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Synthesis, Photophysical and Photochemical Properties of Poly(oxyethylene)-Substituted Phthalocyaninato Oxotitanium(IV) Complexes

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The synthesis, photophysical and photochemical properties of tetra- and chlorotetrapoly(oxyethylene)-substituted oxotitanium(IV) phthalocyanines are reported for the first time. The new compounds were characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy, electronic spectroscopy and mass spectra. These complexes showed monomeric behaviour in solution. General trends are described for photodegradation, singlet oxygen, triplet state and fluorescence quantum yields, and triplet and fluorescence lifetimes of these compounds in dimethyl sulfoxide (DMSO). Photophysical and photochemical properties of phthalocyanine complexes are very useful for PDT applications. The complexes showed high triplet quantum yields and triplet lifetimes in DMSO. The singlet oxygen quantum yields (Φ_Δ), which give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism), were 0.72 and 0.78 for **3a** and **5a**, respectively. Thus, these complexes show potential as Type II photosensitizers. These complexes were also quenched by benzoquinone for fluorescence quenching studies.

Introduction

Recently, phthalocyanine (Pc) chemistry has undergone a renaissance because these compounds and many of their derivatives exhibit properties that are interesting for many applications in material science.[1,2] Current research on phthalocyanines (Pcs) has been rapidly expanding into several applied fields including photovoltaics, electrochromism, optical data storage, laser dyes, liquid crystals, chemical sensors and photosensitizers for photodynamic therapy.[3] Because of their properties as semiconductors as well as their large linear and nonlinear optical responses, Pcs are currently of great scientific and technological interest for designing novel electronic and photonic devices. Pcs with highly delocalized cyclic π-electron systems show intense absorptions in the red region (Q band) and these absorptions can be shifted to the near IR region by making relatively small changes in these molecules.[3,4] Fusion of additional aromatic rings (polybenzannulation) has been proposed as a practical method to enhance the conjugation of π-electrons, thus increasing the wavelength of absorbed electromagnetic radiation. However, there is a decrease in the solubility of the products obtained by increased conjugation.[5] The second way to obtain the same effect has been the addition of electron donating groups (e.g. -OR, -SR, etc.) into the periphery of Pcs.[1] The presence of substituents is an additional advantage, as they address the problem of insolubility by making the complexes soluble in most organic solvents as opposed to unsubstituted Pcs that have limited applications. Tetra-substituted Pcs are usually more soluble than the corresponding octa-substituted Pcs due to the formation of constitutional isomers and the high dipole moment that results from the unsymmetrical arrangement of the substituents at the periphery.[6–9] The other method for changing the absorption wavelength is the use of some special metals in the inner core, and TiO^{2+} is one of them.[10] Unsubstituted oxotitanium phthalocyanine (OTiPc), a well-known near-IR-active photoconductive dye used as xerographic photoreceptor in copiers and laser printers,[11–13] was first synthesised by Taube.[14] Also, this material can be used in optical disc information recording. The high third order optical susceptibility values of OTiPc derivatives are well documented.[15] Specific phthalocyanines can thus be tailored such that they consist of certain properties that are required for various applications since the possibility of combining an unlimited number and type of substituents with a great number of central metals is infinite.

Thiol-derivatized metallophthalocyanine complexes show rich spectroscopic and photochemical properties. For example, they are known to absorb at longer wavelengths[16–21] than other metallo phthalocyanine complexes. To the best of our knowledge, titanium phthalocyanines

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tetra-substituted with poly(oxyethylene) side chains containing S atoms have not been reported.

Photophysical properties of OTiPc are very useful in applications involving nonlinear optics and optical limiters as these titanyl macrocycles are known to have remarkable properties.[22–28] Herein we report the synthesis of new sterically hindered thia-bridged tetrapoly(oxyethylene)-substituted OTiPc phthalocyanine derivatives (Scheme 1). The influence of the presence of the thia bridges in the poly(oxyethylene) side chains on the photophysical (triplet quantum yields and lifetimes, fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen and photodegradation quantum yields) properties were determined. The quenching of fluorescence by benzoquinone is also discussed.

Results and Discussion

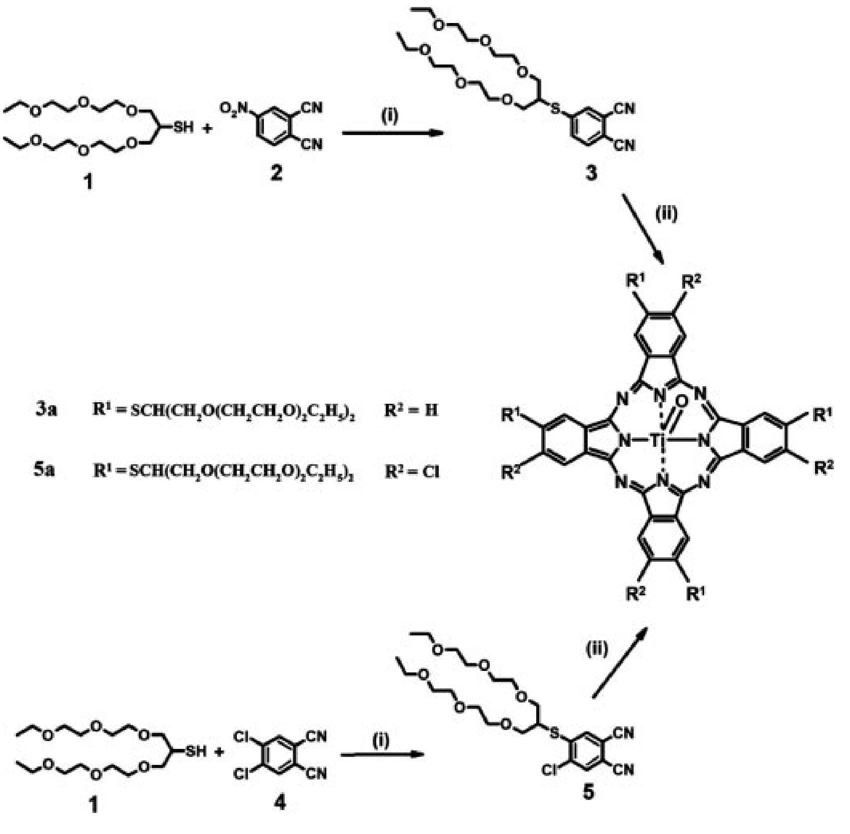
Synthesis and Characterization

Treatment of substituted dinitriles **3** and **5** with Ti(OBu)$_4$, urea and DBU in *n*-pentanol led to the formation of corresponding metallo Pcs **3a** and **5a**, respectively (Scheme 1). This method is similar to that reported by Hanack and co-workers.[22] We expect that **3a** and **5a** were prepared as a statistical mixture of four regioisomers due to the various possible positions of the poly(oxyethylene) side chains relative to one another. The four possible isomers of molecular symmetry D_{4h}, C_{4h}, C_{2v} and C_s and a distribution of 1:1:2:4, respectively, can be obtained.[29] No attempt was made to separate the isomers of complexes **3a** and **5a**.

Thia-bridged tetra- and chlorotetrapoly(oxyethylene)-substituted phthalocyanines **3a** and **5a**, respectively, were purified in each case, by column chromatography (silica gel) and preparative thin-layer chromatography (silica gel) using a mixed solvent system of dichloromethane/methanol as eluent. The waxy products are very soluble in polar and apolar solvents, such as chloroform, benzene, diethyl ether, carbon tetrachloride, *N*,*N*-dimethylformamide, dimethyl sulfoxide (DMSO), ethanol and acetone. They could thus be thoroughly investigated by ^{1}H and ^{13}C NMR in solution. The mass spectra of the phthalocyanine compounds obtained by ESI (electrospray ionisation) showed relatively intense molecular ion peaks.

In the IR spectra characteristic vibrations corresponding to ether groups (C–O–C) at 1120–1100 cm^{-1} and CH$_2$ stretches at ca. 2950–2850 cm^{-1} are common for phthalocyanine compounds **3a** and **5a**. The disappearance of the dinitrile stretches at ca. 2230 cm^{-1} and the presence of Ti=O stretches at ca. 960 cm^{-1} confirmed the formation of MPc.

The ^{1}H and ^{13}C NMR spectra of phthalocyanine compounds **3a** and **5a** in CDCl$_3$ confirmed the proposed structure. The ^{1}H NMR spectra of **3a** and **5a** have broad absorptions relative to those of the phthalonitrile derivative. It is likely that broadness is due to both chemical exchange caused by aggregation–disaggregation equilibria and the



Scheme 1. Synthetic pathway for the preparation of compounds **3a** and **5a**: (i) DMSO, K$_2$CO$_3$, 50 °C, 48 h; (ii) 1-pentanol, urea, Ti(OBu)$_4$, DBU, reflux, 6 h.

fact that the product obtained in this reaction is a mixture of four positional isomers that are expected to show chemical shifts only slightly differing from each other. The poly(oxyethylene)-substituted phthalocyanines were found to be pure by ^{1}H NMR spectroscopy with all the substituents and ring protons observed in their respective regions. Pc complexes **3a** and **5a** both showed the phthalocyanine ring protons as unresolved multiplets (most likely due to the presence of isomers), integrating for a total of 12 and 8 protons, respectively. The phthalocyanine ring protons were observed in the range 8.20–9.40 ppm for **3a** and 8.80–9.56 ppm for **5a**. Although the presence of isomers as well as phthalocyanine aggregation at the concentrations used for the NMR measurements may lead to broadening of the aromatic signals, the observed spectra of all the complexes were relatively well-resolved.

Ground State Electronic Absorption and Fluorescence Spectra

The electronic spectra of phthalocyanine complexes **3a** and **5a** showed intense Q absorption bands around 715 nm (Figure 1). The spectra showed monomeric behaviour as evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes for **3a** and **5a** in DMSO.[30] In DMSO, the Q bands were observed at 714 (**3a**) and 716 nm (**5a**), Tables 1 and 2. The B bands are broad due to the superimposition of the B_1 and B_2 bands in the 350 nm region. The shoulder between 400–500 nm (Figure 1) is tentatively assigned to charge transfer from the electron-rich ring to the electron-poor metal, but it may also be due to intraligand charge transfer between the sulfur groups and the phthalocyanine ring.

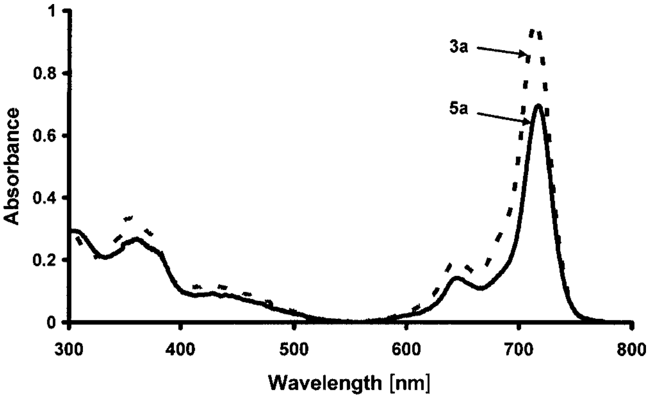


Figure 1. Absorption spectra of substituted oxotitanium phthalocyanines (OTiPc) **3a** and **5a** in DMSO. Concentration = 4×10^{-6} mol dm^{-3}.

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.[31,32] 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.[33] In this study, the aggregation behaviour of phthalocyanine complexes **3a** and **5a** are investigated in different solvents (*n*-hexane, THF, chloroform, MeOH and DMSO), Figure 2. The complexes did not show aggregation in chloroform, THF or DMSO, whereas they showed aggregation in *n*-hexane and MeOH (Figure 2), as judged by the broadening and blueshifting of the Q band. In DMSO, the Beer–Lambert law was obeyed for all of these compounds in the concentrations ranging from 1.4×10^{-5} to 4×10^{-6} mol dm^{-3}, without any distortion of the spectra.

Table 1. UV/Vis spectroscopic data of complexes **3a** and **5a** in different solvents.

Compound	Solvent	Q band [nm] (log ε)	B band [nm]	N band [nm]
3a	*n*-Hexane	705 (4.81)	343	–
	THF	710 (5.46)	352	–
	$CHCl_3$	715 (5.52)	350	307
	MeOH	708 (4.96)	344	–
	DMSO	714 (5.34)	353	–
5a	*n*-Hexane	713 (4.46)	348	307
	THF	716 (5.24)	355	313
	$CHCl_3$	720 (5.27)	353	316
	MeOH	712 (4.70)	349	314
	DMSO	716 (5.11)	361	309

Table 2. Absorption, excitation and emission spectroscopic data for complexes **3a** and **5a** in DMSO.

Compound	Q band λ_{max} [nm]	log ε	Excitation λ_{Ex} [nm]	Emission λ_{Em} [nm]	Stokes shift Δ_{Stokes} [nm]
3a	714	5.34	716	724	10
5a	716	5.11	720	726	10

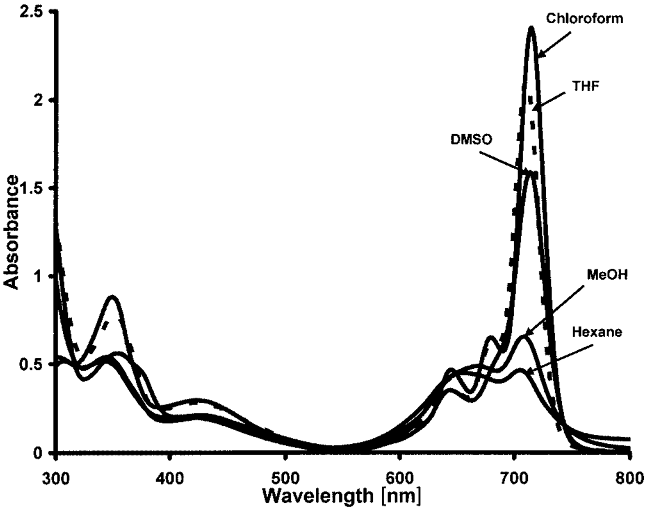


Figure 2. UV/Vis spectrum of **3a** in different solvents. Concentration = 7.20×10^{-6} mol dm^{-3}.

Complexes **3a** and **5a** showed similar fluorescence behaviour in DMSO. Figure 3 shows the absorption, fluorescence emission and excitation spectra for complexes **3a** and **5a** in DMSO. Fluorescence emission peaks were observed at 724 nm for **3a** and 726 nm for **5a** in DMSO (Table 2). The excitation spectra were similar to the absorption spectra and both were mirror images of the fluorescent spectra in DMSO (Figure 3). The proximity of the wavelength of each component of the Q band absorption to the Q band maxima of the excitation spectra for all complexes suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation in DMSO. The observed Stokes shifts (Table 2) were typical of MPc complexes in DMSO.

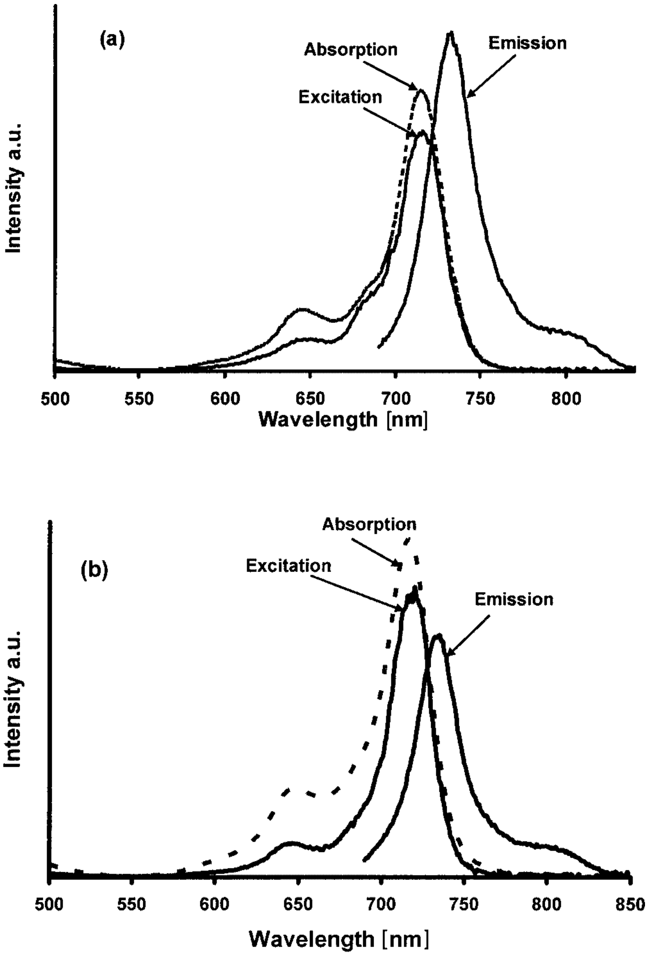


Figure 3. Absorption, excitation and emission spectra of compound **3a** (a), and **5a** (b) in DMSO. Excitation wavelength = 680 nm.

Photophysical and Photochemical Properties

Fluorescence Quantum Yields and Lifetimes

The fluorescence quantum yields (Φ_F) of the complexes were similar and typical for MPc complexes, Table 3. The Φ_F value of complex **3a** was larger than that of complex **5a** in DMSO. Complex **5a** contains chlorine ligands, which would enhance intersystem crossing to the triplet state through the heavy atom effect, hence the slightly lower Φ_F value for **5a** compared to **3a**.

Table 3. Photophysical and photochemical parameters of complexes **3a** and **5a** in DMSO. Triplet absorption wavelength used = 550 nm.

Compound	Φ_F	τ_T [μs]	Φ_T	Φ_{IC}	Φ_d [$\times 10^{-5}$]	Φ_Δ	S_Δ
3a	0.16	150	0.78	0.06	1.31	0.72	0.92
5a	0.10	220	0.85	0.05	3.35	0.78	0.92

Lifetimes of fluorescence (τ_F) were calculated from the radiative lifetime using the Strickler–Berg equation and fluorescence quantum yields. Using this equation, a good correlation was[34] found for the experimentally determined fluorescence lifetimes and the theoretically determined lifetimes for the unaggregated molecules as is the case in this work. Thus we believe that the values obtained using this equation are a good measure of fluorescence lifetimes. The τ_F value for **3a** was larger than that of complex **5a** in DMSO, Table 4. The natural radiative lifetime (τ_0) for **3a** was lower than that of complex **5a** in DMSO, Table 4. The rate constant value for fluorescence (k_F) of **3a** was larger than complex **5a** in DMSO, Table 4. The heavy atom effect due to the chlorine substituent in **5a** discussed above, will affect both the fluorescence lifetime and rate constant for this complex, hence a lower τ_F is observed for **5a** compared to **3a**. Complex **3a** showed a lower rate constant (k_{IC}) but showed approximately the same quantum yields for internal conversion (Φ_{IC}) in DMSO when compared to complex **5a**, Tables 3 and 4. In addition, complex **3a** showed a lower rate constant for intersystem crossing (k_{ISC}) when compared to complex **5a** in DMSO, Table 4.

Triplet Lifetimes and Quantum Yields

The transient spectrum of complex **3a** in DMSO is shown in Figure 4, and shows a maximum at 550 nm; hence the triplet lifetimes and yields were determined at this wavelength for complexes **3a** and **5a**. Figure 5 shows the triplet decay curves of the complexes (using complex **3a** in DMSO as an example). Complexes **3a** and **5a** showed typical triplet lifetimes (τ_T) values for metallophthalocyanines. The triplet lifetime (τ_T) value of complex **5a** was higher than complex **3a** in DMSO, Table 3. This suggests that the triplet state of complex **3a** is quenched more efficiently than that of **5a**.

Table 4. Rate constants for various excited state deactivation processes of complexes **3a** and **5a** in DMSO.

Compound	τ_F[a] [ns]	τ_0[b] [ns]	k_F[c] [s^{-1}, $\times 10^8$]	k_{ISC}[d] [s^{-1}, $\times 10^8$]	k_{IC}[e] [s^{-1}, $\times 10^7$]	k_d[f] [s^{-1}, $\times 10^{-2}$]
3a	1.39	8.71	1.15	5.61	4.31	8.70
5a	1.01	10.12	0.98	8.41	4.95	15.22

[a] Fluorescence lifetime. [b] Natural radiative lifetime. [c] Rate constant for fluorescence. Values calculated using $k_F = \Phi_F/\tau_F$. [d] Rate constant for intersystem crossing. Values calculated using $k_{ISC} = \Phi_T/\tau_F$. [e] Rate constant for internal conversion. Values calculated using $k_{IC} = \Phi_{IC}/\tau_F$. [f] Rate constant for photodegredation. Values calculated using $k_d = \Phi_d/\tau_T$.

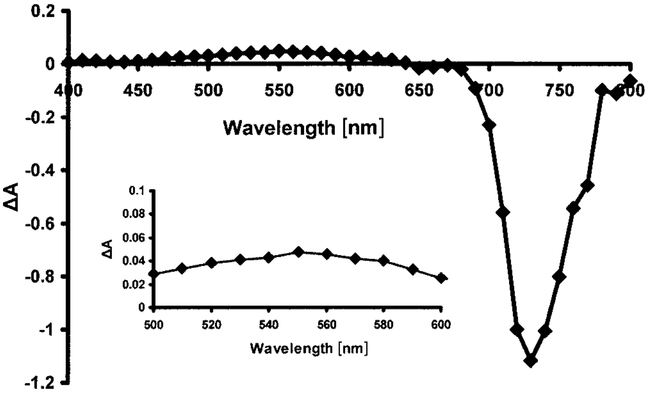


Figure 4. Transient differential spectrum of complex **3a** in DMSO. Excitation wavelength = 714 nm.

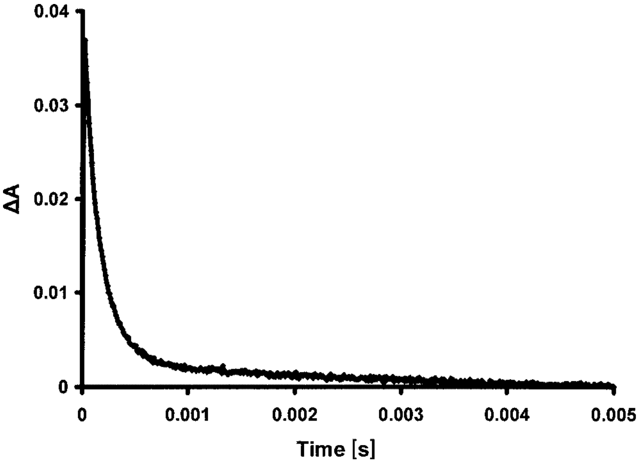


Figure 5. Triplet decay curve of **3a** in DMSO. Excitation wavelength = 714 nm.

The triplet quantum yields (Φ_T) for substituted complexes **3a** and **5a** in DMSO were higher relative to typical[35] metallophthalocyanines in DMSO. For example, ZnPc standard gave Φ_T value of 0.65[36] when compared to 0.78 and 0.85 obtained in this work. Complex **5a** showed a larger Φ_T value when compared to complex **3a** in DMSO, Table 3.

Singlet Oxygen Quantum Yields

Singlet oxygen quantum yields (Φ_Δ) were determined in DMSO using a chemical method [1,3-diphenylisobenzofuran (DPBF)].[37] The disappearance of DPBF was monitored using UV/Vis spectrophotometry. Many factors are responsible for the magnitude of the determined quantum yield of singlet oxygen, including triplet excited 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 determinations, Figure 6, confirming that complexes are not degraded during singlet oxygen studies. The Φ_Δ value of complex **3a** was lower when compared to complex **5a** in DMSO, Table 3. The magnitude of S_Δ (= Φ_Δ/Φ_T) represents the efficiency of quenching of the triplet excited state by ground state (triplet) oxygen. Complexes **3a** and **5a** showed S_Δ of near unity (Table 3), suggesting efficient quenching of the triplet state by triplet molecular oxygen.

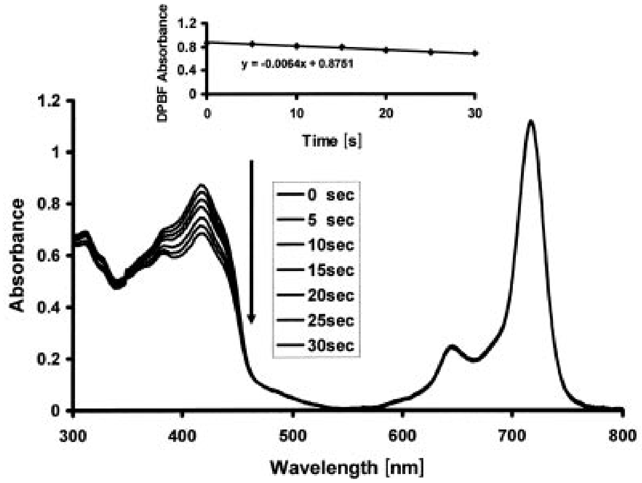


Figure 6. A typical spectrum for the determination of singlet oxygen quantum yield. This determination was for compound **5a** in DMSO at a concentration of 3×10^{-5} mol dm^{-3}.

Photodegradation Studies

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 photocatalysts. The collapse of the absorption spectra without any distortion of the shape confirms clean photodegradation not associated with phototransformation. The spectral changes observed for complexes **3a** and **5a** during irradiation are as shown in Figure 7 (using complex **3a** as an example in DMSO) and hence confirm that photodegradation occurred without phototransformation to new species which absorb in the Q band region. Table 3 shows that complex **3a** was more stable to degradation compared to complex **5a** in DMSO. The rate constant for photodegradation (k_d) of complex **3a** was also lower than that for complex **5a** in DMSO (Table 4).

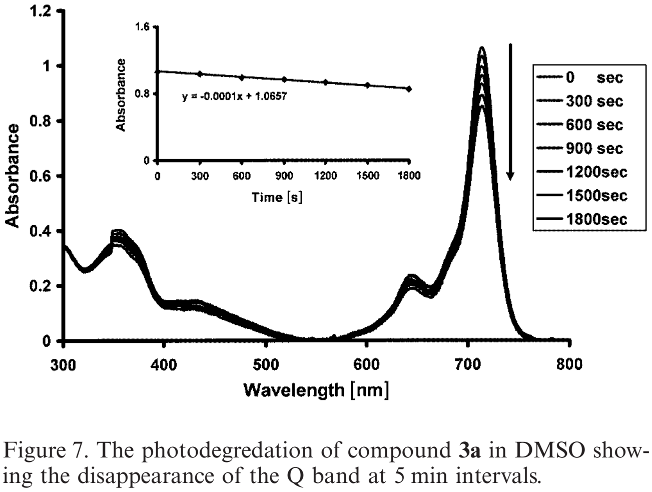


Figure 7. The photodegredation of compound **3a** in DMSO showing the disappearance of the Q band at 5 min intervals.

Fluorescence Quenching Studies by Benzoquinone

In the presence of benzoquinone (BQ) quencher, a reaction takes place between the excited oxotitanium phthalocyanine complexes and the BQ molecules. The fluorescence quenching of oxotitanium phthalocyanine complexes **3a** and **5a** by BQ in DMSO was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Figure 8 shows the quenching of complex **3a** and BQ in DMSO as an example. This figure shows the quenching behaviour of oxotitanium phthalocyanine complexes **3a** and **5a** typical of the nonaggregated complexes. The slope of the plots shown in Figure 9 gave K_{SV} values. The K_{SV} values for the BQ quenching of oxotitanium phthalocyanine complexes are listed in Table 5 in DMSO. The K_{SV} value of complex **3a** was marginally lower than complex **5a** in DMSO. The bimolecular quenching constant (k_q) value of complex **3a** was also lower than complex **5a** in DMSO. Values of k_q near 10^{10} $\text{M}^{-1}\,\text{s}^{-1}$ are in agreement with the theoretical Smoluchowski–Stokes-Einstein approximation at 298 K.[38]

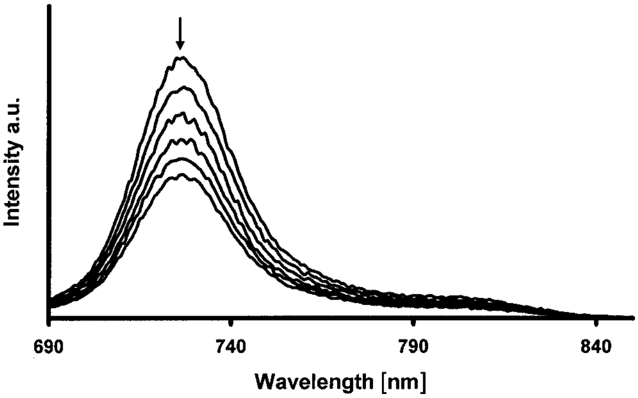


Figure 8. Fluorescence emission spectral changes of **3a** (1.12×10^{-5} mol dm^{-3}) on addition of different concentrations of BQ in DMSO. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 mol dm^{-3}. Excitation wavelength = 680 nm.

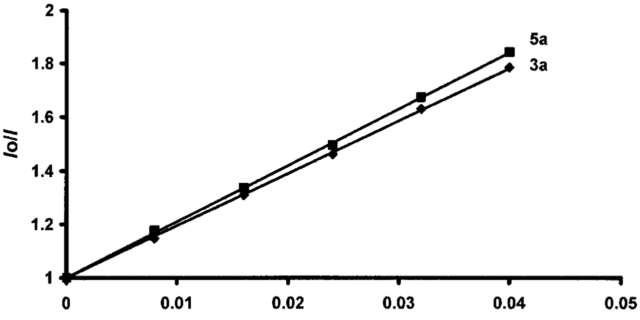


Figure 9. Stern–Volmer plots for BQ quenching of **3a** and **5a**. [MPc] ca. 1.20×10^{-5} mol dm^{-3} in DMSO. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 mol dm^{-3}. Excitation wavelength = 680 nm.

Table 5. Fluorescence quenching data for complexes **3a** and **5a** in DMSO.

Compound	K_{SV} [M^{-1}]	k_q [dm^3 mol^{-1} s^{-1}, $\times 10^{10}$]
3a	19.5	1.4
5a	21.0	2.0

Conclusions

In the present work, the synthesis of new tetra- and chlorotetrathia(polyoxyethylene)-substituted oxotitanium phthalocyanines were described and the compounds were characterized by standard methods (^{1}H and ^{13}C NMR spectroscopy, elemental analysis, IR and UV/Vis spectroscopy and mass spectrometry). The compounds are soluble in most solvents from *n*-hexane to methanol. In solution, the spectra showed monomeric behaviour evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes for **3a** and **5a** in DMSO and the complexes showed charge-transfer bands around 400–500 nm as a shoulder in the UV/Vis spectra. The substituted complexes showed similar and typical fluorescence behaviour in DMSO. The complexes showed higher triplet quantum yields and triplet lifetimes in DMSO than are typical for MPc complexes. Complexes **3a** and **5a** gave high singlet oxygen quantum yields corresponding to high triplet quantum yields. The singlet oxygen quantum yields (Φ_Δ), which give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism), were 0.72 and 0.78 for **3a** and **5a**, respectively. Thus, these complexes show potential as Type II photosensitizers. The stability order among the substituted complexes was **3a** > **5a** in DMSO. The substituted complexes showed similar K_{sv} and k_q values.

Experimental Section

Materials: All solvents were purified as described in Perrin and Armarego.[39] 1,3-Bis[2-(2-ethoxyethoxy)ethoxy]-2-propane-2-thiol (**1**),[40] 4-nitrophthalonitrile (**2**),[41] 4-{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)ethoxymethyl]ethylsulfanyl phthalonitrile (**3**),[42] 1,2-dichloro-4,5-dicyanobenzene (**4**)[16] and, 4-chloro-5-{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)ethoxymethyl]-ethylsulfanyl}phthalonitrile (**5**)[42] were prepared according to the reported procedures. Zinc phthalocyanine (ZnPc) employed as a standard was obtained from Sigma–Aldrich. All other reagents and solvents were of reagent grade quality and obtained from commercial suppliers.

Equipment: Elemental analyses were obtained from Carlo Erba 1106 Instrument. Infrared spectra were recorded with a Bio-Rad FTS 175C FTIR spectrophotometer. Absorption spectra in the UV/Vis region were recorded with an Shimadzu 2001 UV Pc spectrophotometer and a Varian 500 UV/Vis/NIR spectrophotometer. Fluorescence excitation and emission spectra were recorded with a Varian Eclipse spectrofluorometer using 1-cm pathlength cuvettes at room temperature. Mass spectra were recorded with a Thermo LCQ DECA XP-Max spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions with a Varian 500 MHz spectrometer. Photoirradiations were performed 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 infrared radiations. An interference filter (Intor, 700 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. Triplet absorption and decay kinetics were recorded with a laser flash photolysis system, the excitation pulses were produced by a Quanta-Ray Nd: YAG laser providing 400 mJ, 90 ns pulses of laser light at 10 Hz, pumping a Lambda-Physik FL3002 dye (Pyridine 1 dye in methanol). Single pulse energy was 2 mJ. The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as a detector. Signals were recorded with a two-channel digital real-time oscilloscope (Tektronix TDS 360); the kinetic curves were averaged over 256 laser pulses. Solutions for these studies were degassed with nitrogen for at least 30 min before recording the spectra.

Photophysical and Photochemical Parameters – Fluorescence Quantum Yields and Lifetimes: Fluorescence quantum yields (Φ_F) were determined by the comparative method outlined in Equation (1):[34,43]

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

where F and F_{Std} are the areas under the fluorescence curves of samples **3a** or **5a** and the standard, respectively. A and A_{Std} are the respective absorbances of the sample and standard at the excitation wavelengths (which was ca. 0.05), and η and η_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc in DMSO ($\Phi_F = 0.18$)[44] was employed as the standard.

Natural radiative lifetimes (τ_0) were determined using PhotochemCAD Program[45] which uses the Strickler–Berg equation.[46] From τ_0 values, fluorescence lifetimes (τ_F) were determined using Equation (2).

$$\Phi_F = \frac{\tau_F}{\tau_0} \qquad (2)$$

Triplet Quantum Yields and Lifetimes: The deaerated solutions of the respective tetra-substituted oxotitanium phthalocyanine complexes **3a** and **5a** were introduced into a 1-cm pathlength spectrophotometric cell and irradiated at the Q band maxima with the laser system described above. Triplet quantum yields (Φ_T) were determined by a comparative method using triplet decay,[47] Equation (3):

$$\Phi_T^{\mathrm{Sample}} = \Phi_T^{\mathrm{Std}}\,\frac{\Delta A_T^{\mathrm{Sample}} \cdot \varepsilon_T^{\mathrm{Std}}}{\Delta A_T^{\mathrm{Std}} \cdot \varepsilon_T^{\mathrm{Sample}}} \qquad (3)$$

where $\Delta A_T^{\mathrm{Sample}}$ and $\Delta A_T^{\mathrm{Std}}$ are the changes in the triplet state absorbances of samples **3a** or **5a** and the standard, respectively. $\varepsilon_T^{\mathrm{Sample}}$ and $\varepsilon_T^{\mathrm{Std}}$, the triplet state extinction coefficients for samples **3a** and **5a**, and the standard, respectively. The standard employed was zinc phthalocyanine (ZnPc) in DMSO. The triplet quantum yield is $\Phi_T^{\mathrm{Std}} = 0.65$ for ZnPc[36] in DMSO.

Quantum yields of internal conversion (Φ_{IC}) were obtained from Equation (4), which assumes that only three processes (fluorescence, intersystem crossing and internal conversion) jointly deactivate the excited singlet state of tetra-substituted oxotitanium phthalocyanine complexes.

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T) \qquad (4)$$

Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 7.5 software.

Singlet Oxygen and Photodegradation Quantum Yields: Singlet oxygen (Φ_Δ) and photodegradation (Φ_d) quantum yield determinations were carried out using the experimental setup described above.[47–49] Typically, a 2 mL portion of the respective tetra-substituted oxotitanium phthalocyanine **3a** or **5a** solutions (absorbance ca. 1 at the irradiation wavelength) containing the singlet oxygen quencher was irradiated in the Q band region with the photoirradiation setup described in refs.[47–49] Values of Φ_Δ were determined in air using the relative method with 1,3-diphenylisobenzofuran (DPBF) as singlet oxygen chemical quencher in DMSO [Equation (5)]:

$$\Phi_\Delta = \Phi_\Delta^{\mathrm{Std}}\,\frac{R \cdot I_{\mathrm{abs}}^{\mathrm{Std}}}{R^{\mathrm{Std}} \cdot I_{\mathrm{abs}}} \qquad (5)$$

where $\Phi_\Delta^{\mathrm{Std}}$ is the singlet oxygen quantum yield for the standard ZnPc ($\Phi_\Delta^{\mathrm{Std}} = 0.67$ in DMSO,[50] R and R^{Std} are the DPBF photobleaching rates in the presence of respective samples **3a** or **5a**, and the standard, respectively. I_{abs} and $I_{\mathrm{abs}}^{\mathrm{Std}}$ are the rates of light absorption by samples **3a** or **5a** and the standard, respectively. The concentrations of DPBF in the solutions were calculated using the determined values of log $\varepsilon = 4.36$ at 417 nm (DPBF in DMSO). The light intensity used for Φ_Δ determinations was found to be 9.51×10^{15} photons s^{-1} cm^{-2}.

Photodegradation quantum yields were determined using Equation (6):

$$\Phi_d = \frac{(C_0 - C_t) \cdot V \cdot N_A}{I_{\mathrm{abs}} \cdot S \cdot t} \qquad (6)$$

where C_0 and C_t are the concentrations of samples **3a** or **5a** before and after irradiation, respectively, V is the reaction volume, N_A is Avogadro's constant, S is the irradiated cell area and t is the irradiation time. I_{abs} is the overlap integral of the radiation source light intensity and the absorption of samples **3a** or **5a**. A light intensity of 3.17×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

Fluorescence Quenching by BQ: Fluorescence quenching experiments on oxotitanium phthalocyanine complexes **3a** and **5a** were carried out (in air, without degassing) by the addition of different concentrations of BQ to a fixed concentration of the complex, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032, 0.040 and 0.048 mol dm^{-3}. The fluorescence spectra of oxotitanium phthalocyanine complexes **3a** and **5a** at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern–Volmer (S–V) equation [Equation (7)]:[46]

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \tag{7}$$

where I_0 and I are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively. $[Q]$ 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 [Equation (8)].

$$K_{SV} = k_q{\cdot}\tau_F \tag{8}$$

The ratios $\frac{I_0}{I}$ were calculated and plotted against [BQ] according to Equation (7), and K_{SV} was determined from the slope.

Synthesis

Tetrakis{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)ethoxymethyl]ethylsulfanylphthalocyaninato}titanium(IV) Oxide (3a): Under an argon atmosphere, **3** (0.326, 0.7 mmol), urea (18 mg, 0.3 mmol) and three drops of DBU (1,8-diazabicyclo[5.4.0] undec-7-ene) were mixed in *n*-pentanol (3 mL) and heated to 120 °C. At that temperature, $Ti(OBu)_4$ (0.3 mL, 3 mmol) was added, and the reaction mixture was heated at reflux for 6 h at 155 °C. After cooling to room temperature, the mixture was poured into 100 mL hexane and precipitated. The crude product was collected by centrifugation and dried in vacuo. The obtained mixture of metallated and metal-free phthalocyanine was purified by column chromatography on silica gel. Elution with CH_2Cl_2/methanol (50:1) gave the metal-free Pc. The main product, oxotitanium Pc, was obtained by changing the eluent to CH_2Cl_2/methanol (20:1). Yield: 18 mg (11%). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.10 (t, J = 7.1 Hz, 24 H, CH_3), 3.39 (m, 4 H, CH), 3.50–3.80 (m, 80 H, CH_2), 3.95 (m, 16 H, CH_2), 8.20–8.38 (br. m, 4 H, CH_{ar}), 8.85–9.40 (br. m, 8 H, CH_{ar}) ppm. ^{13}C NMR (500 MHz, $CDCl_3$, 25 °C, decoupled): δ = 15.42 (CH_3), 48.75 (CH), 66.88 (CH_2), 70.14 (CH_2), 70.86–71.31 (CH_2), 123.27 (CH_{ar}), 124.32 (CH_{ar}), 125.28 (CH_{ar}), 132.94 (C_{ar}), 134.96 (C_{ar}), 137.62 (C_{ar}), 140.87 (C_{ar}), 151.43 (C_{ar} *C*=N) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3040, 2980–2850, 1600, 1529, 1450, 1400, 1381, 1350, 1310, 1260, 1240, 1120–1080, 959, 880 cm^{-1}. MS (ESI): *m*/*z* (%) = 1930(100) $[M + 1]^+$. $C_{92}H_{136}N_8TiO_{25}S_4$ (1929): calcd. C 57.20, H 7.10, N 5.81; found C 57.35, H 7.05, N 5.53.

Tetrakis(2,9,16,23-{2-[2-(2-ethoxyethoxy)ethoxy]-1-[2-(2-ethoxyethoxy)ethoxymethyl]ethylsulfanyl}-3,10,17,24-chlorophthalocyaninato)titanium(IV) Oxide (5a): Compound **5** (640 mg, 1.27 mmol), urea (36 mg, 0.6 mmol) and three drops of DBU were mixed in *n*-pentanol (5 mL) and heated at 120 °C. At that temperature, $Ti(OBu)_4$ (0.6 mL, 6 mmol) was added, and the reaction mixture was heated at reflux for 6 h at 155 °C. The *n*-pentanol was removed under reduced pressure, and the crude green product was purified by column chromatography (silica gel, CH_2Cl_2/methanol, 30:1) and the metallated and metal-free phthalocyanine were obtained from the crude product. Furthermore, the oxotitanium Pc was purified with preparative TLC (silica gel) using CH_2Cl_2/MeOH (30:1). Yield: 50 mg (9%). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.15 (t, J = 7.2 Hz, 24 H, CH_3), 3.20–3.88 (m, 84 H, CH, CH_2), 4.12 (m, 16 H, CH_2), 8.80–9.56 (br. m, 8 H, CH_{ar}) ppm. ^{13}C NMR (500 MHz, $CDCl_3$, 25 °C, decoupled): δ = 15.44 (CH_3), 49.15 (CH), 66.82 (CH_2), 70.08 (CH_2), 70.93–71.34 (CH_2), 123.27 (CH_{ar}), 125.32 (CH_{ar}), 126.38 (C_{ar}), 134.16 (C_{ar}), 135.86 (C_{ar}), 137.17 (C_{ar}), 141.53 (C_{ar}), 151.00 (C_{ar} *C*=N) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3040, 2980–2850, 1600, 1450, 1410, 1380, 1340, 1280, 1240, 1120–1080, 960, 880 cm^{-1}. MS (ESI): *m*/*z* (%) = 2067 (100) $[M + 1]^+$. $C_{92}Cl_4H_{132}N_8TiO_{25}S_4$ (2066): calcd. C 53.43, H 6.43, N 5.42; found C 53.80, H 6.22, N 5.60.

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