two photochemical processes.

Photoassisted substitution of covalently bound axial groups to the hydroxyls is followed by degradation of the phthalocyanine macrocycle. Photoassisted axial substituent change in silicon Pc to the hydroxyls has not been reported so far. We have studied this process with various axially substituted silicon octaphenoxyphthalocyanines, but obviously it may occur with other rings as well. Phototransformation proceeds under visible light with quantum yields up to 10^{-2} for some derivatives and leads to a blue shift of the phthalocyanine Q-absorption band. The possibility of photoinduced axial substituent change to hydroxyl groups has to be taken into consideration in applications of silicon Pc, based on their interactions with light. Self-sensitized photooxidation by singlet oxygen was suggested to be responsible for the photobleaching of the macrocyclic ring. We have studied some aspects of the mechanism of phototransformation of axial ligands but this is still not completely settled and thus, a few processes that may result in central silicon atom hydroxylation will be discussed below. Obviously nucleophilic photosubstitution of axial ligands by the hydroxyl anion is not significant in DMSO. Photochemical cleavage of Si–C bond has been observed [21]. A possibility is that photoinduced homolytic cleavage of Si–O bond may be supposed as a key step of phototransformation followed by a sequence for dark reactions of radicals with oxygen as follows

$$\mathrm{PcSi\text{-}OR} \xrightarrow{h\nu} \mathrm{PcSi}^{\bullet} + {}^{\bullet}\mathrm{OR}$$

$$\mathrm{PcSi}^{\bullet} + \mathrm{O_2} \rightarrow \mathrm{PcSiO_2}^{\bullet}$$

$$\mathrm{PcSiO_2}^{\bullet} \xrightarrow{\mathrm{RH}} \mathrm{PcSiO_2H}$$

$$\mathrm{PcSiO_2H} \xrightarrow{h\nu,\Delta} \mathrm{PcSiOH}$$

Although the main relationships observed for the phototransformation can be explained in the frames of this mechanism, this route under visible light may be improbable from the thermodynamic point of view. The energy of the filtered light used is too low to induce homolytic cleavage of the Si–O bond (bond energy about 110 kcal/mole [22]).

It is well known that in polar solvents like DMSO heterolysis is the preferred mode of cleavage [23]. Solvation benefits the decrease in activation energy (E_a) of the reaction. Thus, for example, the cluster model of hydrolysis of Si–O bridge predicts a low activation energy of the process, for the $(HO)_3Si–O–Si(OH)_3$ molecule $\Delta E_a = 17$ kcal/mole [24]. Photoinduced heterolytic cleavage leads to radical ion formation and subsequent reactions of this species with oxygen and solvent may result in Si atom hydroxylation as well. However, it is worth mentioning that the low energy phthalocyanine chromophore upon Q-band irradiation results in $\pi\pi^*$-excited states of the ring. Other excited states, responsible for charge transfer between axial ligands and the central metal atom, are supposed to lie at higher energies [10], thus, an intramolecular charge transfer mechanism is doubtful.

Intermolecular electron transfer between phthalocyanine $\pi\pi^*$-excited state and electron acceptors, particularly oxygen, is known [4,10] and may be considered as a first step of photooxidation leading to hydroxylation of Si central metal. A cation radical is formed in this initial photochemical step and these have a propensity to fragment into cation and radical [25]. In the frames of this mechanism the following scheme for photohydrolysis may be proposed

$$\mathrm{PcSi\text{-}OX} \xrightarrow{h\nu} \mathrm{PcSiOX}^{*}$$

$$\mathrm{PcSiOX}^{*} + \mathrm{A} \rightarrow \mathrm{PcSi\text{-}OX}^{\bullet +} + \mathrm{A}^{\bullet -}$$

$$\mathrm{PcSi\text{-}OX}^{\bullet +} \rightarrow \mathrm{PcSi}^{+} + {}^{\bullet}\mathrm{OX}$$

$$\mathrm{PcSi}^{+} + \mathrm{OH}^{-} \rightarrow \mathrm{PcSiOH}$$

$${}^{\bullet}\mathrm{OX} \xrightarrow{\mathrm{RH}} \mathrm{HOX}$$

where A is an electron acceptor and RH is the solvent.

A low influence of axial substituent electronic properties on the rate of one electron ring photooxidation is possible. The observed high deuterium isotope effect of the solvent indicates the important role of hydrogen atom abstraction in the proposed mechanism. This is shown by the interaction of the $\mathrm{XO}^{\bullet}$ radical with the solvent. In the absence of oxygen the radical cation may be produced in a bimolecular electron transfer reaction of the excited phthalocyanine with a ground state phthalocyanine. The finding that 2,4-di-*tert*-butylphenol does not inhibit the process indicates an absence of long radical chains. So far the main peculiarities of phototransformation may be explained by the mechanism above when initiated by intermolecular electron transfer and based upon the above discussion, this mechanism seems to be the most reasonable.

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