Polyhedron 29 (2010) 675–682

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and properties of axially-phenoxycyclotriphosphazenyl substituted silicon phthalocyanine

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ARTICLE INFO

Article history:
Received 3 September 2009
Accepted 30 September 2009
Available online 24 October 2009

Keywords:
Silicon phthalocyanine
Cyclotriphosphazene
Fluorescence
Singlet oxygen
Quantum yield

ABSTRACT

An hydroxyl substituted hexa(phenoxy)cyclotriphosphazene (**3**) is reacted with silicon phthalocyanine (**4**), SiPc(Cl)$_2$, to give an axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**). In this study, an axially phosphazene substituted phthalocyanine complex synthesized at the first time. Newly synthesized silicon phthalocyanine complex has been fully characterized by elemental analysis, ESI mass spectrometry, FT-IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. Photophysical (fluorescence quantum yield and lifetime) and photochemical (singlet oxygen generation and photodegradation quantum yield) properties of complex **5** are reported in DMSO. The fluorescence quenching behaviour of this complex by 1,4-benzoquinone (BQ) is also reported in DMSO.

1. Introduction

Phthalocyanines (Pcs), which were first developed as industrial pigments, have been actively explored in various technological applications [1] such as optical recording photovoltaics, photocopying, gas sensing, liquid crystal and photodynamic therapy (PDT).

Axially-substituted silicon phthalocyanines (SiPcs) are of great interest to scientists because they are not able to aggregate due to their special structural features [2], thus avoiding fluorescence quenching. Therefore, they are very attractive targets to study photophysical processes [3]. In the past few years, different axially-substituted silicon Pcs have been synthesized bearing a wide variety of active moieties such as carotenoid, azo, tetrathiafulvalene, porphyrin and several ester and/or ether derivatives including phenyl, terphenyl, thienyl and pyrenyl system which have been studied to determine energy or electron transfer processes [4–8].

The cyclic and polymeric phosphazenes are an important class of inorganic heterocyclic ring systems in basic and applied science [9]. They are usually prepared by nucleophilic substitution reactions of alkoxides, aryloxides or amines on halocyclophosphazenes or high polymers [10] and their physical and chemical properties can be tailored via appropriate substituted groups on phosphorus atoms. For example, it is possible to design materials with special properties such as inflammable textile fibers and advanced elastomers [11], anticancer agents [12], hydraulic fluids and lubricants [13], electrical conductivity [14], and flame retardant properties [15]. Recently there has been considerable interest in fluorescent compounds based on cyclic phosphazene cores [16] or cyclolinear polymers with the cyclotriphosphazene units [17] for development of electroluminescent devices.

We have previously described the synthesis of cyclotriphosphazenyl-rings substituted on peripheral position of a phthalocyanine macrocycle and their photophysical and photochemical properties have been also investigated [18,19].

To our best knowledge, there is no report that synthesis of cyclotriphosphazene being linked to phthalocyanines as axially groups. The nature of substituents on axially positions can strongly influence essential parameters of a phthalocyanine, such as its solubility, aggregation behaviour, electronic absorption and fluorescence spectral properties. Therefore, we want to investigate the effects of cyclotriphosphazenyl group substituted on axially position of silicon phthalocyanine. In this work, we report the molecular design, synthesis, photophysical and photochemical properties of axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) at the first time. Photophysical (fluorescence quantum yield and lifetime) and photochemical (singlet oxygen generation and photodegradation quantum yield) properties of axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) are reported in DMSO. The fluorescence quenching behaviour of this complex by BQ is also reported in DMSO.

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doi:10.1016/j.poly.2009.09.035

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (Otsuka Chemical Co. Ltd.) was purified by fractional crystallization from *n*-hexane. The deuterated solvents ($CDCl_3$ and toluene-d_8) for NMR spectroscopy and the following chemicals were obtained from Merck; cyclohexene, ethanol, phenol, $Pd(OH)_2$, K_2CO_3, NaH, acetone, triethylamine, silica gel 60, tetrahydrofuran. 1,3-diphenylisobenzofuran (DPBF) were purchased from Fluka. All other reagents and solvents were reagent grade quality and obtained from commercial suppliers. $SiPc(Cl)_2$ [20], 1,1,3,3,5-pentaphenoxy-5-chlorocyclotriphosphazatriene (**1**) [18], 1,1,3,3,5-pentaphenoxy-5-[(4-hydroxy)phenoxy]-cyclotriphosphazatriene (**2**) [18] and 1,1,3,3,5-pentaphenoxy-5-[(4-hydroxy)phenoxy]-cyclotriphosphazatriene (**3**) [18] were synthesized and purified according to the literature procedures.

2.2. Equipment

Elemental analysis was carried out using Thermo Finnigan Flash 1112 Instrument. UV–Vis spectra were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. Infrared spectra were recorded on a Bio-Rad FTS 175C FT-IR spectrophotometer using KBr pellets. The mass analyzer was a Bruker Daltonics (Bremen, Germany) MicrOTOF mass spectrometer equipped with an orthogonal electrospray ionization (ESI) source. The instrument was operated in positive ion mode using a *m*/*z* range of 50–3000. The capillary voltage of the ion source was set at 4500 V and the capillary exit at 210 V. The nebulizer gas flow was 0.6 bar and drying gas flow 4 L/min. The drying temperature was set at 200 °C. The transfer time of the source was 88 ms and the hexapole radiofrequency (RF) was 800.0 Vpp. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh; for 3 g. crude mixture, 100 g. silica gel was used in a column of 3 cm in diameter and 60 cm in length) and preparative thin layer chromatography was performed on silica gel 60 P F_{254}. ^1H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ and toluene-d_8 solutions on a Varian 500 MHz spectrometer.

Photo-irradiations were done using 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 infrared radiations, respectively. An interference filter (Intor, 670 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX5100 (Molelectron detector incorporated) power meter.

2.3. Photophysical parameters

2.3.1. Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method (Eq. (1)) [21,22],

$$\Phi_F = \Phi_F(\mathrm{Std})\frac{F \cdot A_{\mathrm{Std}} \cdot \eta^2}{F_{\mathrm{Std}} \cdot A \cdot \eta^2_{\mathrm{Std}}} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence emission curves of the sample (**5**) and the standard, respectively. A and A_{Std} are the respective absorbances of the sample and standard at the excitation wavelengths, respectively. η^2 and η^2_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [23] was employed as the standard. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Natural radiative lifetimes (τ_0) were determined using PhotochemCAD program which uses the Strickler–Berg equation [24]. The fluorescence lifetimes (τ_F) were evaluated using Eq. (2).

$$\Phi_F = \frac{\tau_F}{\tau_0} \tag{2}$$

The experimental errors in the determination of the Φ_F, τ_F and τ_0 were ~5% (determined several values).

2.4. Photochemical parameters

2.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the experimental set-up described in literature [25–27]. Typically, a 3 ml portion of the respective axially-phenoxycyclotriphosphazenyl substituted silicon phthalocyanine (**5**) solution (absorbance ~ 1.0 at the irradiation wavelength) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in Refs. [25–27]. Singlet oxygen quantum yields (Φ_Δ) were determined in air using the relative method with ZnPc (in DMSO) as reference. DPBF was used as a chemical quencher for singlet oxygen in DMSO. Eq. (3) was employed for the calculations:

$$\Phi_\Delta = \Phi_\Delta^{\mathrm{Std}} \frac{R \cdot I_{\mathrm{abs}}^{\mathrm{Std}}}{R^{\mathrm{Std}} \cdot I_{\mathrm{abs}}} \tag{3}$$

where $\Phi_\Delta^{\mathrm{Std}}$ is the singlet oxygen quantum yield for the standard ZnPc ($\Phi_\Delta^{\mathrm{Std}} = 0.67$ in DMSO) [28]. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective sample (**5**) and standard, respectively. I_{abs} and $I_{\mathrm{abs}}^{\mathrm{Std}}$ are the rates of light absorption by the sample (**5**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [29], the concentration of quencher was lowered to $\sim 3 \times 10^{-5}$ mol dm^{-3}. Solutions of sensitizer (absorbance = 1 at the irradiation wavelength) containing DPBF was prepared in the dark and irradiated in the Q band region using the set-up described above. DPBF degradation at 417 nm was monitored. The light intensity 6.60×10^{15} photons s^{-1} cm^{-2} was used for Φ_Δ determinations.

2.4.2. Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determination of complex **5** was carried out using the experimental set-up described in literature [25–27]. Photodegradation quantum yield of complex **5** was determined using Eq. (4),

$$\Phi_d = \frac{(C_0 - C_t) \cdot V \cdot N_A}{I_{\mathrm{abs}} \cdot S \cdot t} \tag{4}$$

where C_0 and C_t are the sample (**5**) concentrations before and after irradiation, respectively, V is the reaction volume, N_A is the Avogadro's constant, S is the irradiated cell area and t the irradiation time I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the sample (**5**). A light intensity of 2.20×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determination.

2.5. Fluorescence quenching by 1,4-benzoquinone (BQ)

Fluorescence quenching experiments on the axially-phenoxycyclotriphosphazenyl substituted silicon phthalocyanine (**5**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the phthalocyanine complex (**5**), and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032 and 0.040 mol dm^{-3}. The fluorescence spectra of phthalocyanine complex (**5**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (S–V) equation [30] (Eq. (5)):

$$\frac{I_0}{I} = 1 + K_{SV}[BQ] \tag{5}$$

where I_0 and I are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively; [BQ] is the concentration of the quencher, and K_{SV} is the Stern–Volmer constant; and is the product of the bimolecular quenching constant (k_q) and the fluorescence lifetime τ_F, i.e.

$$K_{SV} = k_q \cdot \tau_F \tag{6}$$

The ratios I_0/I were calculated and plotted against [BQ] according to Eq. (5), and K_{SV} determined from the slope (the experimental errors in the determination of the K_{SV} value was ~5%).

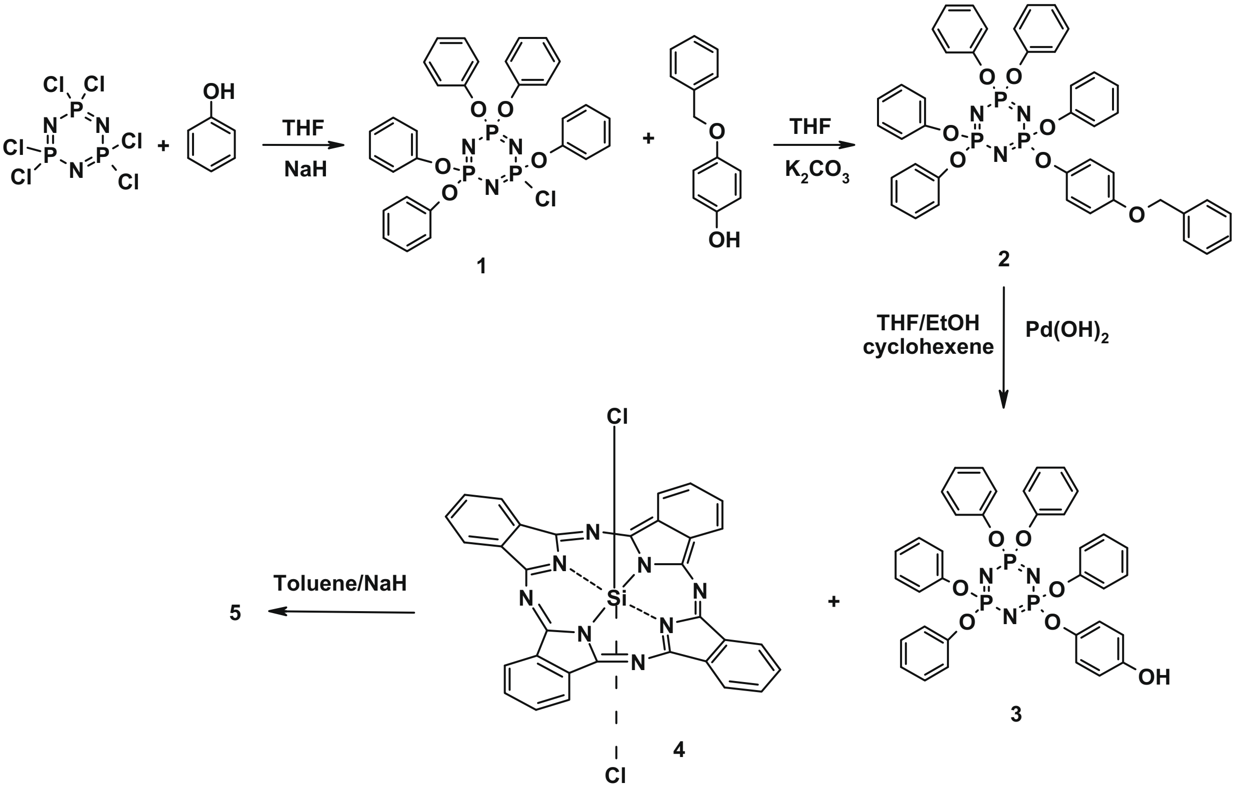
2.6. Synthesis of compound **5**

A mixture of dichloro(phthalocyaninato) silicon (**4**) (100 mg, 0.16 mmol) and **3** (231 mg, 0.33 mmol) in dry toluen (10 ml) was stirred and then sodium hydride (13.2 mg, 0.33 mmol) was added to this mixture. After refluxing under nitrogen for 10 h, the reaction mixture was cooled to room temperature, and than the solvent was evaporated to dryness under reduced pressure. The crude product was purified by preparative TLC on silica gel using hexane: THF (3:2) as the eluent. Dark green product was obtained; Yield: 105 mg (33%). *Anal.* Calc. for $C_{106}H_{74}N_{14}O_{14}P_6Si$ (1957): C, 63.74; H, 3.91; N, 10.01. Found: C, 63.64; H, 3.86; N, 10.05%. FT-IR ν_{max}/cm^{-1} (KBr pellet); 3059 (ArCH), 1591 (ArC=C), 1265 (P=N), 1125 (C–O), 950 (P–O); ^{1}H NMR(CDCl$_3$) δ = 6.21–7.50 (m, 48H, ArH), 8.40 and 9.70 (m, 16H, ArCH of SiPc); {^{1}H}^{13}C NMR (CDCl$_3$) δ = 151.81 (ArC), 149.80 (ArCH), 136.04 (ArC), 129.48 (ArCH), 128.52 (ArCH), 125.79 (ArCH), 124.88 (ArCH), 121.15(ArCH), 121.05 (ArCH), 119.49 (ArCH), 117.91 (ArCH); {^{1}H}^{31}P NMR (toluene-d_8) δ = 9.05 [>P(PhO)$_2$], 9.52 [>P (OPh)SiPc]; ^2J(P,P) = 74.2 Hz; MS (ESI) m/z (%): 1958(100) [M+H]$^+$.

3. Result and discussion

3.1. Synthesis and characterization

The synthetic route of the compounds presented in this work is shown in Scheme 1. Compounds **1** [31], **2** [18], **3** [18] and SiPc(Cl)$_2$ [20] were synthesized according to previously published methods. Compound **5** was obtained from a nucleophilic displacement reaction of **3** with SiPc(Cl)$_2$ under nitrogen atmosphere with sodium hydride as the base. The product was purified by preparative TLC on silica gel using hexane: THF (3:2) as the eluent. The structure of the compound **5** is shown in Fig. 1. The newly synthesized compound **5** was characterized by FT-IR, ^{1}H, ^{13}C and ^{31}P NMR, mass spectrometry and elemental analysis. All the results were consistent with the predicted structure as shown in the experimental section. The FT-IR spectra features peaks at around 1265 cm^{-1} (br) (P=N), 950 cm^{-1} (P–O) for phosphazene ring and aromatic C–H stretching around 3059 cm^{-1} for phthalocyanine skeleton as expected. The elemental analysis results and the mass spectral data for **5** were consistent with the assigned formulation. The mass spectrum of **5** was obtained by ESI mass spectrometry. Mass spectral identification is based on matching measured accurate mass and isotopic pattern of a sample. Theoretical and measured isotopic patterns as an additional identification tool to accurate mass determination of **5** and the positive ion ESI mass spectrum is given in Fig. 2. The peak group representing the protonated molecular ion of **5** was observed at 1958 Da mass (Fig. 2). Since the compound **5** shows non-first order ^{31}P NMR spectrum, it is necessary to carry out simulation analysis to get the appropriate spectral parameters. Following this analysis, the proton-decoupled ^{31}P NMR spectrum



Scheme 1. Chemical structure and synthetic pathway of **1–5**.

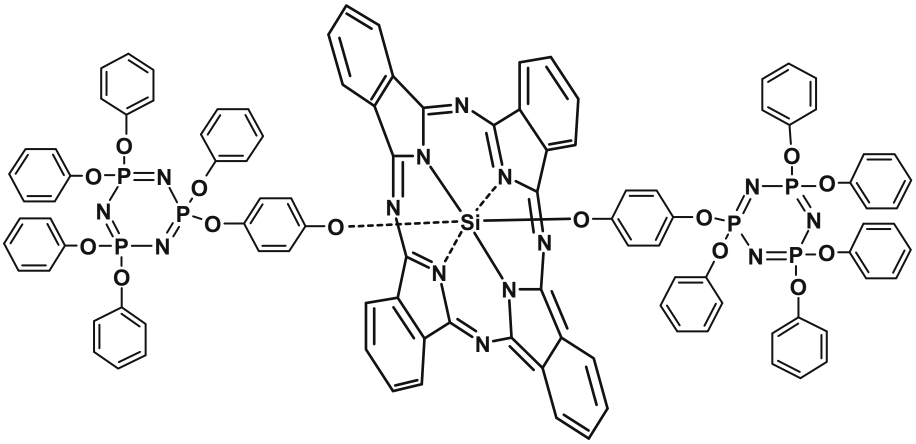


Fig. 1. Structure of the axially-phenoxycyclotriphosphazenyl substituted silicon phthalocyanine complex (**5**).

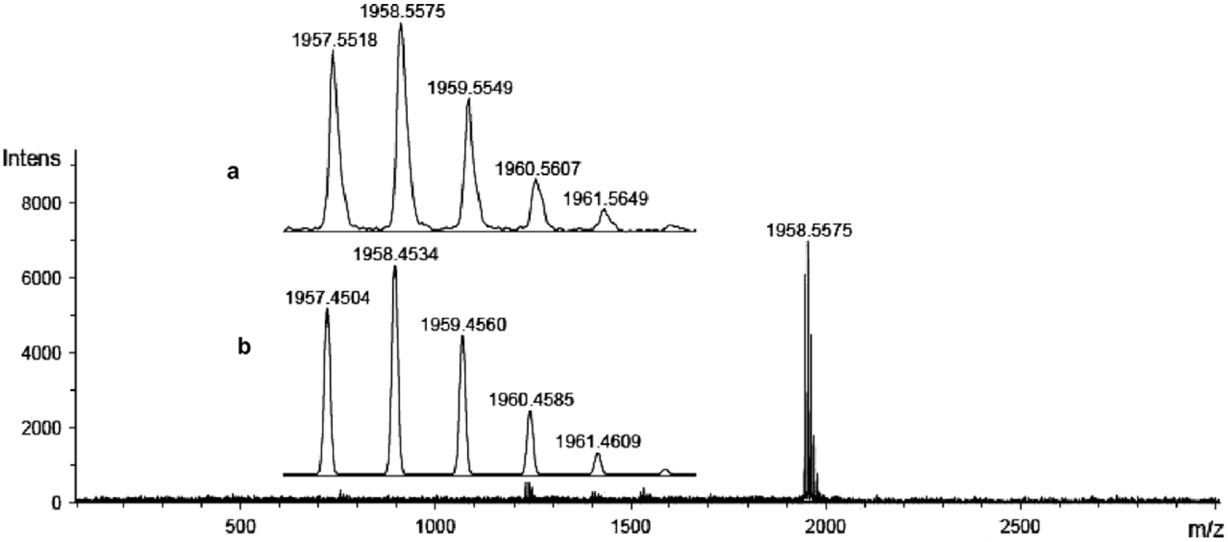


Fig. 2. Positive-ion mode electrospray ionization (ESI) mass spectrum of **5**. See inset: (a) experimental isotopic pattern and (b) theoretical isotopic pattern.

of compound **5** was shown as the expected typical AB_2 pattern [18] and the resonances belonging to phosphorous atoms were observed at ca. 9.05 ppm for >P(PhO)$_2$ and at ca. 9.52 ppm for >P(OPh)SiPc, also the magnitude of the ^2J(P,P) at ca. 74.2 Hz (Fig. 3).

3.2. Ground state electronic absorption and fluorescence spectra

The electronic spectrum of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) showed intense Q absorption band at 684 nm in DMSO (Fig. 4). The spectra showed monomeric behaviour evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes for **5** in DMSO [32]. The B-bands were broad due to the superimposition of the B_1 and B_2 bands at around 350 nm (Fig. 4).

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, peripheral substituents, complexed metal ions and temperature [33,34]. In the aggregated state the electronic structure of the complexed phthalocyanine rings is perturbed resulting in alternation of the ground and excited state electronic structure [35]. In this study, the aggregation behaviour of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) was investigated at different solvents (chloroform, DMF, THF, toluene, dichloromethane and DMSO). The complex **5** did not show aggregation in these solvents suggesting that the substitution effect of the phenoxycyclotriphosphazenyl group as axial substituent on the phthalocyanine ring.

The aggregation behaviour of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) complex was investigated at different concentrations in DMSO (Fig. 5). In DMSO, as the concentration was increased, the intensity of the Q band absorption also increased and there was no new bands (normally blue shifted) due to the aggregated species for complex **5** (Fig. 5). Thus, the complex **5** did not show aggregation in DMSO at different concentrations. Beer–Lambert law was obeyed for this complex (**5**) in the concentrations ranging from 1.4×10^{-5} to 4×10^{-6} mol dm^{-3}.

Fig. 6 shows the absorption, fluorescence emission and excitation spectra for axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) complex in DMSO. Fluorescence emission peak was observed at 692 nm for **5** in DMSO. The excitation spectrum was similar to absorption spectrum and both were mirror images of the fluorescent spectrum in DMSO (Fig. 6). The proximity of the wavelength of each component of the Q band absorption to the Q band maxima of the excitation spectrum for complex **5** suggests that the nuclear configurations of the ground and excited states were similar and not affected by excitation in DMSO. The observed Stokes shift was 8 nm and typical of MPc complexes in DMSO.

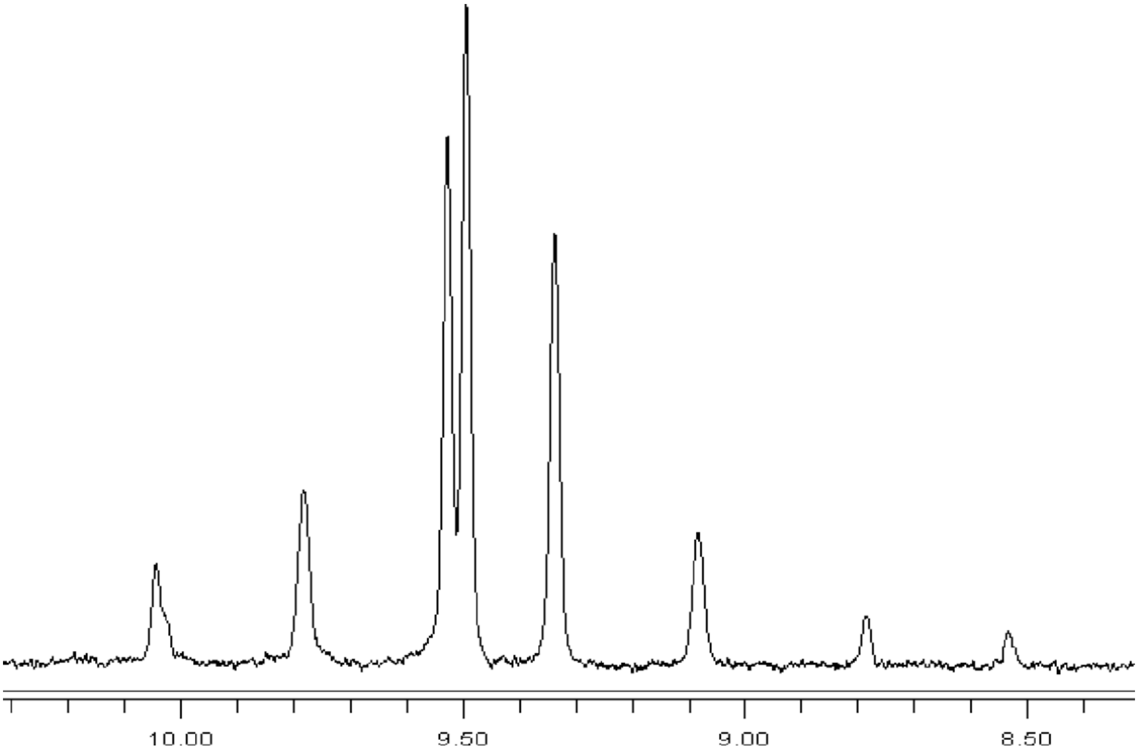


Fig. 3. Proton-decoupled ^{31}P NMR spectrum of **5** in toluene-d_8 solution.

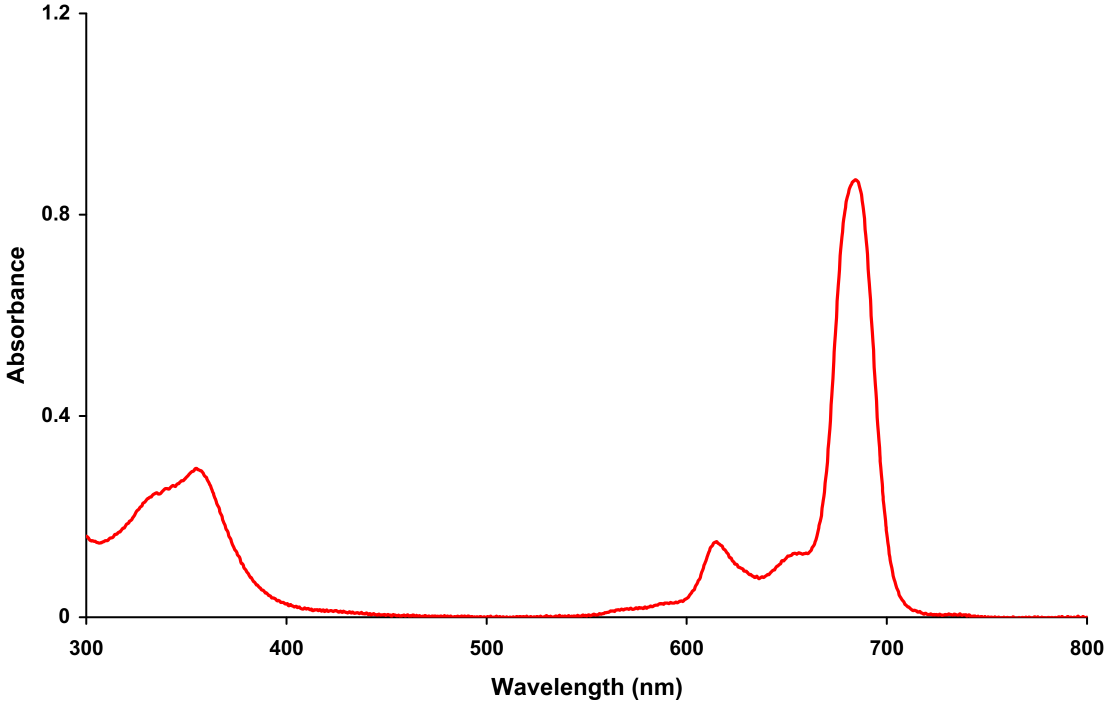


Fig. 4. Absorption spectrum of axially-phenoxycyclotriphosphazenyl substituted silicon phthalocyanine complex (**5**) in DMSO. Concentration = 1.00×10^{-5} mol dm^{-3}.

3.3. Fluorescence quantum yields and lifetimes

The fluorescence quantum yield (Φ_F) of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) complex ($\Phi_F = 0.17$) was typical of MPc complexes in DMSO. The Φ_F value of the substituted complex (**5**) is slightly lower than for unsubstituted ZnPc ($\Phi_F = 0.20$) in DMSO.

Lifetime of fluorescence (τ_F) was calculated using the Strickler–Berg equation. Using this equation, a good correlation has been [22] found for the experimentally and theoretically determined fluorescence lifetimes for the unaggregated molecules as is the case in this work for **5** in DMSO. τ_F value of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) complex ($\tau_F = 3.11$ ns) was longer when compared to unsubstitut-

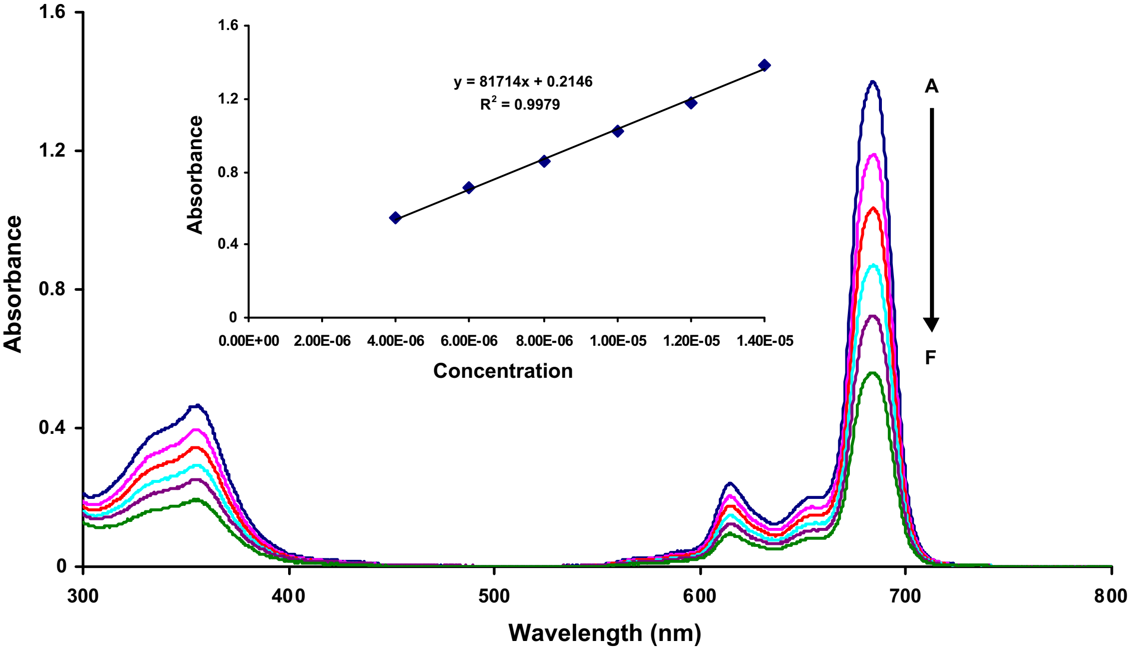


Fig. 5. Aggregation behaviour of **5** in DMSO at different concentrations: 14×10^{-6} (A), 12×10^{-6} (B), 10×10^{-6} (C), 8×10^{-6} (D), 6×10^{-6} (E), 4×10^{-6} (F) mol dm^{-3}.

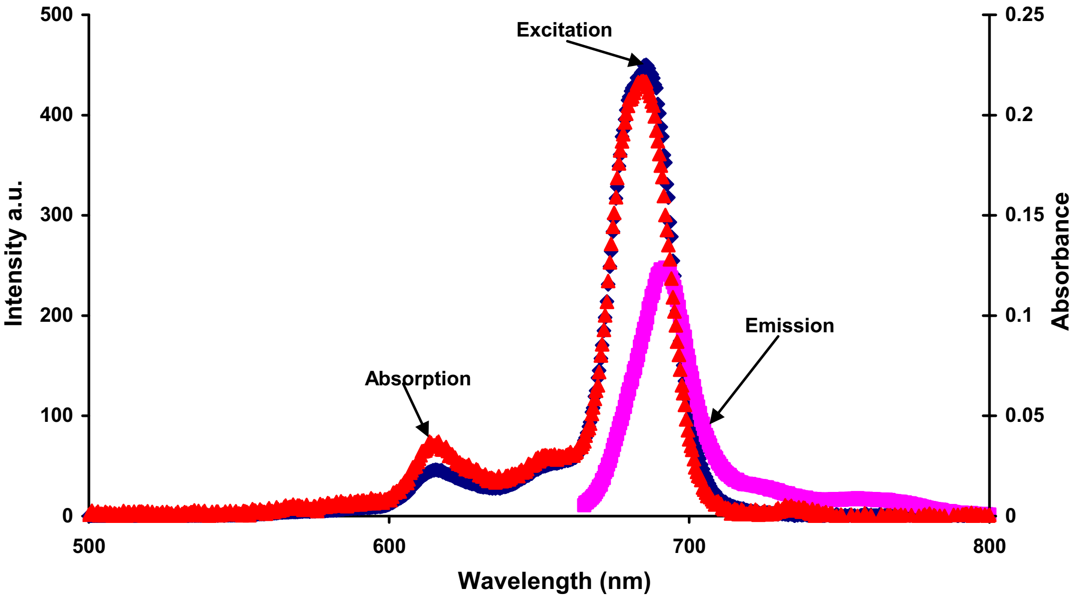


Fig. 6. Absorption, excitation and emission spectra of the compound **5** in DMSO. Excitation wavelength = 655 nm.

ed ZnPc (τ_F = 1.22 ns) [36] in DMSO. The natural radiative lifetime (τ_0) value of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) complex (τ_0 = 18.29 ns) was also longer when compared to unsubstituted ZnPc (τ_0 = 6.80 ns) in DMSO [36]. The rate constant for fluorescence (k_F) value of the complex **5** ($k_F = 5.46 \times 10^7$ s^{-1}) was lower than unsubstituted ZnPc ($k_F = 1.47 \times 10^8$ s^{-1}) in DMSO [36].

Fluorescence quantum yield (Φ_F) and lifetime (τ_F) values of employed axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine complex (**5**) resemble with those of axially substituted silicon phthalocyanine complexes in the literature that ranged from 0.02 to 0.14 for Φ_F and 2.54–5.40 ns for τ_F, respectively [37–40]. The Φ_F value, obtained as a result of this study, is higher than silicon phthalocyanine derivatives having different substituents on the axially position in literature [37–40]. The τ_F value, obtained as a result of this study, is almost similar with axially substituted silicon phthalocyanine derivatives in literature [37–40].

3.4. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) was determined in DMSO using a chemical method using DPBF as a quencher. The disappearance of DPBF spectra was monitored using UV–Vis spectrophotometer. Many factors are responsible for the magnitude of the determined quantum yield of singlet oxygen including; triplet ex-

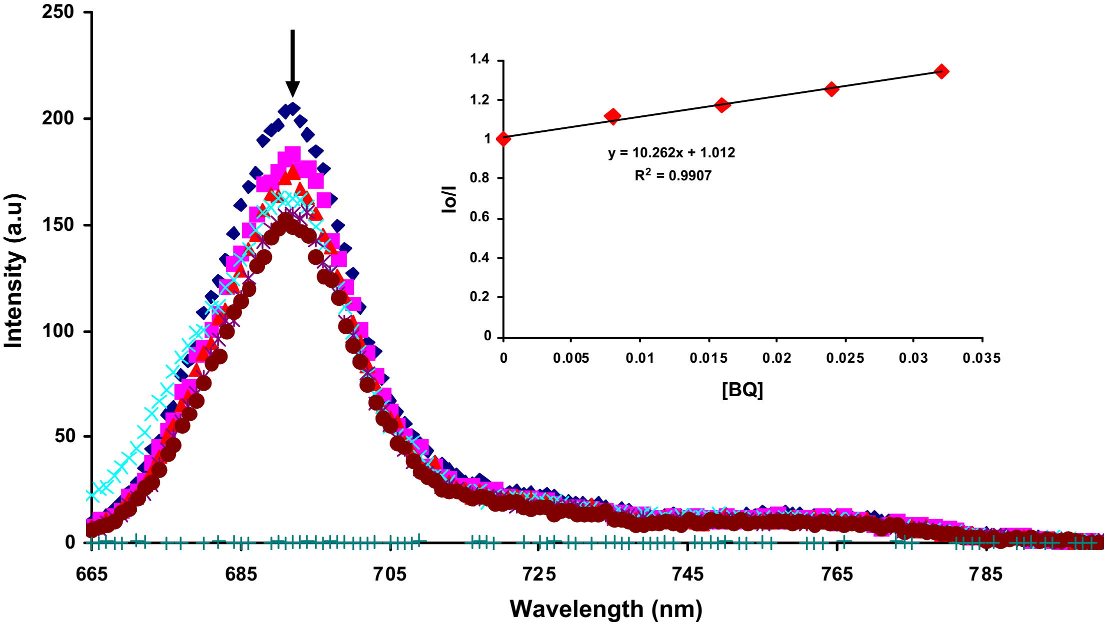


Fig. 7. Fluorescence emission spectral changes of **5** (1.00×10^{-5} mol dm^{-3}) on addition of different concentrations of BQ in DMSO. [BQ] = 0, 0.008, 0.016, 0.024, 0.032 and 0.040 mol dm^{-3} (inset: Stern–Volmer plot for BQ quenching of **5**).

cited state energy, ability of substituents and solvents to quench the singlet oxygen, the triplet excited state lifetime and the efficiency of the energy transfer between the triplet excited state and the ground state of oxygen.

There was no change in the Q band intensity during the Φ_Δ determination, confirming that complex was not degraded during singlet oxygen study. The Φ_Δ value of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) complex is 0.22 in DMSO and it is lower than unsubstituted ZnPc value ($\Phi_\Delta = 0.67$) [28] in DMSO. Singlet oxygen quantum yield (Φ_Δ) value of employed the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine complex (**5**) is similar compared to axially substituted phthalocyanine derivatives in literature that ranged from 0.04 to 0.41 [37–42].

3.5. Photodegradation study

Degradation of the molecules under irradiation can be used to study their stability and this is especially important for those molecules intended for use as photo catalysts. The collapse of the absorption spectra without any distortion of the shape confirms clean photodegradation not associated with phototransformation. The spectral changes observed for axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) during confirmed photodegradation occurred without phototransformation.

Φ_d values indicate that the stability of the molecules towards the light irradiation. Stable phthalocyanine complexes show Φ_d values as low as 10^{-6} and for unstable molecules, values of the order of 10^{-3} have been reported [43]. The photodegradation value of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) is 1.06×10^{-4} and it is less stable to degradation compared to unsubstituted ZnPc ($\Phi_d = 2.61 \times 10^{-4}$) [36] in DMSO. Thus the substitution of silicon phthalocyanine with phenoxycyclotriphosphazenyl group seems to decrease the stability of the complex in DMSO.

3.6. Fluorescence quenching studies by BQ

Pc complexes may also be used as photosynthetic mimickers. An essential requirement for a good photosynthetic mimicker is the ability to undergo excited state charge transfer with ease, and Pc-quinone systems have proved to be favoured candidates in this respect [26,44].

The fluorescence quenching of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) by BQ in DMSO was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Fig. 7 shows the quenching of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) complex by BQ in DMSO. The slope of the plots shown at inset of Fig. 7 gave K_{SV} value of complex **5**. The K_{SV} value of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) is 10.26 dm^3 mol^{-1} and it is lower than unsubstituted ZnPc (31.90 dm^3 mol^{-1}) [36] in DMSO. K_{SV} value of employed the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine complex (**5**) is similar compared to silicon phthalocyanine derivatives in literature [40,45]. The bimolecular quenching constant (k_q) value of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) is 0.351×10^{10} dm^3 mol^{-1} s^{-1} and it is also lower than for unsubstituted ZnPc (2.611×10^{10} dm^3 mol^{-1} s^{-1}) [36] in DMSO, thus axially substitution of the silicon phthalocyanine with phenoxycyclotriphosphazenyl group seems to decrease the k_q values of the complex.

In this work, we present a study of the light harvesting and energy transducing tendencies of mixtures of silicon phthalocyanine (**5**) and BQ. The effective quenching of the complex' fluorescence by BQ suggests that systems that are composite of silicon phthalocyanine (**5**) and quinones could well serve as good light harvesters and energy transducers. We are at present looking at the possibility of architecting silicon phthalocyanine (**5**)-quinone conjugates, which should be more efficient as a mimicker of the natural photosynthesis.

4. Conclusion

In the presented work, the synthesis of new axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) was described and this complex was fully characterized by standard methods (elemental analysis, IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy, electronic spectroscopy and mass spectrum). The photophysical and photochemical properties of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) was also described and compared with unsubstituted ZnPc which was used as standard. This new axially substituted silicon phthalocyanine is soluble in most solvents such as chloroform, toluene, DMSO, etc. In solution, the absorption spectra of the axially-disubstituted phenoxycyclotriphosphazenyl silicon phthalocyanine (**5**) showed monomeric behaviour evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes in used solvents such as DMSO, DMF, THF, chloroform, toluene and dichloromethane. The fluorescence quantum yield of complex **5** was typical for MPcs. This complex (**5**) has average singlet oxygen quantum yields (Φ_{Δ}). The axially substitution of silicon phthalocyanine with phenoxycyclotriphosphazenyl group seems to decrease the stability of this complex when compared to unsubstituted ZnPc in DMSO. The complex **5** showed lower K_{sv} and k_q values when compared to the unsubstituted ZnPc in DMSO.

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