

# Effect of oligomerization on the photochemical properties of silicon octaphenoxypthalocyanine

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## Abstract

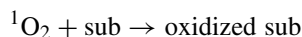
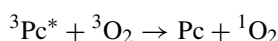
The photochemical properties of silicon octaphenoxypthalocyanines (SiOPPC) oligomerized were studied in dimethylsulfoxide (DMSO) solutions. Oligomers containing 2–5 and 9 SiOPPC rings linked with terephthalate linkages were synthesized. Singlet oxygen quantum yields were found to be in the range 0.11–0.34, and increased with the number of rings up to five rings, a decrease in the quantum yield was observed for nine rings. This is explained in terms of the high aggregation of the oligomer containing nine rings. © 2001 Elsevier Science B.V. All rights reserved.

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

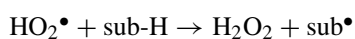
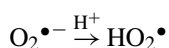
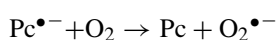
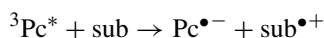
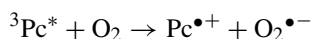
## 1. Introduction

Phthalocyanines (Pcs) are synthetic compounds related to the natural porphyrins. Due to their resemblance to porphyrins and their superior absorption in the red region of the spectrum [1–3] they are being widely investigated as potential photosensitizing agents in the photodynamic therapy (PDT) of cancer [4–6]. The photosensitizing action of the Pcs may be attributed to one of two mechanisms, currently referred to as the Type II and Type I mechanisms, respectively as illustrated below.

Type II mechanism [4–6]:



Type I mechanism [7,8]:



sub<sup>•+</sup>; sub<sup>•</sup>; H<sub>2</sub>O<sub>2</sub> → further reaction, oxidized sub

Where ISC is intersystem crossing from the singlet to the triplet excited state and sub = substrate.

The route via singlet oxygen is considered to be the main process in photosensitized tumor cell inactivation. Currently, the PDT agents, Photofrin and Photofrin II, are utilized as photosensitizers and they are known to contain oligomers of hematoporphyrin [9]. The monomeric units in these oligomers are covalently linked to one another. 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 Pcs and their analogs [10–13]. Several axially ligated silicon Pc (SiPc) complexes have been prepared and studied as PDT agents. The results obtained have shown that SiPc and their annelated analogs are promising dyes for PDT of cancer [14–16] as well as for the inactivation of viruses in blood [17,18]. The effect of axial oligomerization 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 oligomers shown in Fig. 1. Oligomeric and polymeric SiPc have been synthesized by heating dihydroxy SiPc at 400°C with loss of water [19]. The degree of oligomerization was thought to be between 10 and 100 according to the following schematic:



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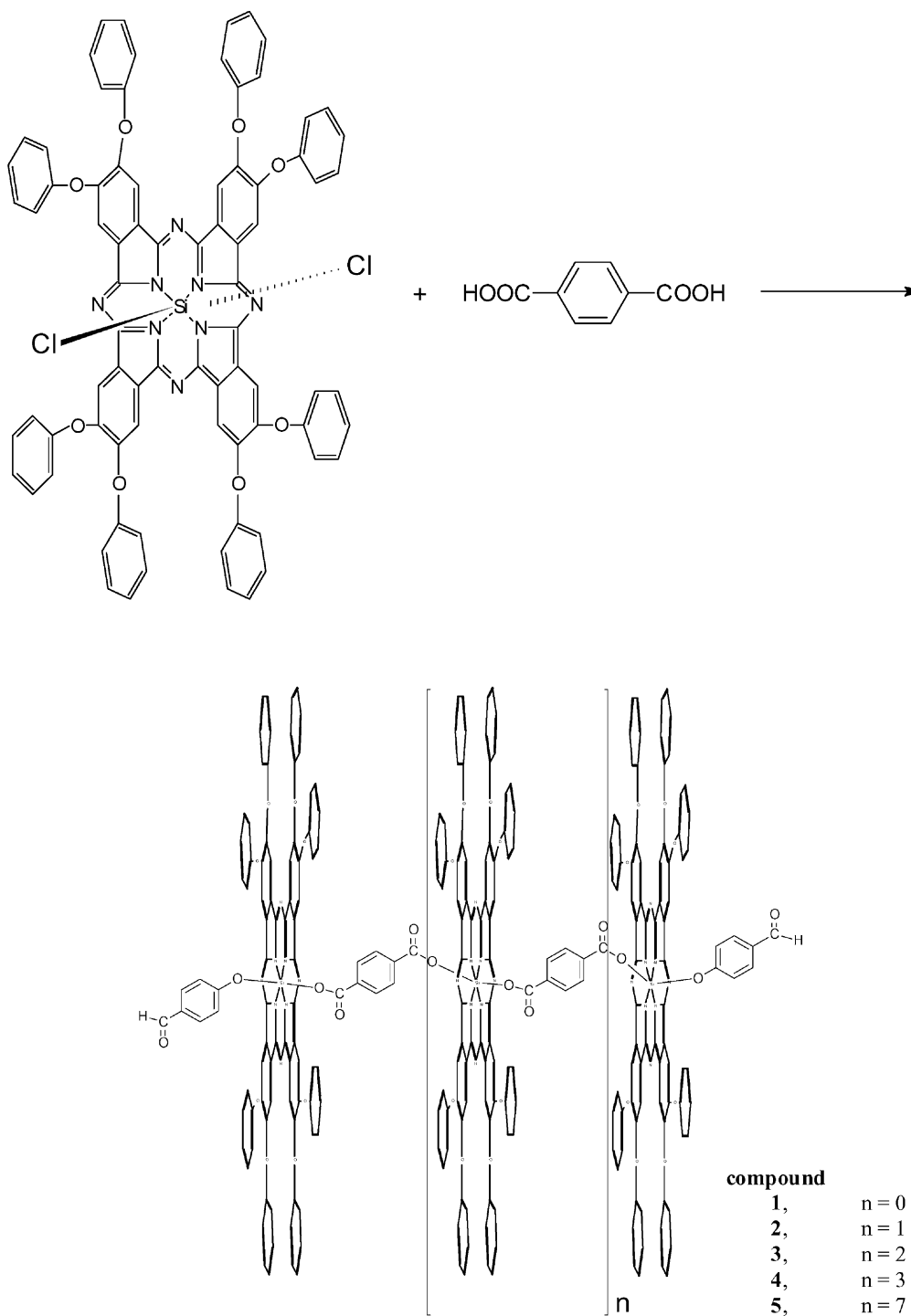


Fig. 1. The structure of compounds 1–5 used in this study with  $n = 0$ –3 and 7.

A Pc trimer has also been made with two aluminum Pc (AlPc) and a SiPc [20] as follows:



The aluminum and SiPc monomers were refluxed in 1-chloronaphthalene for 4 h. The conditions employed were

less harsh due to the relative acidity of the AlPc's axial hydroxyl proton. SiPc have found application as conducting polymers [21,22] and peripherally substituted analogs have been applied as Langmuir Blodgett films [23]. We report on the synthesis and photochemistry of oligomeric silicon octacarboxyphthalocyanines.

## 2. Experimental

### 2.1. Materials and synthesis

Dimethylsulfoxide (DMSO), 1,3-diphenylisobenzofuran (DPBF), diazabicyclooctane (DABCO), *p*-hydroxybenzaldehyde and terephthalic acid were used as supplied (Sigma-Aldrich). Zinc Pc (ZnPc) was a gift from Dr. V. Derkacheva, from the Organic Intermediates and Dyes Institute in Moscow. Bis(chloro) SiOPPC ((Cl)<sub>2</sub>SiOPPC) was synthesized as previously described [24].

Oligomers **1–5** (Fig. 1) were synthesized from (Cl)<sub>2</sub>SiOPPC according to the following general procedure: To a refluxing solution of the (Cl)<sub>2</sub>SiOPPC (for amounts see Table 1) in dry DMF (4 ml) under nitrogen, terephthalic acid completely dissolved in dry DMF (1 ml), was added. The reaction was monitored by thin layer chromatography (TLC) and upon completion of the reaction *p*-hydroxybenzaldehyde (0.1 g) was added to the DMF solution and the reflux was continued for 30 min. The reaction mixture was allowed to cool and water was added to quench the reaction. After filtration the precipitate was washed with a 10% NaOH solution until the phenol and acid were washed out completely. A final wash with water and drying at 60°C under vacuum delivered the impure product which was then further purified by preparative TLC using chloroform as an eluent to deliver products **1–5**.

**Dimer 1:** (2.1 mg, 38%);  $\delta_{\text{H}}$  9.16 (s, 2H, CHO) 9.00 (s, 16H, Pc-H); 7.51 (t, 32H, phenoxy ring-H); 7.29 (m, 48H, phenoxy ring-H); 6.31 (d, 4H, axial Ph-H); 2.87 (d, 4H, axial Ph-H); 2.57 (d, 4H, Ph-H); UV-VIS (DMSO,  $\lambda_{\text{max}}$ ) 684 ( $\epsilon = 1.8 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 650, 613, 354; anal. calc. C, 73.82; H, 3.74; N, 7.57%. Found C, 73.55; H, 3.59; N, 7.83%.

**Trimer 2:** (1.9 mg, 36%);  $\delta_{\text{H}}$  9.15 (s, 2H, CHO) 8.99 (s, 16H, Pc-H); 8.97 (s, 8H, Pc-H); 7.50 (m, 48H, phenoxy ring-H); 7.30 (m, 72H, phenoxy ring-H); 6.30 (d, 4H, axial Ph-H); 2.89 (m, 8H, axial Ph-H); 2.58 (d, 4H, Ph-H); UV-VIS ( $\lambda_{\text{max}}$ ) 682 ( $\epsilon = 1.9 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), 650, 615, 353; anal. calc. C, 73.66; H, 3.71; N, 7.64%. Found C, 73.60; H, 3.66; N, 7.55).

**Tetramer 3:** (1.8 mg, 32%);  $\delta_{\text{H}}$  9.15 (s, 2H, CHO) 9.00 (s, 16H, Pc-H); 8.98 (s, 16H, Pc-H); 7.50 (m, 64H, phenoxy ring-H); 7.30 (m, 96H, phenoxy ring-H); 6.29 (d, 4H, axial Ph-H); 2.87 (m, 12H, axial Ph-H); 2.60 (d, 4H, Ph-H);

UV-VIS ( $\lambda_{\text{max}}$ ) 681 ( $\epsilon = 1.8 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), 615, 354; anal. calc. C, 73.58; H, 3.69; N, 7.67%. Found C, 73.29; H, 3.33; N, 7.81%.

**Pentamer 4:** (1.9 mg, 34%);  $\delta_{\text{H}}$  9.16 (s, 2H, CHO) 8.99 (s, 16H, Pc-H); 8.97 (s, 16H, Pc-H); 8.95 (s, 8-H, Pc-H); 7.49 (m, 80H, phenoxy ring-H); 7.29 (m, 120H, phenoxy ring-H); 6.31 (d, 4H, axial Ph-H); 2.89 (m, 16H, axial Ph-H); 2.57 (d, 4H, Ph-H); UV-VIS ( $\lambda_{\text{max}}$ ) 681 ( $\epsilon = 1.9 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), 614, 354; anal. calc. C, 73.53; H, 3.68; N, 7.69%. Found C, 73.22; H, 3.44; N, 7.81%.

**Nonamer 5:** (1.0 mg), 18%;  $\delta_{\text{H}}$  9.15 (s, 2H, CHO) 9.00 (s, 16H, Pc-H); 8.98 (s, 16H, Pc-H); 8.96 (m, 40H, Pc-H); 7.50 (m, 144H, phenoxy ring-H); 7.30 (m, 216H, phenoxy ring-H); 6.30 (d, 4H, axial Ph-H); 2.89 (m, 32H, axial Ph-H); 2.57 (d, 4H, Ph-H); UV-VIS ( $\lambda_{\text{max}}$ ) 680 ( $\epsilon = 1.7 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 611, 352; anal. calc. C, 73.43; H, 3.66; N, 7.73%. Found C, 73.05; H, 3.17; N, 7.02%.

The complexes were characterized by <sup>1</sup>H-nuclear magnetic resonance (NMR) (<sup>1</sup>H-NMR, 400 MHz), UV-VIS and infrared spectroscopies, and by elemental analysis. UV-VIS spectra were recorded on a Varian 500 UV-VIS/NIR spectrophotometer. <sup>1</sup>H-NMR spectra were recorded in d<sup>6</sup>-DMSO using the Bruker EMX 400 NMR spectrometer. Infra red spectra was recorded with Perkin-Elmer spectrum 2000 FTIR spectrophotometer.

### 2.2. Photobleaching 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 compounds **1–5** ( $\sim 1 \times 10^{-5} \text{ mol l}^{-1}$ ) was introduced to the cell and photolysed 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 ultraviolet 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) and was found to be  $5 \times 10^{16} \text{ photons s}^{-1} \text{ cm}^{-2}$ . The wavelength of the interference filter (670 nm) was chosen such that it was close to the Q-band absorption of the Pc.

The quantum yield for the photobleaching of SiOPPC was determined using the following equation:

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

where  $C_t$  and  $C_0$  in  $\text{mol l}^{-1}$  are the Pc concentration after and prior to irradiation, respectively.  $V$  is the reaction volume,  $S$  the irradiated area ( $1.4 \text{ cm}^2$ ) of the cell,  $t$  the irradiation time,  $N_A$  the Avogadro's number and  $I_{\text{abs}}$  the overlap integral of the radiation source light intensity and the absorption of the

Table 1  
Details of synthesis for compounds **1–5**

Compound	Phthalic acid (mg)	Phthalocyanine (mg)
<b>1</b>	0.31	5.1
<b>2</b>	0.39	4.8
<b>3</b>	0.47	5.1
<b>4</b>	0.50	5.1
<b>5</b>	0.55	5.0

Pc (the action spectrum) in the region of the interference filter transmittance and is defined as

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

Where  $I_{\lambda}$  is the intensity of light and  $A_{\lambda}$  the absorbance of the Pc at wavelength  $\lambda$ . Values of  $C_0$  and  $C_t$  were obtained from using the extinction coefficients of the Q-band dye absorbance 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, 2,4-di-*tert*-butylphenol ( $1 \times 10^{-2} \text{ mol l}^{-1}$ ) and DABCO ( $2 \times 10^{-3} \text{ mol l}^{-1}$ ) being 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  $\sim 3 \times 10^{-5} \text{ mol l}^{-1}$ . These conditions resulted in first order kinetics being observed.

The typical procedure was as follows. DMSO solutions containing the Pc derivatives (absorbance below 1 at the irradiation wavelength) and DPBF ( $3 \times 10^{-5} \text{ mol l}^{-1}$ ) 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 2.2. 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  $\phi_{\Delta}$  were calculated using the following relationship:

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

where  $\phi_{\Delta}^{\text{PcZn}}$  is the singlet oxygen quantum yield for ZnPc in DMSO (0.67 [13]),  $W$  and  $W^{\text{ZnPc}}$  are the DPBF photobleaching rates in the presence of SiPc derivatives under investigation and ZnPc, respectively.  $I_{\text{abs}}$  and  $I_{\text{abs}}^{\text{ZnPc}}$  are the rates of light absorption by the SiPc derivative and ZnPc, respectively. 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

Table 2  
Singlet oxygen photosensitization  $\phi_{\Delta}$  of compounds 1–5

Compound	Singlet oxygen quantum yield ( $\phi_{\Delta}$ )
1	0.23
2	0.28
3	0.31
4	0.34
5	0.11

accuracy of  $\sim 10\%$ . All the experiments were carried out at room temperature (21–23°C).

## 3. Results and discussion

### 3.1. Synthesis

The synthetic procedures used are similar to polymerization reactions [25] using exact molar amounts of substance and, thus, it is vitally important to have all components dissolved before attempting reactions. The use of *p*-hydroxybenzaldehyde is a convenient way to terminate the oligomers to enable simple  $^1\text{H-NMR}$  determination of the degree of oligomerization. The best results were obtained by slow addition of the terephthalic acid to a solution of the dichloro SiOPPc, thus, minimizing monomer formation. Due to the very low amounts of terephthalic acid used in the reactions, a 10 ml solution was generally made with a 10-fold excess of the required acid and then 1 ml of this solution was added to the reaction mixture. The solubility of the Pcs generally decreased with an increase in degree of oligomerization. The yields of 1–5 are low but acceptable in comparison to the axial ligation reactions of monomeric species due to the statistical nature of the reactions and the effect of reagent purity which is especially more prominent for the formation oligomer 5.

### 3.2. Spectral characterization

All the compounds could be analyzed by  $^1\text{H-NMR}$  spectroscopy and this was the principle method for the determination of degree of oligomerization. The compounds displayed similar  $^1\text{H-NMR}$  behavior, as expected, with slight differences for the Pc ring protons. The  $^1\text{H-NMR}$  spectrum of compound 3 is shown in Fig. 2 with the relevant structures that represent each resonance. The deshielded protons responsible for the singlet near 9 ppm were due to the non-peripheral protons of the Pc ring and integrated for 8 protons for each Pc ring. The integrals of these peaks could actually allow confirmation of the number of rings in a complex, for example compound 1 displayed a singlet of 16 protons near 9 ppm, showing that there are two rings involved and both rings are in the same environment. Compound 3 displayed a singlet for the non-peripheral Pc protons at 9.00 and 8.98 ppm, each integrating for 16 protons, hence, confirming a total of four rings. The fact that two singlets were observed for the non-peripheral Pc protons, shows that the rings are not in the same environment. The phenoxy ring protons nearest the ether bond were more deshielded than their neighboring protons and exhibited a triplet for 1 and multiplets for the rest of the oligomers at  $\sim 7.5$  ppm. All compounds displayed a multiplet of phenoxy protons at 7.3 ppm. The  $^1\text{H-NMR}$  data for the axial ligands on each of the compounds displayed very similar shifts and all the linking aromatic terephthalate protons displayed

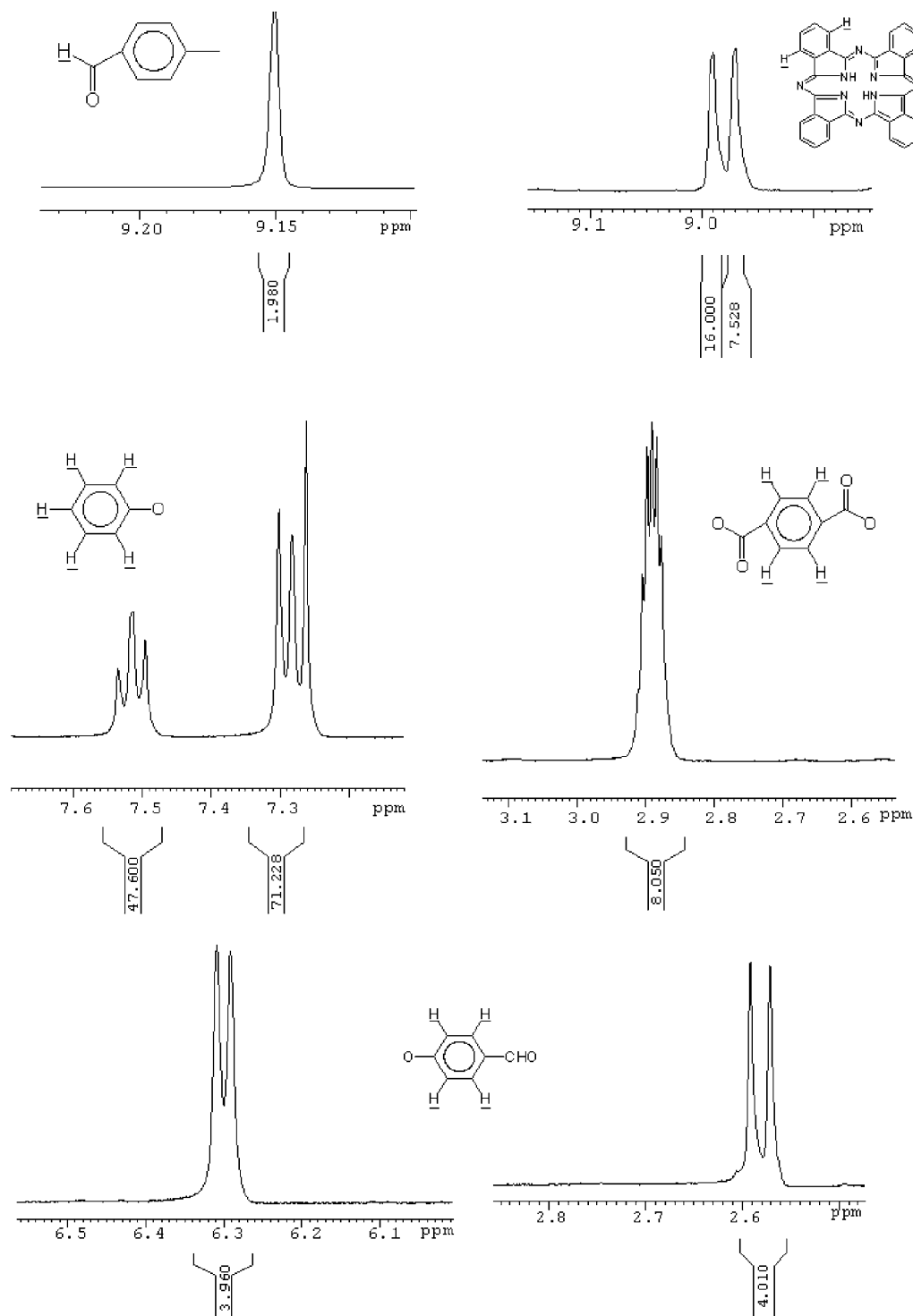


Fig. 2. The  $^1\text{H-NMR}$  spectrum of compound 3.

multiplets at  $\sim 2.9$  ppm which is indicative of the extreme high shielding of these aromatic protons by the Pc rings. The terminal aldehyde groups provided an easy method of determining the degree of oligomerization by comparison of the area integral of their resonances at  $\sim 9.15$  ppm to the combined non-peripheral Pc ring resonances at  $\sim 9$  ppm.

The UV–VIS absorption spectra are typical of Pcs and consist of two main bands — Q and Soret at about 681 and 345 nm, respectively (Fig. 3). The wavelengths of absorption maxima and molar extinction coefficients for Q-bands are given in Section 2. A slight shift of the Q-band from 684 to 680 nm is observed on going from compound 1–5.

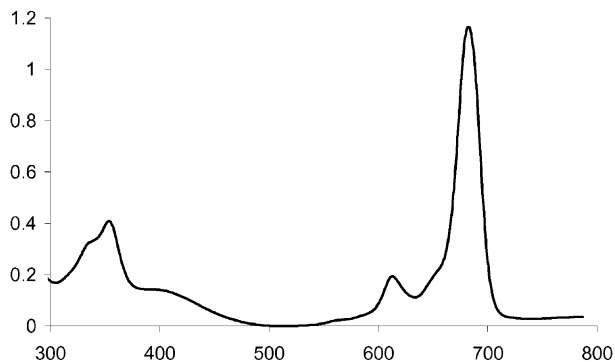


Fig. 3. The UV-VIS spectrum of compound **5** in DMSO.

Photochemical processes are known to occur more readily when photosensitizers are in an unaggregated state [1,20]. The compounds do, however, show a slight increase in aggregation behavior as the oligomerization degree increases with oligomer **5** showing the highest non-dependence of the Beer's law (Fig. 4).

### 3.3. Photobleaching studies

Under Q-band excitation of complexes **1–5** in air and in DMSO solutions, the first step is a slow transformation of the oligomers into the hydrolyzed monomer,  $(\text{OH})_2\text{SiOPPc}$ , with a new Q-band at 678 nm. This is the same wavelength which was observed for monomeric  $(\text{OH})_2\text{SiOPPc}$  in DMSO, thus, confirming the monomerization and hydrolysis of the oligomers. Photolysis of all the oligomers gave the same spectra after hydrolysis confirming that the same compound is formed. Hydrolysis of  $(\text{Cl})_2\text{SiPc}$  to  $(\text{OH})_2\text{SiPc}$  in pyridine solutions has been reported [26]. The  $(\text{OH})_2\text{SiOPPc}$  species is formed with a low quantum yield ( $\phi_P$ ) of  $\sim 7.9 \times 10^{-5}$ .

Photobleaching (the degradation of the Pc macrocycle) of  $(\text{OH})_2\text{SiOPPc}$  then followed with a quantum yield of  $\sim 4.7 \times 10^{-6}$ . The mechanism of this bleaching was found to involve singlet oxygen. This was confirmed by performing the photobleaching studies in the presence of the singlet oxygen quencher DABCO, in nitrogen saturated DMSO, in oxygen saturated DMSO and in deuterated DMSO. Singlet

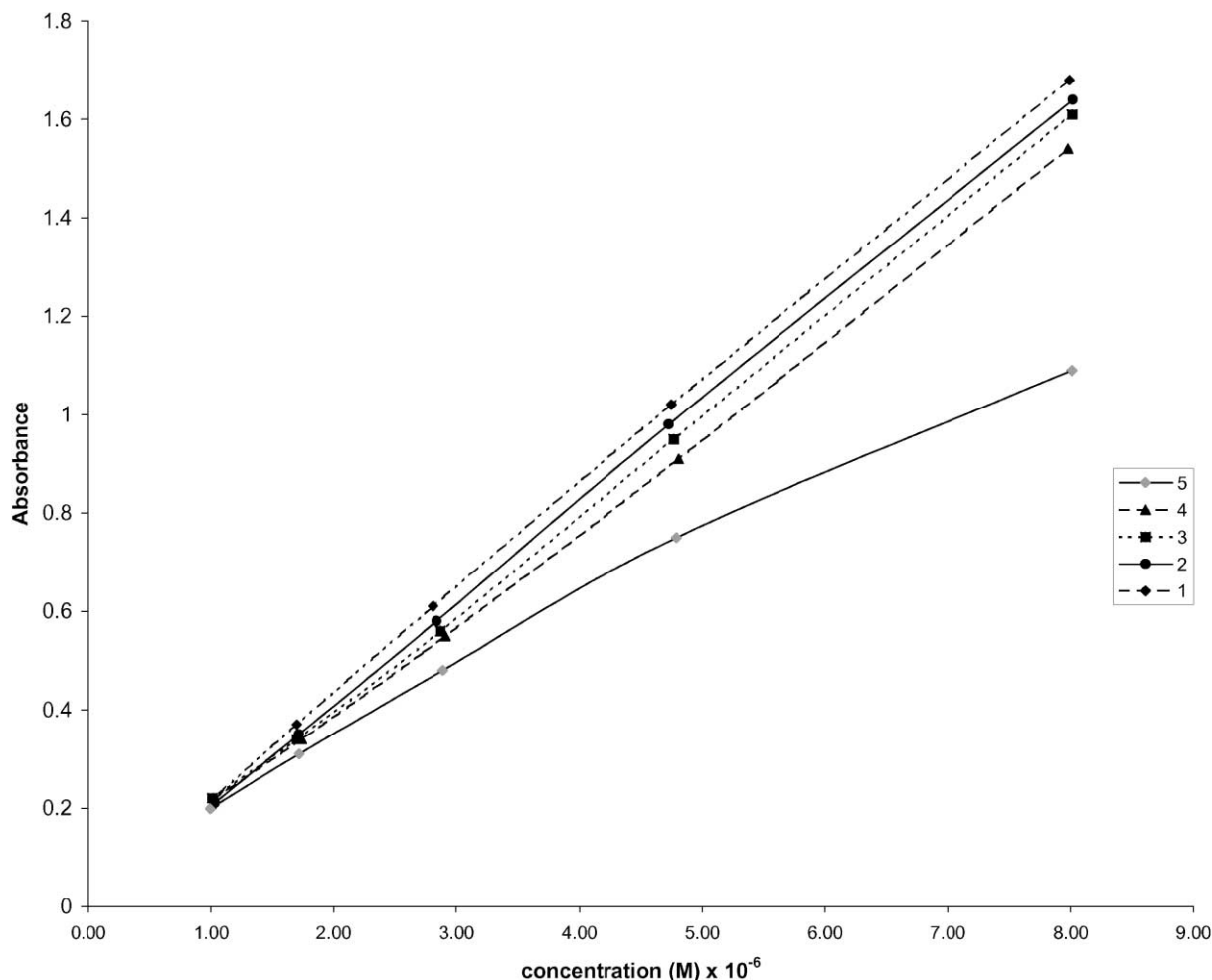


Fig. 4. Beer's law deviation for the oligomers **1–5**.

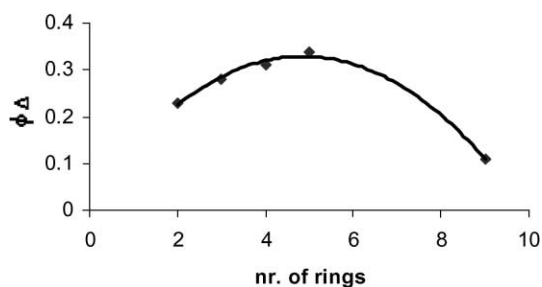


Fig. 5. Relationship of degree of oligomerization with singlet oxygen quantum yield ( $\phi_{\Delta}$ ).

oxygen has longer life-times in deuterated solvents. It was found that the rate of photobleaching increased in oxygen saturated DMSO and deuterated DMSO and decreased in DABCO and nitrogen saturated DMSO. These experiments prove that a singlet oxygen is involved in the photobleaching mechanism.

#### 3.4. Singlet oxygen quantum yields

Quantum yields of singlet oxygen photogeneration ( $\phi_{\Delta}$ ) of compounds 1–5 are presented in Table 2. No photobleaching or phototransformation of the complexes was observed during the determination of singlet oxygen quantum yields, since these processes occur much slower than singlet oxygen production. It is well known that intermolecular interactions between Pc rings result in decreased photochemical activity due to enhanced probability of radiationless decay of excited states. In this case, however, aggregation is largely prevented by the linking groups as well as the terminal groups. An interesting trend is observed in the generation of singlet oxygen as seen in Fig. 5 where an increase in singlet oxygen generation is observed up to compound 4 (with five rings) and a drop is observed to 5 (with nine rings). The lower  $\phi_{\Delta}$ -values for 5 is most likely due to the increased aggregation for this oligomer.

#### 4. Conclusions

In this study single isomers of complex molecules were synthesized although in low yields of ~30%. The use of hydroxybenzaldehyde in terminating the reaction enabled a more controlled degree of oligomerization compared to other reported oligomerization reactions [19]. The isolation of these oligomers from various side-products was achieved with relative ease using preparative TLC. Slow transformation of the oligomers into the hydrolyzed monomer is observed. The mechanism of this phototransformation process has been proposed earlier [27], and it is believed to involve fragmentation of the hydrolyzed monomer into cationic and anionic fragments in the initial step. This phototransformation process is followed by the photobleaching of the hydrolyzed product. The quantum yield of the photobleaching

process is smaller than that of the phototransformation process. This work has also surprisingly shown that singlet oxygen generation may be increased in SiPc by an increase in the degree of oligomerization, even though solvent solubility does decrease. This is an important observation since the currently used PDT agent, Photofrin is known to contain oligomers of hematoporphyrin. Our observation of increase in the singlet oxygen quantum yield with the increase in the number of oligomers shows that oligomeric Pcs may be more effective PDT agents than their monomeric counterparts. There is, however, a limit as to how many rings are beneficial in this regard. In our work the octaphenoxy SiPc have the highest singlet oxygen quantum yield as a pentamer (five ring oligomer). The complex containing nine rings gave the lowest singlet oxygen quantum yield, this may be explained by the observed high aggregation in this complex. The triplet state quantum yields and triplet state life times of the oligomers will also affect the magnitudes the singlet oxygen quantum yields. Photophysical studies on the oligomeric complexes discussed in this work are underway.

#### Acknowledgements

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