

The photochemistry and photophysics of a series of alpha octa(alkyl-substituted) silicon, zinc and palladium phthalocyanines

Cite this: *Photochem. Photobiol. Sci.*, 2014, **13**, 62

Magda van Leeuwen,^a Andrew Beeby,^b Isabelle Fernandes^a and Stephen H. Ashworth^{*a}

Photophysical and photochemical measurements have been made on a series of novel alpha octa(alkyl-substituted) silicon, zinc and palladium phthalocyanines for which the synthesis is outlined. Fluorescence quantum yields and lifetimes, triplet quantum yields and lifetimes and singlet delta oxygen quantum yields were measured in 1% v/v pyridine in toluene. The effects of varying central atom and addition of alkyl substituents relative to unsubstituted parent molecules, zinc phthalocyanine (ZnPc) and silicon phthalocyanine (SiPc), are discussed. All phthalocyanines studied exhibit absorption and emission maxima in the region of 680–750 nm with molar absorptivity of the Q-band $\sim 10^5 \text{ M}^{-1} \text{ cm}^{-1}$. The series of compounds also exhibited triplet quantum yields of 0.65–0.95 and singlet oxygen quantum yields of 0.49–0.93.

Received 8th July 2013,
Accepted 25th October 2013

DOI: 10.1039/c3pp50219h

www.rsc.org/pps

Introduction

Phthalocyanines and metallophthalocyanines are large macrocyclic molecules consisting of four modified pyrrole units, similar in structure to the naturally occurring porphyrins. Originally of interest in the dyes and pigments industries due to the bright blue colour exhibited, research now has a stronger focus on the unique photochemical and photophysical properties of these compounds. Current research is primarily concerned with the application of these molecules in a variety of fields including chemical sensors,^{1,2} catalysts,³ non-linear optics⁴ and as photosensitizers in photodynamic therapy.^{5–7}

Photodynamic therapy, PDT, is the treatment of a variety of cancerous diseases, infections and age-related macular degeneration using light and a photosensitizer.^{8,9} The ideal photosensitizer has preferential absorption by malignant cells and remains dormant until activated by targeted laser light, whereby it reacts with ground state molecular oxygen to generate the highly reactive and toxic singlet delta oxygen species ($^1\Delta \text{O}_2$).^{10,11} The optical window of such treatments is defined by the penetration of light in tissue, with wavelengths between 650 and 800 nm exhibiting maximum penetration. The

success of the technique is largely dependent upon the photosensitizer used. There are a select few compounds, including the drug Photofrin, a hematoporphyrin derivative, that have undergone successful medical trials and been approved for treatment^{12,13} another is PhotoSens.^{14,15} However, a compound that satisfies all desired properties completely has yet to be found. Predominant problems associated with clinically used photosensitizers include a complex synthesis resulting in a compound that comprises a complex mixture of isomers with a limited understanding of the active component of the mixture, followed by poor selectivity and weak extinction coefficients in the optical window.

Phthalocyanines, on the other hand, have great potential as photosensitizers and can be synthesized with a variety of non-metal and metal centres.^{16–19} Such compounds hold great promise due to a straightforward synthesis and high stability under a variety of conditions. Other favourable characteristics include: intense absorbance between 600–750 nm, high molar extinction coefficients, ϵ , of typically $\sim 10^5 \text{ M}^{-1} \text{ cm}^{-1}$,^{20,21} and relatively long triplet lifetimes, 10–100 μs ,²² all ideal properties for candidates of PDT.

A number of systematic steps can be taken to enhance the photophysical and photochemical properties of these molecules including an appropriate selection of the central metal. Metal–ligand spin–orbit coupling²³ is likely to increase the probability of the spin-forbidden transition to the triplet state, a key step in the formation of singlet delta oxygen. In a similar way, if the system allows, axial ligands on a metal centre or alpha (non-peripheral) and beta (peripheral) substituents can

^aSchool of Chemistry, University of East Anglia, Norwich Research Park, Norwich, UK. E-mail: S.Ashworth@uea.ac.uk; Fax: +44 (0)1603 592003; Tel: +44 (0)1603 593031

^bDepartment of Chemistry, Durham University, University Science Laboratories, South Road, Durham, UK. E-mail: Andrew.Beeby@durham.ac.uk; Fax: +44 (0)191 38 44737; Tel: +44 (0)191 33 42023



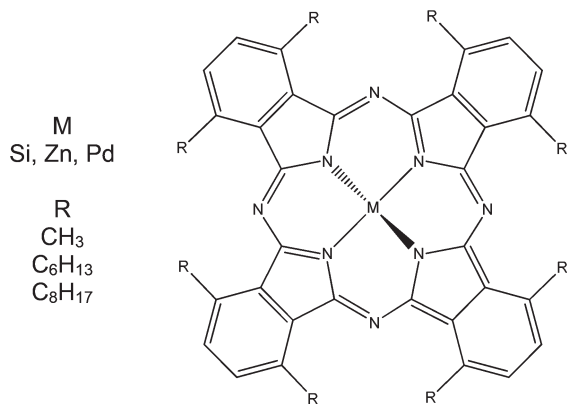


Fig. 1 Molecular structure of alpha-substituted metallophthalocyanines.

be used to fine-tune both the physical and photophysical properties, fluorescence, triplet state characteristics and solubility in a variety of solvents.^{24,25}

A key drawback to phthalocyanines, however, is their insolubility in many solvent systems and a strong propensity towards aggregation.²⁶ Aggregation occurs due to π - π stacking of the molecules and leads to quenching of the excited singlet state, which significantly decreases the yield of triplet state and hence the efficiency of the compound as a photosensitizer.²⁷ One method of minimising this is by the addition of bulky substituents and long chains, which are both known to hinder stacking.²⁸

Herein, we report on a series of alpha-substituted phthalocyanines with varying metal centers that have the potential to serve as photosensitizers. We examined alkyl substituted SiPc, ZnPc and PdPc having eight alpha alkyl groups with chain lengths of 1, 6 and 8, illustrated in Fig. 1, and made comparisons with parent compounds where available. Fluorescence quantum yields, radiative lifetimes, triplet quantum yields, triplet lifetimes and singlet delta oxygen quantum yields, are reported.

Results

Spectroscopic data

The absorption spectra of all compounds exhibit the maximum Q-band in the desired optical range, 650–850 nm, and are typical of other phthalocyanines. All exhibit 2 bands, a broad band (B-bands) at 355 nm and a sharp Q-band in the near-IR. The latter is indicative that no aggregation is occurring in solution. Aggregation results in a mixing of the two bands in the Q-band region due to perturbations of the ground and excited states of the aggregates. For all compounds measured, where a parent compound or relevant data is available, a bathochromic shift of 20–30 nm was observed. This is clearly illustrated in Fig. 2 where spectra of unsubstituted silicon and zinc phthalocyanine are plotted on the same axis as the absorption spectrum of the substituted compounds.

Emission and excitation spectra for the substituted silicon phthalocyanines (1a, 1b) are similar, with maximum emission at 724 nm and maximum absorption at 710 nm: a Stokes shift

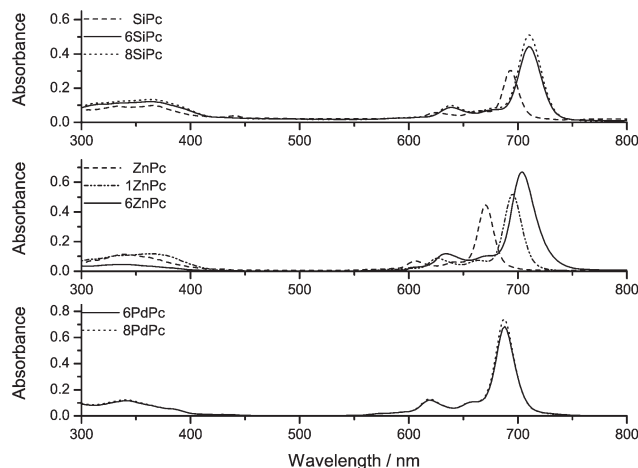


Fig. 2 UV-Vis spectra of the parent compounds, where available, and alpha-substituted compounds.

of 14 nm. This is similar to the previously observed substituted zinc phthalocyanines. However, addition of the methyl group instead of long alkyl chains on the zinc phthalocyanine leads to a smaller Stokes shift of 10 nm, with emission maximum at 704 nm and absorption maximum at 694 nm. Furthermore, no broadening of the emission spectra was observed. No fluorescence was observed for the substituted palladium phthalocyanines.

Photophysics

Fluorescence lifetimes were determined using time-correlated single photon counting. The values obtained can be seen in Table 1. It can be seen that for all compounds measured the lifetimes are relatively short. Alkyl-substituted SiPc exhibit the longest lifetimes at 3.8 ns, and substitution of ZnPc with a methyl group shortens the lifetime from 3.1 ns to 2.5 ns and further to 1.8 ns with addition of long alkyl chains.³¹ An example of a typical decay is given in Fig. 3. Fluorescence quantum yields were determined using the comparative method. The standards used were ZnPc in ethanol ($\Phi_F = 0.28$)³² and ZnPc in toluene ($\Phi_F = 0.2$).³³ The values obtained for the silicon and zinc phthalocyanines were 0.27 and 0.16 respectively and are typical of alpha substituted metallophthalocyanines.¹⁷

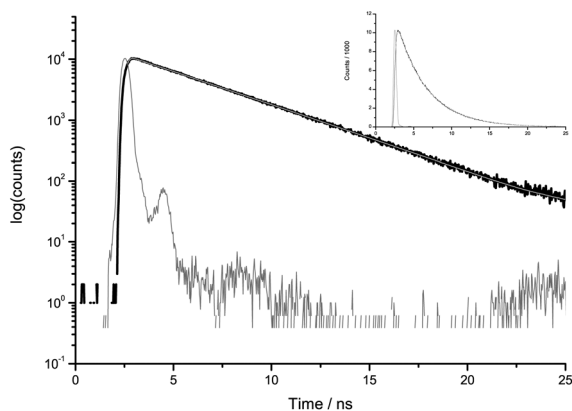
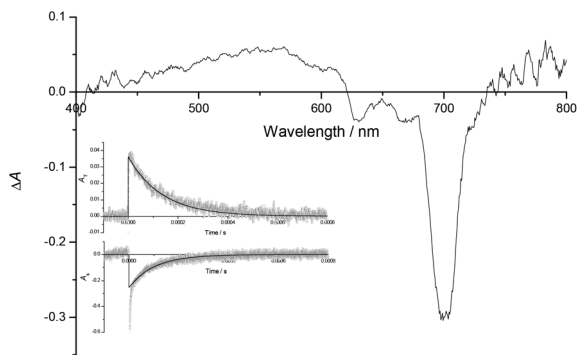
The transient absorption spectra of all compounds were similar in shape and an example is shown in Fig. 4. This transient absorption spectrum is typical of the series and shows a broad absorption peak with a maximum at 534 nm. Triplet lifetimes were determined by fitting an exponential to the decay of transient absorption measured at 530 nm and gave values between 161–196, 113 and 4–5 μ s for SiPc, ZnPc and PdPc compounds respectively. Long triplet lifetimes are typical for silicon phthalocyanines. The triplet extinction coefficients were determined using the expression,

$$\epsilon_T = \epsilon_S \frac{\Delta A_T}{\Delta A_S} \quad (1)$$



Table 1 Photophysical properties of alpha-substituted *n*MPcs

Compound	λ_Q/nm	$\epsilon_S/\text{M}^{-1} \text{cm}^{-1} \times 10^5$	λ_T/nm	τ_T/ns	Φ_F	k_f/s^{-1}
ZnPc ²⁹	671	2.8	676	3.1	0.34	1.1×10^8
1ZnPc	694	2.5 ± 0.2	704	2.5 ± 0.1	0.16 ± 0.02	
6ZnPc	704	1.8 ± 0.2	718	1.8 ± 0.1	0.12 ± 0.02	6.67×10^7
8ZnPc	704	1.8 ± 0.2	718	1.8 ± 0.1	0.12 ± 0.02	6.67×10^7
Si(OH) ₂ Pc	692		702			
6Si(OH) ₂ Pc	710	2.3 ± 0.2	724	3.8 ± 0.1	0.27 ± 0.02	6.32×10^7
8Si(OH) ₂ Pc	710	2.3 ± 0.2	724	3.8 ± 0.1	0.27 ± 0.02	6.32×10^7
PdPc ³⁰	660		664			
6PdPc	688	0.67 ± 0.2	—	—	—	—
8PdPc	688	0.67 ± 0.2	—	—	—	—

**Fig. 3** Typical fluorescence signal for 6SiPc with fit measured at 728 nm. The lighter line indicates the instrument response function. The decay is shown on a linear scale in the inset.**Fig. 4** Transient triplet-triplet absorption of 1ZnPc in 1% v/v toluene-pyridine at 1×10^{-5} M, excitation wavelength 355 nm. The broad absorption with peak at 530 nm is due to T-T* absorption. Transient decay with fits are shown in the inset, ΔA_T (upper trace) measured at 530 nm and ΔA_S (lower trace) measured at 694 nm.

where A_T and A_S were found by fitting exponential functions to the decay of signals at 534 nm for the triplet and 710 nm for the singlet. Both of these fits are shown in Fig. 4.

The decay of the transient absorption was found to be a single exponential, with the same time constant as the recovery of absorption in the singlet state. The spike in the decay of the

singlet observed in SiPc and ZnPc compounds is due to fluorescence saturating the detection system and is treated as phenomenological in the fit. Absence of this peak in the singlet decay of the PdPc compounds is further evidence to suggest that there is minimal or no fluorescence exhibited by these compounds. It is possible to determine ϵ_T using this technique as the singlet and triplet states have no absorption at the triplet and singlet wavelengths, respectively. Triplet extinction values were determined to be 4.3, 3.2, and 1.2×10^4 M cm⁻¹ for 6SiPc, 1ZnPc and 6PdPc respectively. These values were then used to determine the triplet quantum yields using the comparative method and the following expression,

$$\Phi_T = \Phi_T^{\text{std}} \frac{\epsilon_T^{\text{std}} \Delta A_T}{\Delta A_T^{\text{std}} \epsilon_T} \quad (2)$$

where Φ_T and Φ_T^{std} are the triplet quantum yields of the sample and standards respectively. The standards used were unsubstituted ZnPc in toluene ($\Phi_T = 0.65$)³⁴ and ZnTPP in toluene ($\Phi_T = 0.88$).^{35,36} The values obtained for the range of compounds investigated were in the range 0.65–0.99 and are summarized in Table 2.

Photochemistry, Φ_Δ

Singlet delta oxygen quantum yields, Φ_Δ , were determined using time-resolved singlet oxygen phosphorescence detection. The phosphorescence was measured for a series of solutions with A between 0.05–0.2 at the excitation wavelength and at a series of powers ranging from 0.1–1 mJ, the maximum singlet oxygen intensity, S_0 , at t_0 was plotted as a function of laser power, E_l . The gradients of the five graphs were then plotted against the absorbance factor of each of the solutions. A typical set of data is shown in Fig. 5. The samples were compared to two standards, perinaphthenone in pyridine-toluene ($\Phi_\Delta = 0.95 \pm 0.05$)³⁷ and zinc phthalocyanine in pyridine-toluene ($\Phi_\Delta = 0.61 \pm 0.05$).³⁸ A value of Φ_Δ for each compound was calculated using an average of the values determined by each standard. The results are summarized in Table 2, where it can be seen that the values increase with increasing central substituent mass and also increase with the addition of the alkyl substituent in the alpha position.



Table 2 Photochemical properties of alpha-substituted series of *n*MPCs

Compound	$\tau_T/\mu\text{s}$	T-T _{max} /nm	$\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}\times 10^4$	Φ_T	Φ_Δ	$S_\Delta = \Phi_\Delta/\Phi_T$	E_T/nm
ZnPc	330	480	3.4	0.65	0.58	0.89	1092@77K
1ZnPc	113 ± 5	530 ± 10	3.0 ± 0.2	0.73 ± 0.07	0.54 ± 0.05	0.74	
6ZnPc	51 ± 5	534 ± 10	2.8 ± 0.2	0.84 ± 0.07	0.73 ± 0.05	0.87	
8ZnPc	50 ± 5	534 ± 10	2.6 ± 0.2	0.81 ± 0.07	0.71 ± 0.05	0.88	
Si(OH) ₂ Pc	103 ± 5						
6Si(OH) ₂ Pc	161 ± 5	534 ± 10	4.3 ± 0.2	0.65 ± 0.07	0.52 ± 0.05	0.80	
8Si(OH) ₂ Pc	196 ± 5	534 ± 10	4.6 ± 0.2	0.72 ± 0.07	0.50 ± 0.05	0.70	
PdPc	25 ± 5						1007@300K
6PdPc	5 ± 5	528 ± 10	1.0 ± 0.2	0.94 ± 0.07	0.92 ± 0.05	0.98	1048@300K
8PdPc	6 ± 5	529 ± 10	1.2 ± 0.2	0.96 ± 0.07	0.93 ± 0.05	0.97	1052@300K

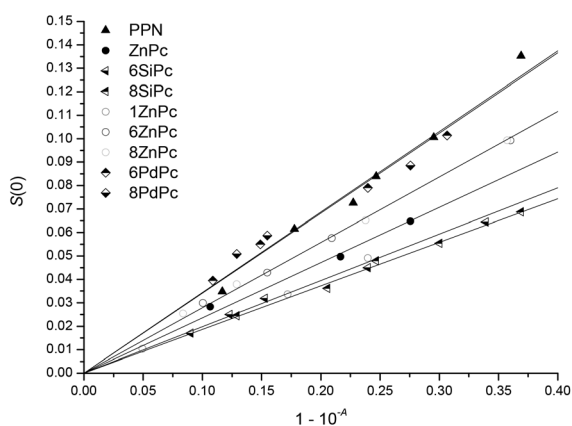


Fig. 5 The gradients of the singlet delta oxygen phosphorescence relationship with laser power, $S(0)$, plotted against the absorption factor, $1 - 10^{-A}$, for the substituted phthalocyanines and reference compounds, PPN and ZnPc, in 1% v/v toluene-pyridine solutions. $\lambda_{\text{ex}} = 355\text{ nm}$.

The ratio of the quantum yield of the triplet state to that of $^1\Delta\text{O}_2$, S_Δ , is also reported in Table 2. S_Δ gives a measure of the efficiency of $^1\Delta\text{O}_2$ production relative to the triplet state production.

Discussion

The shift in Q-band observed between the unsubstituted metallophthalocyanine and all substituted metallophthalocyanines has been attributed to the substitution of an alkyl group in the alpha position.^{31,39–41} This has been previously observed in zinc and palladophthalocyanines with alkyl, thioalkyl and alkoxy groups in alpha positions^{42–44} and is ascribed to the electron-donating nature of the groups, which has been reported to reach a maximum at a chain length of 3 carbons in zinc alkoxy systems.⁴⁵ Previous density functional theory studies have shown that the substitution of an electron-donating group in the alpha position, where the HOMO has a large amplitude, results in an effective upward shift of the orbital and, therefore, in a diminished HOMO–LUMO gap.^{40,46} This is in contrast to the beta position where the HOMO has a relatively small amplitude, hence the influence of any group

substituted into this position is a lot less significant with respect to the parent compound.^{46,47} Hence, an identical red-shift of 18, 30 and 28 nm is observed for Si, Zn and Pd respectively with substitution of long alkyl chains regardless of chain length. However, 1ZnPc results in a smaller shift of 20 nm in accordance with the reduced electron-donating nature of the methyl group. The red-shift in Q-band with decrease in central metal size is typical of the phthalocyanine molecule and is ascribed to a destabilization of the HOMO.³⁰ The red-shift of the absorbance in all substituted phthalocyanines makes them attractive as potential photosensitizers in PDT as the Q-band lies firmly in the range of the optical window of 650–800 nm.

The fluorescence quantum yields of 0.27 and 0.16 for the substituted SiPc and ZnPc, respectively, are significantly lower than values obtained for unsubstituted parent compounds. This is indicative that alpha substitution of the electron-donating alkyl groups goes some way in promoting intersystem crossing from the excited state to triplet state. A decrease in Φ_F is complemented by an increase in Φ_T values for all compounds investigated. A low fluorescence quantum yield is desired as it means that absorbed energy is being transferred efficiently within the molecule to the triplet state and hence generating high triplet quantum yields. A decrease in fluorescence lifetimes has been noted for all alpha-substituted systems compared to the parent compound, where data was available. The SiPc series exhibits significantly longer lifetimes than the ZnPc, both substituted and unsubstituted, and for ZnPc the substitution follows the trend ZnPc > 1ZnPc > 6/8ZnPc. This must be, in part, due to the electron-donating nature of the substituents. In terms of metal centres we have observed that SiPc > ZnPc > PdPc in terms of fluorescence lifetime and the opposite trend is observed in terms of the triplet quantum yield. This is as expected. ZnPc is known to be a closed-shell system, $3d^{10}$ configuration, hence there is more effective shielding of nuclear charges than SiPc and also an increase in spin-orbit coupling which lends itself to an increase in triplet yields and subsequent decrease in fluorescence yield. PdPc on the other hand is an open-shell diamagnetic system with $4d^8$ configuration. This configuration is known for low fluorescence due to the considerable d– π interactions, hence relatively high triplet quantum yields.



The singlet oxygen quantum yield, Φ_{Δ} , is a measure of the efficiency of singlet oxygen generation by photosensitizers. In a given solvent the value of Φ_{Δ} could be dependent on several factors: (i) triplet state properties, including quantum yield, lifetime and triplet energy, E_T , (ii) the ability of substituents to quench singlet oxygen and (iii) the efficiency of energy transfer from the excited state to ground state molecular oxygen. In terms of the phthalocyanines presented here it is clear to see from the values in Table 2 that Φ_T and Φ_{Δ} follow a general trend whereby increasing the mass of the central atom leads to larger quantum yields which is further enhanced by alpha alkyl substitution such that $\text{SiPc} < 6/8\text{SiPc} < \text{ZnPc} \sim 1\text{ZnPc} < 6/8\text{ZnPc} < 6/8\text{PdPc}$. The high triplet state quantum yields, determined by the nature of the metal centre, and triplet lifetimes are all within the desired range. Preliminary data observed for E_T of 6 and 8PdPc indicates the triplet state to lie at approximately 1050 nm, some 60 nm red-shifted compared to the parent compound,³⁰ though further work is required to confirm the nature of this emission. However, ZnPc measurements have shown the triplet state emission to be around 1100 nm, hence high S_{Δ} values are obtained for ZnPc despite an average triplet yield. This may be in part due to the longer τ_T of ZnPc complexes compared to the alpha-substituted analogues.

Experimental methods

Synthesis

Compounds 1ZnPc, 6ZnPc, 8ZnPc, 6PdPc and 6SiPc were synthesised according to literature procedures.^{48–51}

¹H NMR spectra were recorded at 270 MHz using a JEOL EX 270 spectrometer or at 300 MHz on a Varian Gemini 2000 spectrometer. Tetramethylsilane was used as the internal standard and the positions of the peaks are reported in ppm. The UV-Vis spectra were recorded using a Hitachi U-3000-X spectrophotometer. Low resolution matrix-assisted laser desorption ionisation (MALDI) mass spectra were obtained using a dithranol matrix at the University of Manchester, UK or on a Shimadzu spectrometer at UEA. Elemental analysis was carried out by the microanalytical service provided at the University of East Anglia by Mr A. W. Saunders. Silica gel (Merck grade 7734) was used in chromatographic separations. TLC was performed using Merck 5554 silica gel on aluminium sheets.

Preparation of 1,4,8,11,15,18,22,25-octakis(octyl)phthalocyaninatodihydroxysilicon, 8SiPc. A mixture of metal-free 1,4,8,11,15,18,22,25-octakis(octyl)phthalocyanine (200 mg, 0.15 mmol) and tri-*n*-butylamine (2 mL) was refluxed in benzene (50 mL) under nitrogen. The solution was dried by distilling off some of the solvent (15 mL). The solution was left to cool to room temperature and trichlorosilane (1 mL) was injected *via* a syringe directly into the solution. This was then stirred in the dark for 6 hours. More trichlorosilane (0.5 mL) was added and the solution left to stir in the dark for 12 hours. TLC analysis (eluent: petroleum ether (bp. 40–60 °C)) showed some starting material was left. More

trichlorosilane (0.5 mL) was added and the solution left to stir in the dark for another 12 hours. The mixture was then poured cautiously into water (100 mL) and triethylamine (60 mL) was added slowly. The white precipitate was removed by filtration and washed with toluene until the washings were almost clear. The organic phase was separated, washed with 20% aqueous HCl (5 × 100 mL), brine and dried (MgSO₄). The drying agent was removed by filtration and the solvent was removed under reduced pressure. The green residue was chromatographed over silica (eluent: petroleum ether (bp. 40–60 °C)) to remove traces of starting material. The eluent was then changed to petroleum ether (bp. 40–60 °C)–THF 4 : 1. This afforded a blue-green fraction which contained 1,4,8,11,15,18,22,25-octakis(octyl)phthalocyaninatodihydroxysilicon (110 mg, 54%) which appeared soluble in most organic solvents (acetone, methanol, ethanol, petroleum ether, toluene and THF). [¹H NMR (270 MHz, C₆D₆) 7.89 (s, 8H), 4.45 (t, 16H), 2.08 (m, 16H), 1.52 (m, 16H), 1.0–2.0 (m, 64H), 0.74 (t, 24H), –5.41 (br s, 2H) ppm. λ_{max} (abs. $\epsilon \times 10^5$) 703.5 (2.3) nm (THF). MALDI-MS: isotopic clusters at 1472 [M⁺, 60%] and 1455 [M⁺–H₂O, 100%]. Found: C, 78.15; H, 10.03; N, 7.38%. C₉₆H₁₄₆N₈O₂Si requires: C, 78.31; H, 9.99; N, 7.61%].

Preparation of 1,4,8,11,15,18,22,25-octakis(octyl)phthalocyaninatopalladium(II), 8PdPc. Metal-free 1,4,8,11,15,18,22,25-octakis(octyl)phthalocyanine (320 mg, 0.23 mmol) was dissolved in pentan-1-ol (10 mL) and heated to reflux. Excess metal salt, palladium(II) acetate (0.2 g, 0.9 mmol), was added and reflux was continued for 4 h. After the reaction mixture had cooled, methanol (10 mL) was added and the precipitate collected and chromatographed over silica gel (eluent: petroleum ether (bp. 40–60 °C)–THF 2 : 1), collecting the green fraction which was recrystallised from THF–methanol to give the title product (270 mg, 77%) as a blue powder. [¹H NMR (300 MHz, C₆D₆) 7.28 (8H, s), 4.02 (16H, t), 1.82 (16H, m), 1.4 (16H, m), 0.9 (64H, m), 0.55 (24H, t) ppm. λ_{max} (abs.) 690 nm (cyclohexane). Found: C, 75.94; H, 9.67; N, 7.56; C₉₆H₁₄₄N₈Pd requires: C, 76.03; H, 9.57; N, 7.39%. MALDI-MS: isotopic cluster at 1514.9 (M⁺, 100%)].

Materials and instruments

All photophysics experiments were carried out in 1% v/v pyridine in toluene unless otherwise stated. The substituted zinc, silicon and palladium phthalocyanine derivatives under investigation were synthesised as described above. Each compound has a different length alkyl substituent in the alpha position. The compounds are shown in Fig. 1 and referred to as *n*MPc, whereby *n* represents the number of carbons on the alkyl chain and M refers to the metal centre. The standards used in this work were zinc phthalocyanine, ZnPc (97%), perinaphthenone, PPN (97%), and zinc tetraphenylpyridine, ZnTPP, which were obtained from Aldrich and used without further purification. HPLC grade toluene (99.99%) and pyridine (≥99.5%) were obtained from Aldrich.

Spectroscopic studies

UV-visible spectra were recorded on a Hitachi U-3000 spectrophotometer using 1 cm matched quartz cuvettes. The molar



absorptivity was calculated from a least squares fit of absorbance against concentration, with an absorption spectrum of the reference solvent subtracted from the acquired data. Steady-state fluorescence spectra were acquired on a Horiba Jobin Yvon Fluoromax-2 with 2 nm slit width for both excitation and emission monochromators.

Photophysics

Fluorescence quantum yields. Fluorescence quantum yields, Φ_F , were determined using the comparative method described in detail elsewhere.⁵² The fluorescence quantum yield is related to that of a standard by:

$$\Phi_F = \Phi_{F,\text{std}} \frac{A_{\text{std}} F n^2}{F_{\text{std}} n_{\text{std}}^2 A} \quad (3)$$

where F and F_{std} are the areas under the fluorescence emission curves of the samples (a–h) and the standard, respectively. A and A_{std} are the respective absorbances of the samples and standard at the excitation wavelength, respectively, and n and n_{std} are the refractive indexes of solvents: $n_{\text{toluene}} = 1.4961$ (at 20 °C and 589 nm); $n_{\text{ethanol}} = 1.3611$ (at 20 °C and 589 nm); $n_{\text{pyridine}} = 1.5095$ (at 20 °C and 589 nm); $n_{\text{tol/py}}$ taken to be 1.50.⁵³ Unsubstituted ZnPc (in EtOH, $\Phi_F = 0.28$)⁵⁴ was employed as the standard. The absorbance of the solutions at the excitation wavelength ranged between 0.02 and 0.1.

Fluorescence lifetimes. The technique of time correlated single photon counting (TCSPC) was used to record fluorescence lifetimes of the samples. All solutions under study were prepared with a concentration so as to give a maximum absorbance at the Q-band of no greater than 0.05, in order to eliminate the effects of re-absorption. The excitation source consisted of a pulsed 635 nm diode laser (IBH NanoLED Model-02) providing output pulses of <200 ps at a repetition rate of 1 MHz. The fluorescence emission was collected at 90° to the excitation source, and the emission at $\lambda = 716$ nm recorded using a cooled, red sensitive photomultiplier tube (IBH Model TBX-04) linked to a time-to-amplitude converter (Ortec 567) and multichannel analyzer (E.G. & G. Trump Card and Maestro for Windows V.5.10). The instrument response function (IRF) of the apparatus was measured using a dilute suspension of milk powder in water as a scattering medium giving an IRF with a duration of 450 ps full width at half maximum (FWHM). The time per channel was typically ~25 ps giving a full range of ~50 ns over the 2048 point data set. All fluorescence decays were recorded to a minimum of 10 000 counts in the peak channel of the pulse height analyzer. The data were transferred to a computer and analysed by using the standard method of iterative reconvolution and non-linear least squares fitting in a Microsoft Excel spreadsheet. The quality of calculated fits was judged using statistical parameters including the Durbin–Watson parameter, reduced χ^2 , random residuals and autocorrelated residuals.

Photochemistry

Triplet quantum yields and lifetimes. Triplet–triplet absorption spectra, triplet extinction coefficients, lifetimes and

quantum yields were measured using a standard method, described in detail elsewhere.⁵⁵ Briefly, the data were recorded on a laser flash photolysis system. The excitation pulses were provided by the third-harmonic of a Q-switched Nd:YAG laser (JK 2000). Pulse energies were between 0.1–1 mJ and the excitation beam was directed through the sample without focussing. The analyzing source was a tungsten-halogen lamp imaged into the sample cuvette at right angles to the excitation beam. The analyzing source was subsequently relay imaged onto the entrance slits of a 50 cm monochromator and detected with a photomultiplier tube (EMI 9529B). Transient absorption spectra were collected by measuring two gates, from 0–25 μs and 30–80 μs . These were simultaneously recorded onto computer from the two-channel digital real-time oscilloscope (LeCroy Waverunner LT262). Transient decay signals were averaged for 1024 pulses using the oscilloscope and written directly to disk. All the sample solutions were degassed, using the freeze–pump–thaw technique and irradiated in a 1 cm path-length quartz cell.

Time-resolved singlet oxygen phosphorescence detection (TRPD). The singlet delta oxygen quantum yield, Φ_Δ , was determined using a similar method to those described in previous work.^{56,57} Samples dissolved in 1% v/v toluene–pyridine and allowed to equilibrate with air were excited using the third harmonic of a Q-switched Nd:YAG laser (355 nm). A CuSO_4 filter was used upstream of the solution to remove residual 1064 nm radiation. Typical pulse energies used were in the range 0.1–1 mJ per pulse. A North Coast E0-817P Ge photodiode/amplifier combination detected the singlet oxygen phosphorescence at right angles to the incident laser beam. The sample was placed in a fluorescence cuvette with a 10 mm path length close to the detector. The singlet oxygen luminescence was selected with a 1270 nm silicon interference filter (bandpass, 30 nm) placed close to the detector.

Conclusions

The absorption properties, triplet quantum yields and singlet oxygen quantum yields of a series of alpha-substituted metallophthalocyanines have been measured. The results indicate that all compounds exhibit an improvement in the desired properties, relative to the parent compounds.

Acknowledgements

MVL thanks the School of Chemistry and the EPSRC for a DTA award.

Notes and references

- 1 G. Guillaud, J. Simon and J. P. Germain, Metallophthalocyanines - Gas sensors, resistors and field effect transistors, *Coord. Chem. Rev.*, 1998, **178**, 1433–1484.



- 2 R. A. Collins and K. A. Mohammed, Gas sensitivity of some metal phthalocyanines, *J. Phys. D: Appl. Phys.*, 1988, **21**, 154–161.
- 3 C. W. Tang, Two-layer organic photovoltaic cell, *Appl. Phys. Lett.*, 1986, **48**, 183.
- 4 G. de la Torre, P. Vazquez, F. Agullo-Lopez and T. Torres, Phthalocyanines and related compounds: organic targets for nonlinear optical applications, *J. Mater. Chem.*, 1998, **8**, 1671–1683.
- 5 H. Ali and J. E. van Lier, Metal complexes as photo- and radiosensitizers, *Chem. Rev.*, 1999, **99**, 2379–2450.
- 6 C. M. Allen, W. M. Sharman and J. E. Van Lier, Current status of phthalocyanines in the photodynamic therapy of cancer, *J. Porphyrins Phthalocyanines*, 2001, **5**, 161–169.
- 7 D. Phillips, The photochemistry of sensitizers for photodynamic therapy, *Pure Appl. Chem.*, 1995, **67**, 117–126.
- 8 J. Moan and Q. Peng, An outline of the hundred-year history of PDT, *Anticancer Res.*, 2003, **23**, 3591–3600.
- 9 D. Phillips, Light relief: photochemistry and medicine, *Photochem. Photobiol. Sci.*, 2010, **9**, 1589–1596.
- 10 M. C. DeRosa and R. J. Crutchley, Photosensitized singlet oxygen and its applications, *Coord. Chem. Rev.*, 2002, **233**, 351–371.
- 11 A. A. Gorman and M. A. J. Rodgers, Singlet molecular-oxygen, *Chem. Soc. Rev.*, 1981, **10**, 205–231.
- 12 R. Bonnett, Photosensitizers of the porphyrin and phthalocyanine series for photodynamic therapy, *Chem. Soc. Rev.*, 1995, **24**, 19–33.
- 13 J. Moan and K. Berg, Photochemotherapy of cancer - experimental research, *Photochem. Photobiol.*, 1992, **55**, 931–948.
- 14 O. I. Apolikhin, I. V. Chernishov, A. V. Sivkov, D. V. Altunin, S. G. Kuzmin and G. N. Vorozhtsov, in *Therapeutic Laser Applications and Laser-Tissue Interaction III*, ed. A. Vogel, 2007, pp. 63213–63213.
- 15 Y. E. Efremova, E. R. Andreyeva, G. N. Soboleva, N. V. Radyukhina, D. F. Beloyartsev, Y. A. Karpov and E. M. Tararak, In vitro accumulation of the photosensitizer Photosens in the atherosclerotic plaque of the human carotid artery, *Arkhiv Patologii*, 2012, **74**, 18–22.
- 16 L. M. Moreira, F. V. dos Santos, J. P. Lyon, M. Maftoum-Costa, C. Pacheco-Soares and N. S. da Silva, Photodynamic therapy: porphyrins and phthalocyanines as photosensitizers, *Aust. J. Chem.*, 2008, **61**, 741–754.
- 17 T. Nyokong, Effects of substituents on the photochemical and photophysical properties of main group metal phthalocyanines, *Coord. Chem. Rev.*, 2007, **251**, 1707–1722.
- 18 D. Phillips, Chemical mechanisms in photodynamic therapy with phthalocyanines, *Prog. React. Kinet. Mech.*, 1997, **22**, 175–300.
- 19 S. Ogura, K. Tabata, K. Fukushima, T. Kamachi and I. Okura, Development of phthalocyanines for photodynamic therapy, *J. Porphyrins Phthalocyanines*, 2006, **10**, 1116–1124.
- 20 M. Hu, N. Brasseur, S. Z. Yildiz, J. E. van Lier and C. C. Leznoff, Hydroxyphthalocyanines as potential photodynamic agents for cancer therapy, *J. Med. Chem.*, 1998, **41**, 1789–1802.
- 21 R. Langlois, H. Ali, N. Brasseur, J. R. Wagner and J. E. Vanlier, Biological-activities of phthalocyanines .4. Type-II sensitized photooxidation of L-tryptophan and cholesterol by sulfonated metallo phthalocyanines, *Photochem. Photobiol.*, 1986, **44**, 117–123.
- 22 J. D. Spikes, Phthalocyanines as photosensitizers in biological-systems and for the photodynamic therapy of tumors, *Photochem. Photobiol.*, 1986, **43**, 691–699.
- 23 T. H. Huang, K. E. Rieckhoff and E. M. Voigt, Spin-orbit effects in metalphthalocyanines, *Chem. Phys.*, 1977, **19**, 25–33.
- 24 M. Hanack and M. Lang, Conducting stacked metallo-phthalocyanines and related-compounds, *Adv. Mater.*, 1994, **6**, 819–833.
- 25 S. M. Huang, L. M. Dai and A. W. H. Mau, Patterned growth and contact transfer of well-aligned carbon nanotube films, *J. Phys. Chem. B*, 1999, **103**, 4223–4227.
- 26 W. F. Law, R. C. W. Liu, J. H. Jiang and D. K. P. Ng, Synthesis and spectroscopic properties of octasubstituted (phthalocyaninato)titanium(IV) complexes, *Inorg. Chim. Acta*, 1997, **256**, 147–150.
- 27 C. C. Leznoff, L. S. Black, A. Hiebert, P. W. Causey, D. Christendat and A. B. P. Lever, Red manganese phthalocyanines from highly hindered hexadecaalkoxyphthalocyanines, *Inorg. Chim. Acta*, 2006, **359**, 2690–2699.
- 28 M. T. M. Choi, P. P. S. Li and D. K. P. Ng, A direct comparison of the aggregation behavior of phthalocyanines and 2,3-naphthalocyanines, *Tetrahedron*, 2000, **56**, 3881–3887.
- 29 S. M. Bishop, A. Beeby, A. W. Parker, M. S. C. Foley and D. Phillips, The Preparation and Photophysical Measurements of Perdeutero Zinc Phthalocyanine, *J. Photochem. Photobiol., A*, 1995, **90**, 39–44.
- 30 P. S. Vincett, E. M. Voigt and K. E. Rieckhof, Phosphorescence and fluorescence of phthalocyanines, *J. Chem. Phys.*, 1971, **55**, 4131–4140.
- 31 M. van Leeuwen, A. Beeby and S. H. Ashworth, The photochemistry and photophysics of a series of non-peripherally substituted zinc phthalocyanines, *Photochem. Photobiol. Sci.*, 2010, **9**, 370–375.
- 32 M. N. Sibata, A. C. Tedesco and J. M. Marchetti, Photophysicals and photochemicals studies of zinc(II) phthalocyanine in long time circulation micelles for photodynamic therapy use, *Eur. J. Pharm. Sci.*, 2004, **23**, 131–138.
- 33 A. Ogunsipe, D. Maree and T. Nyokong, Solvent effects on the photochemical and fluorescence properties of zinc phthalocyanine derivatives, *J. Mol. Struct.*, 2003, **650**, 131–140.
- 34 W. Chidawanyika, A. Ogunsipe and T. Nyokong, Syntheses and photophysics of new phthalocyanine derivatives of zinc, cadmium and mercury, *New J. Chem.*, 2007, **31**, 377–384.
- 35 I. Carmichael and G. L. Hug, Triplet-Triplet Absorption-Spectra of Organic-Molecules in Condensed Phases, *J. Phys. Chem. Ref. Data*, 1986, **15**, 1–250.
- 36 V. A. Walters, J. C. Depaula, B. Jackson, C. Nutaitis, K. Hall, J. Lind, K. Cardozo, K. Chandran, D. Raible and



- C. M. Phillips, Electronic-structure of triplet-states of zinc(II) tetraphenylporphyrins, *J. Phys. Chem.*, 1995, **99**, 1166–1171.
- 37 R. Schmidt and M. Bodesheim, Time-resolved measurement of O₂ (¹Σ_g⁺) in solution - phosphorescence from an upper excited-state, *J. Phys. Chem.*, 1994, **98**, 2874–2876.
- 38 A. Ogunsipe, J. Y. Chen and T. Nyokong, Photophysical and photochemical studies of zinc(II) phthalocyanine derivatives - effects of substituents and solvents, *New J. Chem.*, 2004, **28**, 822–827.
- 39 M. Aoudia, G. Z. Cheng, V. O. Kennedy, M. E. Kenney and M. A. J. Rodgers, Synthesis of a series of octabutoxy- and octabutoxybenzophthalocyanines and photophysical properties of two members of the series, *J. Am. Chem. Soc.*, 1997, **119**, 6029–6039.
- 40 G. Cheng, X. Z. Peng, G. L. Hao, V. O. Kennedy, I. N. Ivanov, K. Knappenberger, T. J. Hill, M. A. J. Rodgers and M. E. Kenney, Synthesis, photochemistry, and electrochemistry of a series of phthalocyanines with graded steric hindrance, *J. Phys. Chem. A*, 2003, **107**, 3503–3514.
- 41 M. Durmus, C. Lebrun and V. Ahsen, Synthesis and characterization of novel liquid and liquid crystalline phthalocyanines, *J. Porphyrins Phthalocyanines*, 2004, **8**, 1175–1186.
- 42 T. B. Ogunbayo and T. Nyokong, Photophysical and photochemical properties of Ni(II), Pd(II) and Pt(II) aryloxo and alkylthio derivatised phthalocyanine, *J. Mol. Struct.*, 2010, **973**, 96–103.
- 43 T. B. Ogunbayo, A. Ogunsipe and T. Nyokong, The syntheses, characterization and fluorescence spectra of novel, octakis(alkylthiophthalocyanato) nickel(II) and palladium(II) complexes, *Dyes Pigm.*, 2009, **82**, 422–426.
- 44 T. B. Ogunbayo and T. Nyokong, Synthesis and Pd(II) binding studies of octasubstituted alkyl thio derivatised phthalocyanines, *Polyhedron*, 2009, **28**, 2710–2718.
- 45 R. W. Boyle, Biological-activities of phthalocyanines. 16. Tetrahydroxy- and tetraalkylhydroxy zinc phthalocyanines - effect of alkyl chain-length on invitro and invivo photodynamic activities, *Br. J. Cancer*, 1993, **67**, 1177–1181.
- 46 G. Ricciardi, A. Rosa and E. J. Baerends, Ground and excited states of zinc phthalocyanine studied by density functional methods, *J. Phys. Chem. A*, 2001, **105**, 5242–5254.
- 47 G. Cheng, X. Z. Peng, G. L. Hao, V. O. Kennedy, I. N. Ivanov, K. Knappenberger, T. J. Hill, M. A. J. Rodgers and M. E. Kenney, Synthesis, photochemistry, and electrochemistry of a series of phthalocyanines with graded steric hindrance, *J. Phys. Chem. A*, 2003, **107**, 3503.
- 48 M. J. Cook, I. Chambrier, S. J. Cracknell, D. A. Mayes and D. A. Russell, Octa-alkyl zinc phthalocyanines - potential photosensitizers for use in the photodynamic therapy of cancer, *Photochem. Photobiol.*, 1995, **62**, 542–545.
- 49 M. J. Cook and D. A. Russell, ed. P. I. Appl., 1995.
- 50 A. Auger, W. J. Blau, P. M. Burnham, I. Chambrier, M. J. Cook, B. Isare, F. Nekelson and S. M. O'Flaherty, Non-linear absorption properties of some 1,4,8,11,15,18,22,25-octaalkylphthalocyanines and their metallated derivatives, *J. Mater. Chem.*, 2003, **13**, 1042–1047.
- 51 M. J. Cook and I. Fernandes, ed. P. I. Appl., 2002.
- 52 A. T. R. Williams, S. A. Winfield and J. N. Miller, Relative fluorescence quantum yields using a computer-controlled luminescence spectrometer, *Analyst*, 1983, **108**, 1067–1071.
- 53 *Handbook of Chemistry and Physics*, CRC Press, Boca Baton, Florida, 1979.
- 54 M. N. Sibata, A. C. Tedesco and J. M. Marchetti, Photo-physicals and photochemicals studies of zinc(II) phthalocyanine in long time circulation micelles for photodynamic therapy use, *Eur. J. Pharm. Sci.*, 2004, **23**, 131.
- 55 I. Carmichael and G. L. Hug, *J. Phys. Chem. Ref. Data*, 1986, **15**, 1.
- 56 S. Nonell and S. E. Braslavsky, Time resolved singlet oxygen detection, Singlet Oxygen, UV-A and Ozone, *Methods Enzymol.*, 2000, 319.
- 57 R. Schmidt, K. Seikel and H. D. Brauer, Determination of the phosphorescence quantum yield of singlet molecular-oxygen (¹Δ_g) in 5 different solvents, *J. Phys. Chem.*, 1989, **93**, 4507–4511.

