

The synthesis and photophysical properties of low-symmetry zinc phthalocyanine analogues

Wadzanai Chidawanyika, Tebello Nyokong*

Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

ARTICLE INFO

Article history:

Received 22 April 2009

Received in revised form 8 June 2009

Accepted 12 June 2009

Available online 25 June 2009

Keywords:

Zinc phthalocyanine

Fluorescence

Triplet yield

Singlet oxygen

Photodegradation

ABSTRACT

The synthesis of a low-symmetry derivative, zinc mono-carboxy substituted phthalocyanine, ZnPc-COOH (**4**) has been reported. The photochemical and photophysical properties of ZnPc-COOH (**4**), ZnTMPyPc (**5**), ZnttbPc (**6**) and a previously synthesized low-symmetry derivative, ZnttbIPc (**7**), in various organic solvents are reported. The red-shifting of the spectra of **4** and **5** (relative to that of unsubstituted zinc phthalocyanine, ZnPc) is a function of the electron-donating sulfur-containing substituents attached to the periphery of the molecule. High triplet quantum yields (Φ_T) generally occur in response to substitution on the zinc phthalocyanine ring periphery. The highest Φ_T values and triplet lifetimes (τ_T) occur in DMSO for all derivatives as a result of the solvent's high viscosity. The strongly electron-withdrawing imido fused ring of ZnttbIPc (**7**) stabilizes it against photo-oxidative degradation relative to the other derivatives.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

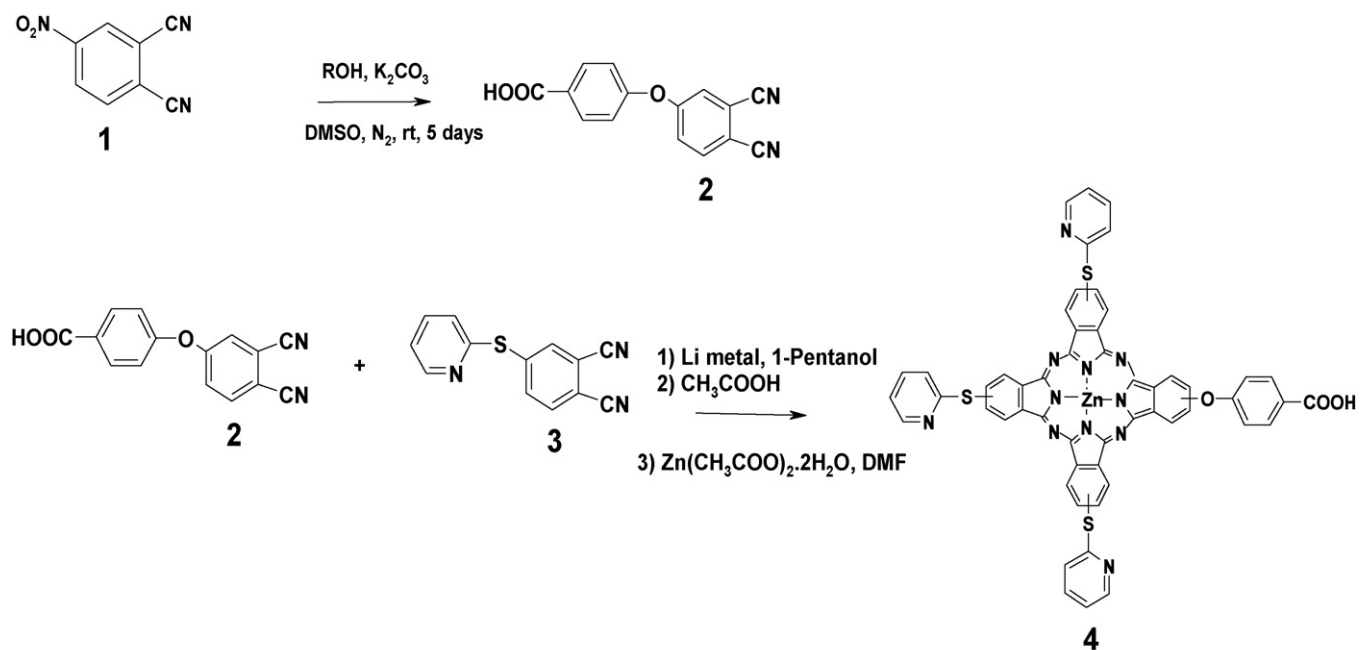
Until recently phthalocyanine research has been centered mainly on the development of symmetrical derivatives substituted either with four or eight substituent groups [1–3]. However, at times such high symmetry derivatives present limitations for various purposes. Low-symmetry or monosubstituted phthalocyanine derivatives [4] allow for the fine-tuning of many physical properties responsible for enhancing technological applications of phthalocyanines and have thus become of increasing interest in fields such as non-linear optics [5], photodynamic therapy (PDT) of cancer [6,7] and in the development of ordered phthalocyanine Langmuir–Blodgett thin films [8]. Of particular importance are derivatives bearing one reactive electrophilic or nucleophilic substituent [9]. For PDT applications, phthalocyanines tend to show poor selectivity for tumours. This may be overcome by incorporating a substituent group (such as carboxyl, sulfo or amino group) capable of covalently binding the molecule to a suitable carrier, e.g. antibodies or lipoproteins, which directs the sensitizer to the tumour without affecting the normal surrounding tissue [10]. Several approaches exist to obtain such monofunc-

tional phthalocyanines, i.e. statistical condensation employing two different phthalonitriles [4,11,12], ring opening of a subphthalocyanine [13–16] or reaction of a polymer-bonded phthalonitrile with differently substituted dicarbonitriles in solution followed by cleavage of the formed phthalocyanine [17,18]. Statistical condensation was employed in this work to synthesize tris{9 (10), 16 (17), 23 (24)-4-(2-mercaptopyridine)-2-(4-carboxyphenoxy)phthalocyaninato}zinc(II)-(ZnPc-COOH, **4**) (Scheme 1).

The molecule contains one COOH group and the rest of the molecule is substituted with quaternizable groups, i.e. 2-mercaptopyridine. The photophysical properties of this complex are reported in this work together with those of the corresponding symmetrical analogue, tetrakis{2,(3)-(2-mercaptopyridine)phthalocyaninato}zinc(II) (ZnTMPyPc, **5**) whose synthesis has been reported before [19]. Also reported here for the first time are the spectroscopic and photophysical properties (in various solvents) of a previously synthesized unsymmetrically substituted molecule tris{9 (10), 16 (17), 23 (24)-[*tert*-butyl]imidophthalocyaninato}zinc(II) (ZnttbIPc, **7**) [20] and of its tetra-substituted derivative tetrakis{2,(3)-(tert-butyl)phthalocyaninato}zinc(II) (ZnttbPc, **6**), whose synthesis has been reported previously [21]. The results are compared with those of unsubstituted zinc phthalocyanine (ZnPc) to ascertain the effect of lowering in symmetry and/or change in substitution pattern. Medicinal applications, such as PDT, often require the use of biocompatible and diamagnetic metals therefore zinc has been used as the central metal for this.

* Corresponding author at: Department of Chemistry, Rhodes University, P.O. Box 94, Grahamstown 6140, South Africa. Tel.: +27 46 6038260; fax: +27 46 6225109.

E-mail address: t.nyokong@ru.ac.za (T. Nyokong).



Scheme 1. Synthesis of ZnPc-COOH (4).

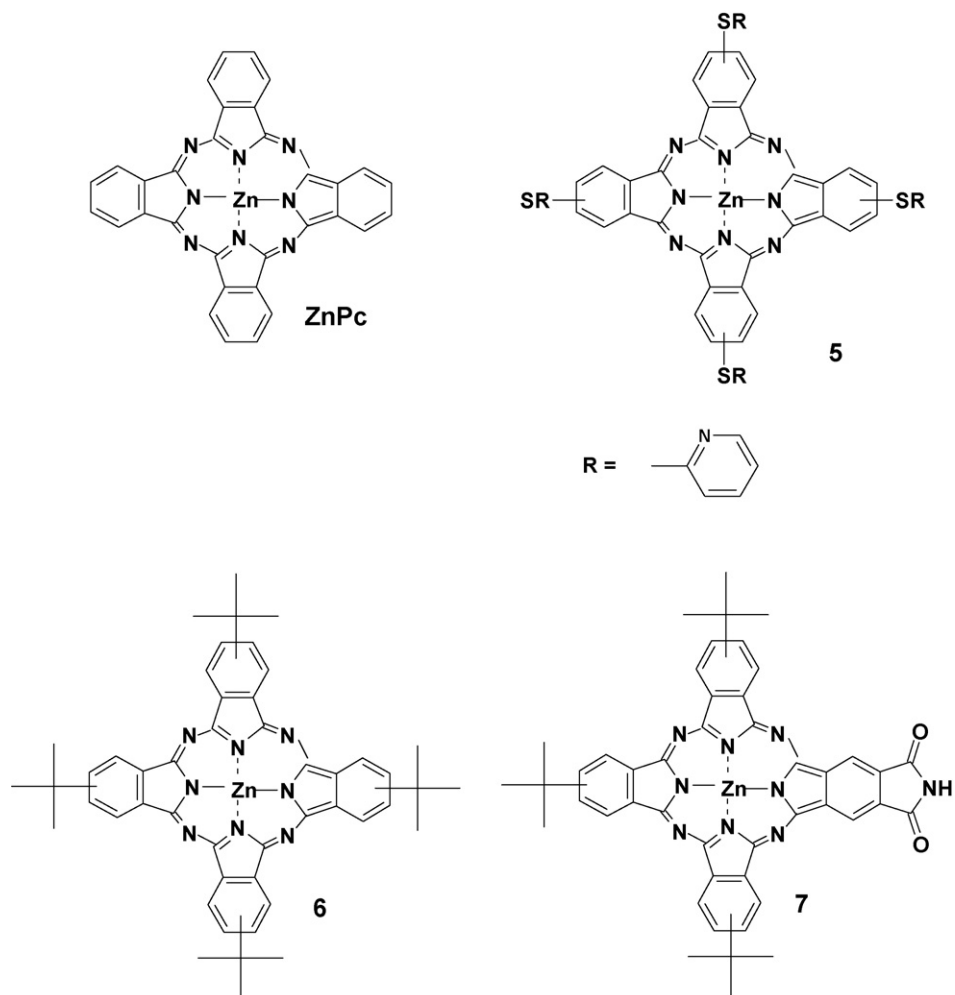


Fig. 1. Molecular structure of ZnPc, ZnTMPyPc (5), ZnttbPc (6) and ZnttbIPc (7).

2. Experimental

2.1. Materials

Acetone, chloroform (CHCl₃), dichloromethane (DCM), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), methanol (MeOH), pyridine, tetrahydrofuran (THF) and toluene were dried prior to use. 4-Hydroxybenzoic acid, potassium carbonate, diphenylisobenzofuran (DPBF), deuterated dimethylsulfoxide (DMSO-d₆), 2-mercaptopyridine, potassium bromide (KBr) and Triton X-100 were purchased from Aldrich. Zinc phthalocyanine was synthesized following literature methods [22]. ZnPc is also available commercially (Aldrich). Silica gel 60 (0.063–0.200 mm) was used for column chromatography.

2.2. Instrumentation

FT-IR spectra (KBr pellets) were recorded on a Perkin-Elmer spectrum 2000 FT-IR spectrometer. UV–vis (ultraviolet-visible) spectra were recorded on a Cary 500 UV/Vis/NIR spectrophotometer and fluorescence emission and excitation spectra on Varian Eclipse spectrofluorimeter. ¹H NMR spectra were obtained, in deuterated solvents, using a Bruker EMX 400 MHz NMR spectrometer. Elemental analyses were carried out at Rhodes University using a Vario Elementar EL111 Series. MALDI-TOF mass spectrometry was carried out at the University of Stellenbosch using an ABI Voyager DE-STR MALDI TOF instrument.

Photo-irradiations for photodegradation or singlet oxygen determinations 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 MAX 5100 (Molelectron detector incorporated) power meter and found to be 9.74×10^{16} photons s⁻¹ for photodegradation and 2.97×10^{16} photons s⁻¹ for singlet oxygen studies.

A laser flash photolysis system was used for the determination of triplet absorption and decay kinetics. The excitation pulses were produced by a Quanta-Ray Nd:YAG laser (1.5 J/90 ns), pumping a Lambda Physik FL 3002 dye laser (Pyridin 1 in methanol). The analyzing beam source was from a Thermo Oriol 66902 xenon arc lamp, and a Kratos Lis Projekte MLIS-X3 photomultiplier tube was used as the detector. Signals were recorded with a two-channel digital real-time oscilloscope (Tektronix TDS 360); the kinetic curves were averaged over 256 laser pulses. Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 7.5 software.

2.3. Syntheses and characterization

The syntheses and characterization of ZnTMPyPc (**5**) [19], ZnttbPc (**7**) [20] and ZnttbPc (**6**) [21], Fig. 1, have been reported elsewhere. The syntheses of 4-nitrophthalonitrile (**1**) [23,24] and 4-(2-mercaptopyridine)phthalonitrile (**3**) [25] were carried out according to previously reported methods.

2.3.1. 4-(3,4-Dicyanophenoxy)benzoic acid, (**2**)

To dry DMSO (30 ml) under nitrogen, 3.5 g (25 mmol) of K₂CO₃ was added. 4-Hydroxybenzoic acid (2.36 g, 17.1 mmol) and 4-nitrophthalonitrile (**1**) (2.0 g, 11.5 mmol) were added to the suspension. After 4 and 24 h, more K₂CO₃ (3.5 g, 25 mmol) was added to the mixture. The mixture was stirred at room temperature for 5 days, following which the formed precipitate was then dissolved in water (600 ml), and the pH of the solution adjusted to 1 by addition of HCl to give a beige coloured product. Yield: 3.10 g, 69%. IR [(KBr)

$\nu_{\max}/\text{cm}^{-1}$]: 3088 ($\nu_{\text{C-H}}$), 2231 ($\nu_{\text{C}\equiv\text{N}}$), 1678, 1591 ($\nu_{\text{C=O}}$), 1491, 1254 ($\nu_{\text{C-O-C}}$), 851 ($\nu_{\text{C-H}}$). ¹H NMR (400 MHz, DMSO-d₆) δ /ppm: 13.09 (1H, s, -COOH), 8.13 (1H, d, 6'-H), 8.03 (2H, m, 3,5-H), 7.89 (1H, d, 3'-H), 7.58 (1H, dd, 5'-H), 7.29 (2H, m, 2,6-H).

2.3.2. Tris(9 (10), 16 (17), 23 (24)-4-(2-mercaptopyridine)-2-(4-carboxyphenoxy)phthalocyaninato}zinc(II) (ZnPc-COOH, **4**)

Phthalonitriles **2** (1.80 mmol) and **3** (5.40 mmol) were suspended in 25 ml of dry 1-pentanol and heated at 140 °C, under nitrogen gas. At this temperature, 250 mg (35 mmol) of lithium metal was added and the solution stirred for 15 min. On cooling to room temperature glacial acetic acid (50 ml) was added and the resulting precipitate centrifuged and washed several times with water. The product at this stage is the metal free substituted derivative. To give the metallated derivative the above product was heated at 80 °C in DMF (30 ml) for 5 h in the presence of excess zinc(II) acetate dihydrate. The DMF solution was evaporated to dryness and the solid residue washed with water. The product was dissolved in a minimum amount of DMF and chromatographed on a silica gel Si60 column with diethyl ether/DMF (9:1) eluent, initially and gradually increasing to 100% DMF at which point the second desired fraction was collected. Further chromatographic separations with CHCl₃/MeOH (9:1) were conducted several times with the second fraction containing the desired product **4**.

Yield: 0.40 g (21%). UV–vis (DMSO) λ_{\max}/nm (log ϵ): 366 (4.85), 619 (5.61), 687 (5.41). IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3437 (s, $\nu_{\text{O-H}}$), 1676 (m, $\nu_{\text{C=O}}$), 1573 (s, $\nu_{\text{C=C}}$), 1096 (m, $\nu_{\text{C-O-C}}$), 682, 617 (m, $\nu_{\text{C-S-C}}$). ¹H NMR (400 MHz, DMSO-d₆) δ /ppm: 9.00–8.70 (m, 8H, ring-H), 8.59–8.49 (d, 4H, ring-H), 8.28–8.12 (m, 4H, Ar-H), 7.82–7.70 (m, 4H, Ar-H), 7.52–7.41 (m, 4H, Ar-H), 7.29–7.17 (m, 4H, Ar-H). Anal. Calcd. for C₅₄H₂₉N₁₁O₃S₃Zn: C, 62.28; H, 2.81; N, 14.79; S, 9.24. Found: C, 62.24; H, 3.49; N, 14.79; S, 9.79. MALDI-TOF MS m/z : Calcd: 1041.4 amu. Found: (M+1) 1042.5 amu.

2.4. Photochemical and photophysical parameters

2.4.1. Fluorescence quantum yields

Fluorescence quantum yields (Φ_{F}) were determined by the comparative method [26] (Eq. (1)),

$$\Phi_{\text{F}} = \Phi_{\text{F(Std)}} \frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n_{\text{Std}}^2} \quad (1)$$

where F and F_{Std} are the areas under the fluorescence curves of the MPc and the reference, respectively. A and A_{Std} are the absorbances of the sample and reference at the excitation wavelength, respectively, and n and n_{Std} are the refractive indices of solvents used for the sample and reference, respectively. Chlorophyll a in ether ($\Phi_{\text{F}} = 0.32$ [27]) was employed as a reference. Both the sample and reference were excited at the same wavelength (610 nm). The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

2.4.2. Triplet quantum yields and lifetimes

For triplet determinations, de-aerated solutions of the respective MPc complexes were introduced into a 1 cm pathlength spectrophotometric cell and irradiated at the Q-band with the laser system described above. Triplet quantum yields (Φ_{T}) of the MPc complexes were determined by the triplet absorption method. A comparative method, based on triplet decay [28] using ZnPc as standard, was employed for the calculations, Eq. (2).

$$\Phi_{\text{T}} = \Phi_{\text{T}^{\text{Std}}} \cdot \frac{\Delta A_{\text{T}} \cdot \epsilon_{\text{T}}^{\text{Std}}}{\Delta A_{\text{T}}^{\text{Std}} \cdot \epsilon_{\text{T}}} \quad (2)$$

where ΔA_T and ΔA_T^{Std} are the changes in the triplet state absorbances of the MPC derivative and the standard, respectively; ε_T and $\varepsilon_T^{\text{Std}}$, the triplet state molar extinction coefficients for the MPC derivative and the standard, respectively; Φ_T^{Std} , the triplet quantum yield for the standard ($\Phi_T^{\text{Std}} = 0.65$ for ZnPc in DMSO [28], 0.58 for ZnPc in DMF [29] and 0.65 for ZnPc in toluene [30]).

Quantum yields of internal conversion (Φ_{IC}) were obtained from Eq. (3), which assumes that only three intrinsic processes (fluorescence, intersystem crossing and internal conversion); jointly deactivate the excited singlet state of an MPC molecule.

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T) \quad (3)$$

The fraction of the excited triplet state quenched by ground state molecular oxygen S_Δ was calculated using Eq. (4):

$$S_\Delta = \frac{\Phi_\Delta}{\Phi_T} \quad (4)$$

2.4.3. Singlet oxygen quantum yields

Singlet oxygen quantum yield values (Φ_Δ) were determined in air using the relative method with DPBF acting as a singlet oxygen chemical quencher in DMSO, using Eq. (5):

$$\Phi_\Delta = \Phi_\Delta^{\text{Std}} \frac{R \cdot I_{\text{abs}}^{\text{Std}}}{R^{\text{Std}} \cdot I_{\text{abs}}} \quad (5)$$

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard ZnPc ($\Phi_\Delta^{\text{Std}} = 0.56$ in DMF [31], 0.67 in DMSO [32], 0.53 in THF [33] and 0.58 in toluene [34]); R and R^{Std} are the DPBF photobleaching rates in the presence of MPC derivative and standard, respectively; I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the MPC and standard, respectively. The concentration of DPBF was lowered to $\sim 3 \times 10^{-5} \text{ mol dm}^{-3}$ for all solutions, to avoid chain reactions [31]. DPBF degradation was monitored at $\sim 417 \text{ nm}$.

2.4.4. Photodegradation quantum yields

Eq. (6) was employed for the determination of photodegradation quantum yields:

$$\Phi_{\text{Pd}} = \frac{(C_0 - C_t) V N_A}{I_{\text{abs}} S t} \quad (6)$$

where C_0 and C_t (mol dm^{-3}) are the respective MPC derivative's concentrations before and after irradiation, respectively; V is the reaction volume; N_A the Avogadro's number; S the irradiated cell area (2.0 cm^2); t the irradiation time (in s) and I_{abs} , the overlap integral of the radiation source intensity and the absorption of the MPC.

3. Results and discussion

3.1. Syntheses and characterizations

The procedure used to obtain 4-alkoxy substituted phthalonitriles is well known in the literature [23,24] and a similar synthetic route was used for the preparation of phthalonitriles **2** and **3** with yields higher than 65% [9,23,25]. Using the statistical condensation approach, 4-(3,4-dicyanophenoxy)benzoic acid (**2**) and 4-(2-mercaptopyridine) phthalonitrile (**3**) were reacted in a 3:1 molar ratio, in the presence of 1-pentanol and lithium metal, to give the metal free substituted phthalocyanine which was reacted with an excess of zinc acetate to afford the desired low-symmetry derivative (**4**). Purification of the crude product was done by column chromatography. Characterization techniques used include IR, UV-vis, ^1H NMR and mass spectra, and elemental analyses, giving data that is in accordance with the predicted structure of

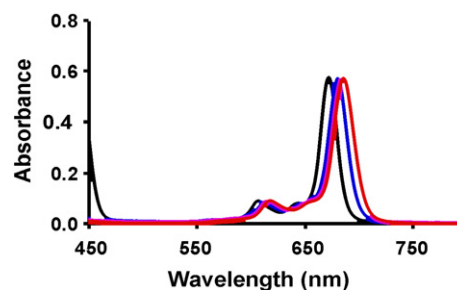


Fig. 2. Normalized ground state electronic absorption spectra of ZnPc (—) in CHCl_3 , ZnTMPyPc (**5**) (—) in THF (concentration = $1.31 \times 10^{-5} \text{ mol dm}^{-3}$), ZnPc-COOH (**4**) (—) in THF (concentration = $1.31 \times 10^{-5} \text{ mol dm}^{-3}$), ZnPc-COOH (**4**) (—) in CHCl_3 (concentration = $4.74 \times 10^{-6} \text{ mol dm}^{-3}$).

the molecule. The ^1H NMR spectrum of **4** shows the eight non-peripheral protons as a poorly resolved multiplet between 8.70 and 9.00 ppm. The peripheral ring protons are found between 8.49 and 8.59 ppm and are followed by a series of aromatic protons pertaining to the 2-mercaptopyridine and carboxyphenoxy groups. The terminal proton of the carboxyl group is often difficult to observe, as in this case which accounts for its absence in the ^1H NMR spectrum. The IR spectra show the $\text{C}=\text{O}$ (at 1676 cm^{-1}) and $\text{C}-\text{S}-\text{C}$ (at 617 cm^{-1}) vibrations. The $\text{C}-\text{O}-\text{C}$ vibration was also observed at 1096 cm^{-1} .

3.2. Ground state electronic absorption spectra and fluorescence spectra

Solvent studies reveal that all phthalocyanine derivatives, **4**, **5**, **6** and **7** show good solubility in most organic solvents, and in particular those selected for this study, namely CHCl_3 , DCM, DMF, DMSO and THF. Complexes **6** and **7** also show solubility in toluene. The ground state electronic absorption spectrum corresponding to **4** in CHCl_3 is shown in Fig. 2 and indicates a slightly broadened but typical monomeric phthalocyanine spectra with no splitting of the Q-band [9,35,36]. Table 1 shows that complexes **4** and **5** have the same Q-band maximum (considering the same solvent), the presence of one extra sulfur does not result in red-shifting in **5** compared to **4**. The use of electron-donating sulfur substituents is largely responsible for the red-shifted spectra of **4** and **5** (relative to ZnPc) (Fig. 2 and Table 1) as sulfur donates electron density to the phthalocyanine ring, resulting in an extension of the ring π -conjugation. In DCM, **4** shows broadening associated with aggregation, Fig. 3. The addition of a surfactant, Triton X-100, to the DCM solution of **4** results in disaggregation to give a slightly blue shifted monomeric peak.

Of note, with regard to compound **4**, is its unsplit Q-band in all solvents used for this study (similar to that of the symmetrical analogue **5**). The spectrum of low-symmetry derivatives is often characterized by a split in the main phthalocyanine Q-band due to transitions to non-degenerate orbitals. However, only slight

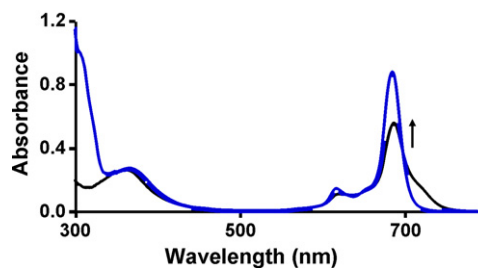


Fig. 3. Electronic absorption spectrum of ZnPc-COOH (**4**) in DCM (i) in the absence of Triton X-100 (—) (concentration = $4.41 \times 10^{-6} \text{ mol dm}^{-3}$) and (ii) in the presence of Triton X-100 (—).

Table 1Solvent properties, absorption, fluorescence emission and excitation spectral data for **4**, **5**, **6**, **7** and **ZnPc** in various solvents.

Solvent	Dielectric constant, ^a ϵ_T	Viscosity, ^a η	MPC	Q-band, λ_{\max}/nm	Log ϵ	Emission, ^c λ_{\max}/nm	Excitation, λ_{\max}/nm	Stoke's shift/nm
Toluene	2.38	1.097	ZnPc	672	5.25	675	672	3
			4	^b	^b	^b	^b	^b
			5	^b	^b	^b	^b	^b
			6	677	4.95	683	678	6
			7	708, 668	4.92, 4.79	719	709, 667	11
CHCl ₃	4.81	1.438	ZnPc	673	^b	680	673	7
			4	686	5.43	696	686	10
			5	686	4.97	694	686	8
			6	678	4.99	687	679	9
			7	715, 668	4.90, 4.67	728	717, 668	13
THF	7.58	1.406	ZnPc	668	5.48	672	668	4
			4	681	5.06	691	682	10
			5	680	5.10	689	680	9
			6	671	5.44	679	672	8
			7	701, 661	4.96, 4.82	711	703, 662	10
DCM	8.93	1.4969	ZnPc	671	^b	681	671	10
			4	685	5.10	694	683	9
			5	686	4.84	694	684	8
			6	677	5.03	685	677	8
			7	712, 667	4.85, 4.70	725	713, 668	13
DMF	36.71	1.430	ZnPc	670	5.37	676	670	6
			4	683	5.45	695	685	12
			5	684	5.06	694	684	10
			6	674	5.42	684	674	10
			7	707, 665	4.90, 4.80	721	712, 666	14
DMSO	46.45	1.479	ZnPc	672	5.38	682	672	10
			4	687	5.41	700	687	13
			5	687	5.02	698	686	11
			6	678	5.44	687	678	9
			7	708, 668	4.90, 4.81	721	713, 667	13

^a Reproduced from Ref. [38].^b Values undetermined due to limited solubility.^c Excitation at 610 nm for MPC complexes.

broadening is observed for **4**, suggesting only a slight lowering of the symmetry.

Compound **7**, however shows a spectrum more typical of a low-symmetry derivative, i.e. a lowering in the symmetry of the phthalocyanine molecule (from ZnttbPc-*D*_{4h} to ZnttbIPc-*C*_{2v}) is accompanied by a split in the phthalocyanine Q-band giving rise to a Q_x and Q_y band at 715 and 668 nm, respectively in CHCl₃ (Fig. 4) as a result of two separate transitions from the highest occupied molecular orbital (HOMO; a_{1u}) to the lowest unoccupied molecular orbitals (LUMO; e_{gx}^{*} and e_{gy}^{*}) [20]. The terminal fused imido-ring may have resulted in the red-shifting of the main Q-band at 715 nm compared to the Q-band position of symmetrical tetra *tert*-butyl substituted ZnttbPc (**6**). Solvents of different polarity have been found to affect the position, shape and intensity of absorption bands [37]. In chlorinated solvents such as CHCl₃ and DCM the Q-band exists at slightly longer wavelengths for **7**. Often

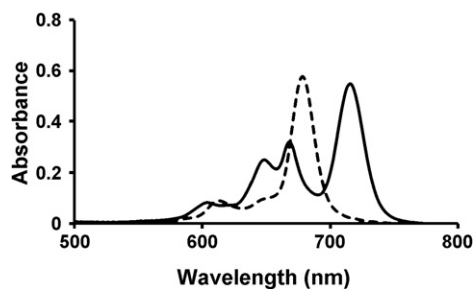


Fig. 4. Ground state electronic absorption spectra of ZnttbPc (**6**) (---) in CHCl₃ (concentration = 7.38×10^{-6} mol dm⁻³) and ZnttbIPc (**7**) (—) in the Q-band region in CHCl₃ (concentration = 6.90×10^{-6} mol dm⁻³).

such a bathochromic shift is a function of an increase in solvent polarity; however this then brings to question the behaviour in DMF and DMSO, which are solvents of even higher polarity (Table 1) and are expected to have longer wavelength absorption bands. The low absorption coefficients of **7** (versus those of **6**) as listed in Table 1 may be of concern; however it has been found in earlier literature that the absorption coefficients of Q-bands tend to decrease with a decrease in molecular symmetry [14].

The emission and excitation spectra of **4**, **5** and **6** are typical of metal phthalocyanine complexes where the excitation spectra are identical to absorption and emission spectra are mirror images of the absorption spectra. For **7**, there is a lack of mirror symmetry in the absorption and fluorescence emission spectra in all solvents; although the excitation spectra are similar to the absorption. A single red-shifted monomeric peak as shown in Fig. 5 characterizes the emission spectrum of **7**. This is because fluorescence occurs from the lowest energy vibrational band (ν_0) of S₁ (i.e. a transition

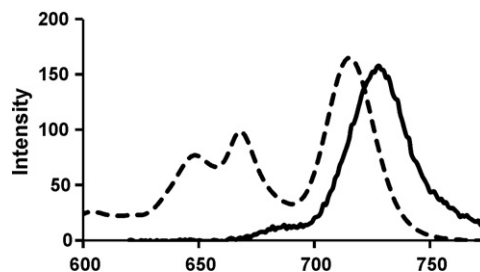


Fig. 5. Electronic absorption (---) and fluorescence emission (—) spectra of ZnttbIPc (**7**) in CHCl₃ (concentration of **7** = $\sim 5.19 \times 10^{-6}$ mol dm⁻³). Excitation wavelength = 610 nm.

from one energy level rather than two as is the case for the absorption of **7**). The emission is thus of lower energy than the absorption band, i.e. the short-lived excited singlet state (S_1) relaxes to a lower energy conformation before it emits [38]. Stokes shifts are small as is typical of MPc complexes, Table 1.

3.3. Photophysical studies

3.3.1. Fluorescence quantum yields

The fluorescence quantum yields (Φ_F) of low-symmetry **4** are higher than for symmetrical **5** in both DMF and DMSO (Table 2). This is reversed for **6** and **7**, where the low-symmetry derivative (**7**) is less fluorescent than the symmetrical (**6**) compound in toluene, DMF and DMSO.

With respect to the low-symmetry derivatives, compound **4** is more fluorescent than **7** in DMF and DMSO (Table 2). A comparison of the symmetrical analogues, **5** and **6** reveals that the sulfur-containing derivative **5** has about the same Φ_F as **6**.

A higher fluorescence yield is obtained for ZnPc in all solvents in comparison to the substituted derivatives **4**, **5**, **6** and **7**, thus it is possible that the substituents on the ring periphery deactivate fluorescence more effectively via intersystem crossing to the triplet state. The data for **7** does not vary significantly, with a change in solvent, although the yields are considerably low compared to the other complexes. The low fluorescence quantum yields for **7** could be a result of intramolecular quenching of the excited singlet state by the amino group [39,40]. The low solvent viscosity of toluene can be used to account for the low Φ_F values obtained for **6** and **7** in this solvent relative to data obtained in higher viscosity solvents such as DMF and DMSO. There is increased possibility of deactivation of the excited state by radiationless transitions such as internal conversion (IC) in low viscosity solvents [34].

3.3.2. Triplet quantum yields and lifetimes

The determination of the triplet quantum yields (Φ_T) and triplet lifetimes (τ_T) is based on the maximum triplet state absorption that occurs between 500 and 600 nm. This absorption is in response to the transition from the lowest triplet state (T_1) to higher triplet states (T_n) of the MPc molecule [41]. Transient absorption curves can be obtained for the various complexes by using argon degassed solutions and exciting at the Q-band maximum wavelength. The point of maximum triplet absorption is determined using a plot similar to that of **7** in toluene (Fig. 6). The maxima for the complexes studied ranged between 490 and 545 nm. Φ_T values provide a measure of the fraction of absorbing molecules that undergo inter-

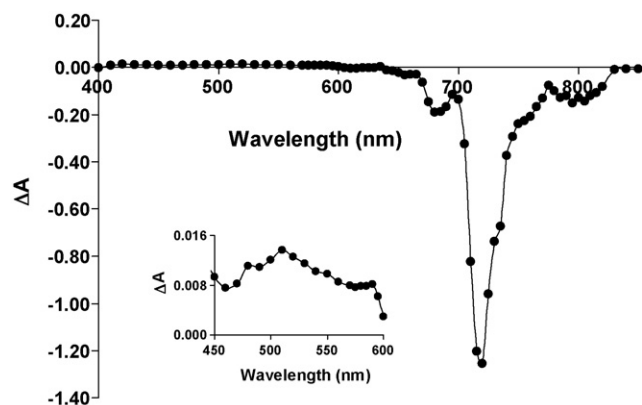


Fig. 6. Transient absorption spectrum of ZnTtpPc (**7**) in toluene (concentration = 1.80×10^{-5} mol dm $^{-3}$) (insert = magnified triplet absorption between 450 and 600 nm).

system crossing (ISC) to the triplet state. The data pertaining to all the compounds, including ZnPc is listed in Table 2. ZnPc shows the lowest triplet quantum yields in DMF and DMSO, which is in good agreement with the highest Φ_F values obtained in these solvents. However, in toluene, the triplet quantum yield of ZnPc is higher than that of **6** and **7**, suggesting that there is less efficient population of the triplet state in toluene due to energy loss via internal conversion as shown by the high internal conversion quantum yields (Φ_{IC}) (Table 2). The triplet lifetimes corresponding to the complexes are listed in Tables 2 and 3 and ranged between 3 and 350 μ s in all solvents. For most solvents (except for DMF and DMSO, Table 3), **6** tends to spend the least time in the triplet states. These low lifetimes may be in response to the presence of numerous C–H bonds which cause extensive C–H vibrations and thus gives rise to increased internal conversion (IC) and a subsequent decrease in the triplet lifetime. This has been referred to in literature as the “loose bolt effect” [42]. In general, ring substituents reduce the lifetime of the molecules in the triplet state, since there is a reduction in lifetime in going from an unsubstituted molecule, i.e. ZnPc to the peripherally ring substituted derivatives **4**, **5**, **6** and **7** in toluene, CHCl $_3$, THF, DMF and DMSO. This is as a result of the presence of heavy atoms (heavy atom effect) within the modified phthalocyanine structure. For all complexes, the highest lifetimes occur in DMSO. MPc molecules tend to spend more time in the triplet state in highly viscous solvents such as DMSO. In such solvents non-radiative transitions, i.e. vibrational relax-

Table 2
Photophysical parameters of **4**, **5**, **6**, **7** and ZnPc in toluene, DMF and DMSO.

Solvent	MPc	Φ_F	Φ_T	Φ_{IC}	Φ_{Δ}	S_{Δ}	τ_T (μ s)
Toluene	ZnPc	0.13	0.65 [30]	0.22	0.58 [34]	0.89	340 [45]
	4	^a	^a	^a	^a	^a	^a
	5	^a	^a	^a	^a	^a	^a
	6	0.081	0.40	0.52	0.54	1.35	4
	7	0.049	0.41	0.54	0.51	1.24	6 ^b
DMF	ZnPc	0.30	0.58 [29]	0.12	0.56 [31]	0.96	330 [46]
	4	0.25	0.68	0.07	0.63	0.93	8
	5	0.19	0.74	0.07	0.40	0.54	4 ^b
	6	0.23	0.71	0.06	0.46	0.65	20 ^b
	7	0.084	0.77	0.15	0.45	0.58	70
DMSO	ZnPc	0.17	0.65 [28]	0.18	0.67 [32]	1.03	350 [46]
	4	0.16	0.82	0.02	0.64	0.78	230
	5	0.10	0.73	0.17	0.48	0.66	160
	6	0.14	0.73	0.13	0.55	0.75	200
	7	0.097	0.82	0.08	0.59	0.72	180

^a Values undetermined due to limited solubility.

^b Lifetime determined by second order kinetics.

ation, become deactivated thus giving rise to longer-lived triplet states.

3.3.3. Singlet oxygen quantum yields (Φ_{Δ})

The cytotoxic species, singlet dioxygen ($^1\text{O}_2$; $^1\Delta_g$) is believed to be the product of an energy transfer process from the triplet excited state of a metallated phthalocyanine molecule ($^3\text{MPC}^*$) to triplet ground state dioxygen ($^3\text{O}_2$; $^3\Sigma_g^-$). Initially, during photosensitization, the MPC molecule is excited to the singlet state and then forms the triplet state via intersystem crossing (a non-radiative process). Using UV–vis spectroscopy, the absorption decay of a singlet oxygen quencher, 1,3-diphenylisobenzofuran (DPBF), was monitored (at ~ 417 nm) over a period of time and the values of singlet oxygen generated determined using Eq. (5). The data was collected for all complexes **4**, **5**, **6** and **7** in the organic solvents CHCl_3 , DMF, DMSO, THF and in toluene (the latter for **6** and **7** only). The data for ZnPc has also been included for comparative purposes. The lack of suitable reference standard inhibited determination in DCM. No photobleaching effects were observed during the determinations for all compounds in the Q-band region. The singlet oxygen yields for **4** in DMSO, DMF and THF are similar (0.64, 0.63 and 0.62, respectively). Although lower singlet oxygen quantum yields prevail for **5**, similarly there is not much variation in the same solvents (0.48, 0.40 and 0.47, for DMSO, DMF/ CHCl_3 and THF, respectively) (Table 3). In the case of **6** and **7**, the highest yields occur in DMSO, with the lowest values occurring in DMF for both compounds. There is not much variation in the Φ_{Δ} values generated by the two compounds (**6** and **7**) in each solvent. In THF, DMSO and DMF, compound **4** generates more singlet oxygen than the other complexes (Table 3) suggesting that the effect of the substituents attached to **5**, **6** and **7** have a quenching effect on its singlet oxygen production capa-

bilities. Overall there is efficient generation of singlet oxygen as reflected by the S_{Δ} values in Table 2. In most solvents, the values obtained are close to unity (with the exception of **5**, **6** and **7** in DMF and **5** in DMSO) indicating efficient quenching of the triplet excited state by triplet oxygen to produce singlet oxygen. In some cases the S_{Δ} values are slightly larger than 1, but are acceptable within experimental error.

3.3.4. Photodegradation quantum yields

Photobleaching studies are often conducted to establish the stability of phthalocyanine molecules on exposure to intense light and hence determine their efficacy for application in various fields. Oxidative attack of the molecule by singlet oxygen is often responsible for the light-induced degradation process, which is characterized by a decrease in absorption intensity in the Q- and B-band regions without a concomitant shift in position or emergence of new peaks in the visible region. Earlier studies [39,43] have found that electron-withdrawing substituents, such as the terminal carboxyl group on ZnPc-COOH (**4**) and the imido fused ring of ZnttblPc (**7**), should stabilize the phthalocyanine ring against oxidative attack as such groups make the phthalocyanine entity more resistant to oxidative degradation. This is generally reflected in the data listed in Table 3, which reflects data within the range expected of stable phthalocyanines. Direct comparison reveals that **7** exhibits greater stability in all solvents relative to **6**. It may thus be concluded that the terminal fused imido portion has a more profound shielding effect thus resulting in lower photobleaching quantum yields. Although **4** and **5** are generally less stable than **7**, they exhibit greater stability when compared with ZnPc in THF and DMSO. The lack of substituents on the ZnPc molecule leaves it open to oxidative degradation and accounts for its much lower stability. The oxidizing properties of chlorinated solvents such as CHCl_3 and DCM are expected to enhance photodegradation quantum yields in these solvents (lowest stability). This holds true in the case of CHCl_3 . However in DCM complexes **4**, **5** and **7** are more stable than in less oxidizing solvents such as DMF, which often protect against oxidative attack [44]. This feature may be related to the phthalocyanine molecular structure and the resultant solvating effects of the solvents. For **4** this may be a response to the aggregating tendencies discussed earlier.

4. Conclusions

A low-symmetry derivative tris{9 (10), 16 (17), 23 (24)-4-(2-mercaptopyridine)-2-(4-carboxyphenoxy)phthalocyaninato} zinc(II) (ZnPc-COOH, **4**) has been successfully synthesized by the statistical condensation approach. Triplet quantum yields (Φ_T) have been determined and comparisons have been made with those of an unsubstituted derivative-ZnPc. The effect of substitution is a general increase in the Φ_T values (in DMSO and DMF) and a concomitant decrease in the triplet lifetimes (τ_T). A lowering in molecular symmetry (**5** to **4** and **6** to **7**) results in high triplet yields and long lived triplet states in DMSO. The strong electron-withdrawing effects of the fused imido-ring of **7** has been used to account for the greater photostability (low Φ_{Pd}) of this complex. The newly synthesized low-symmetry derivative **4** and the previously developed compound **7**, thus show good photosensitizing properties which may make them useful in medicinal (PDT) and industrial (catalysis) applications.

Acknowledgements

This work has been supported by the Department of Science and Technology (DST) and National Research Foundation (NRF), South Africa through DST/NRF Chairs Initiative for Professor of Medicinal

Table 3
Photochemical parameters of **4**, **5**, **6**, **7** and ZnPc.

Solvent	MPC	$\Phi_{Pd}/10^5$	Φ_{Δ}	$\tau_T/\mu\text{s}$
Toluene	ZnPc	0.19	0.58 [34]	340 [45]
	4	^a	^a	^a
	5	^a	^a	^a
	6	21.4	0.54	4
	7	0.19	0.51	6 ^c
CHCl_3	ZnPc	^a	0.57	10 ^c
	4	8.37	0.49	5 ^c
	5	3.99	0.40	6 ^c
	6	1350	0.51	5 ^c
	7	2.49	0.57	8
THF	ZnPc	3.05	0.53 [33]	230 [46]
	4	0.27	0.62	5 ^c
	5	0.036	0.47	10 ^c
	6	0.17	0.53	3 ^c
	7	0.051	0.51	10
DCM	ZnPc	^a	^b	7 ^c
	4	0.17	^b	10
	5	1.67	^b	9 ^c
	6	89.96	^b	6 ^c
	7	0.64	^b	70
DMF	ZnPc	2.35	0.56 [31]	330 [46]
	4	6.93	0.63	8 ^c
	5	6.26	0.40	4 ^c
	6	4.68	0.46	20 ^c
	7	1.65	0.45	70
DMSO	ZnPc	2.38	0.67 [32]	350 [46]
	4	0.11	0.64	230
	5	0.31	0.48	160
	6	0.40	0.62	200
	7	0.066	0.59	180

^a Values undetermined due to limited solubility.

^b Values undetermined due to lack of a reference standard.

^c Lifetimes determined by second order kinetics.

Chemistry and Nanotechnology and Rhodes University. WC thank the Andrew Mellon Foundation and NRF for scholarships.

References

- [1] C.C. Leznoff, A.B.P. Lever, Phthalocyanines, Properties and Applications, vol. 1, VCH Publishers, New York, 1989;
- [2] C.C. Leznoff, A.B.P. Lever, Phthalocyanines, Properties and Applications, vol. 2, VCH Publishers, New York, 1993;
- [3] C.C. Leznoff, A.B.P. Lever, Phthalocyanines, Properties and Applications, vol. 3, VCH Publishers, New York, 1993.
- [4] P. Tau, T. Nyokong, J. Porphyr. Phthalocya. 10 (2006) 1040.
- [5] M. Durmus, T. Nyokong, Polyhedron 26 (2007) 3323.
- [6] M.S. Rodríguez-Morgade, G. de la Torre, T. Torres, in: K.M. Kadish, K.M. Smith, R. Guillard (Eds.), The Porphyrin Handbook, vol. 15, Academic Press, New York, 2003 (Chapter 99).
- [7] D.A. Li, M.A. Ratner, T.J. Marks, J. Am. Chem. Soc. 110 (1988) 1707.
- [8] I. Rosenthal, Photochem. Photobiol. 53 (1991) 859.
- [9] T.J. Dougherty, Photochem. Photobiol. 58 (1993) 895.
- [10] M.J. Cook, R. Hersans, J. McMurdo, D.A. Russell, J. Mater. Chem. 6 (1996) 149.
- [11] H. Kliesch, A. Weitemeyer, S. Muller, D. Wöhrle, Liebigs Ann. 7 (1995) 1269.
- [12] J. Morgan, H. Lottman, C.C. Abbou, D.K. Chopin, Photochem. Photobiol. 60 (1994) 486.
- [13] C.C. Leznoff, C.R. McArthur, Y. Qin, Can. J. Chem. 71 (1995) 1319.
- [14] S.V. Kudrevich, H. Ali, J.E. van Lier, J. Chem. Soc. Perkin Trans. 1 (1994) 2767.
- [15] M. Geyer, F. Plenzig, J. Rauschnabel, M. Hanack, B. del Rey, A. Sastre, T. Torres, Synthesis (1996) 1139.
- [16] N. Kobayashi, R. Kondo, S. Nakajima, T. Osa, J. Am. Chem. Soc. 112 (1990) 9640.
- [17] S. Dabak, A. Gul, O. Bekaroglu, Chem. Ber. 127 (1994) 2009.
- [18] A. Weitemeyer, H. Kliesch, D. Wöhrle, J. Org. Chem. 60 (1995) 4900.
- [19] C.C. Leznoff, T.W. Hall, Tetrahedron Lett. 23 (1982) 3023.
- [20] C.C. Leznoff, P. Snirskaya, B. Khouw, R.L. Cerny, P. Seymour, A.B.P. Lever, J. Org. Chem. 56 (1991) 82.
- [21] S. Moeno, T. Nyokong, J. Photochem. Photobiol. A: Chem. 201 (2009) 228.
- [22] W. Chidawanyika, J. Mack, S. Shimizu, N. Kobayashi, T. Nyokong, J. Porphyr. Phthalocya., in press.
- [23] J. Metz, O. Schneider, M. Hanack, Inorg. Chem. 23 (1984) 1065.
- [24] H. Tomada, S. Saito, S. Shiraishi, Chem. Lett. 12 (1983) 313.
- [25] T.M. Keller, T.R. Price, J.R. Griffith, Synthesis 74 (1980) 613.
- [26] W.M. Sharman, J.E. van Lier, in: K.M. Kadish, K.M. Smith, R. Guillard (Eds.), The Porphyrin Handbook, vol. 15, Academic Press, New York, 2003 (Chapter 97).
- [27] N. Sehlotho, M. Durmus, V. Ahsen, T. Nyokong, Inorg. Chem. Commun. 11 (2008) 479.
- [28] S. Frey-Forgues, D. Lavabre, J. Chem. Educ. 76 (1999) 1260.
- [29] J. Fu, X.Y. Li, D.K.P. Ng, C. Wu, Langmuir 18 (2002) 3843.
- [30] T.H. Tran-Thi, C. Desforge, C. Thiec, J. Phys. Chem. 93 (1989) 1226.
- [31] J. Kossanyi, D. Chahraoui, Int. J. Photoenergy 2 (2000) 9.
- [32] S.M. Bishop, A. Beeby, A.W. Parker, M.S.C. Foley, D. Phillips, J. Photochem. Photobiol. A: Chem. 90 (1995) 39.
- [33] W. Spiller, H. Kliesch, D. Wöhrle, S. Hackbarth, B. Roder, G. Schnurpfeil, J. Porphyr. Phthalocya. 2 (1998) 145.
- [34] N. Kuznetsova, N. Gretsova, E. Kalmykova, E. Makarova, S. Dashkevich, V. Negrimovskii, O. Kaliya, E. Lukyanets, Russ. J. Gen. Chem. 70 (2000) 133.
- [35] L. Kaestner, M. Cesson, K. Kassab, T. Christensen, P.D. Edminson, M.J. Cook, I. Chambrier, G. Jori, Photochem. Photobiol. Sci. 2 (2003) 131.
- [36] A. Ogunsipe, D. Maree, T. Nyokong, J. Mol. Struct. 650 (2003) 131.
- [37] J. Chen, N. Chen, J. Huang, J. Wang, M. Huang, Inorg. Chem. Commun. 9 (2006) 313.
- [38] A. Hirth, A.K. Sobbi, D. Wöhrle, J. Porphyr. Phthalocya. 1 (1997) 275.
- [39] C. Reichardt, in: H.F. Ebel (Ed.), Solvents and Solvent Effects in Organic Chemistry, VCH, Germany, 1988.
- [40] R. Bonnett, in: David Phillips (Ed.), Chemical Aspects of Photodynamic Therapy, Gordon and Breach Science, Canada, 2000.
- [41] S. Maree, T. Nyokong, J. Porphyr. Phthalocya. 5 (2001) 782.
- [42] A.K. Sobbi, D. Wöhrle, D. Schlettwein, J. Chem. Soc. Perkin Trans. 2 (1993) 481.
- [43] T. Nyokong, J. Porphyr. Phthalocya. 12 (2008) 1005.
- [44] J. Turro, Modern Molecular Photochemistry, The Benjamin/Cummings Publishing Co. Inc., New York, 1978.
- [45] H. Xu, T. Shen, O. Zhou, S. Shen, J. Liu, L. Li, S. Zhou, X. Zhang, Q. Yu, Z. Bi, X. Xias, J. Photochem. Photobiol. A: Chem. 65 (1992) 267.
- [46] G. Winter, H. Heckmann, P. Haisch, W. Eberhardt, M. Hanack, L. Luer, H.-J. Egelhaaf, D. Oelkrug, J. Am. Chem. Soc. 120 (1998) 11663.
- [47] A. Ogunsipe, Photophysical and photochemical studies of non-transition metal phthalocyanine derivatives, Ph.D. Thesis, 2004.
- [48] A. Ogunsipe, J.-Y. Chen, T. Nyokong, New. J. Chem. 28 (2004) 822.