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Synthesis and spectral properties of soluble trimethylsilyl substituted metal-phthalocyanines

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Abstract

By in situ trapping of lithiated phthalocyanines with chlorotrimethylsilane, several highly soluble trimethylsilyl non-peripherally substituted phthalocyanines were synthesized. The photodegradation of the resultant ZnPcs in different organic solvents was found to follow quasi-first order kinetics and the degradation products were determined with the aid of GC–MS. A mechanism for the photodegradation process has been proposed and is supported by results from MO calculations. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Soluble phthalocyanines; Synthesis; Photodegradation; MO calculations

1. Introduction

For many years various substituted phthalocyanines (Pcs) have been developed for use as commercial dyes and pigments. During the past 30 years, increasing investigation of the magnetic, catalytic, and photochemical properties of metal-containing Pcs has resulted in potential or new applications outside of traditional areas. For the more recent applications, the low solubility of the various Pcs has limited their potential utility. The insolubility of the Pc system arises from its ability to form stacked oligomers of considerable molecular weights.

To increase the solubility of Pc compounds significantly, two approaches are possible. One involves incorporating solubility-enhancing substituents and the other involves altering the Pc structure in a manner that reduces its stacking ability. In addition, certain judiciously positioned substituents can dramatically increase Pc solubility by utilizing a combination of these two approaches. In this regard, certain peripherally substituted Pcs are much more soluble in organic solvents [1–5]. Solvent soluble macrocycles are of interest to the energy research community because of their potential application in the preparation of sensors, electrode coatings, catalysts, and oxygen transporting agents. Since soluble Pcs are also photosensitizing agents, they may prove useful in photodynamic therapy (PDT) [6]. The use of soluble Pcs as photosensitizers in PDT offers the following advantages: (1) better photostability and thermal stability than porphyrins, (2) photo-biological activity, (3) a high extinction coefficient in the 600–800

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nm range, and (4) higher triplet quantum yields. When Pcs form insoluble aggregates, photosensitizing activity is reduced and their utility for PDT is somewhat limited [6, 7].

Substituted Pcs have generally been prepared by the condensation of phthalonitriles and phthalimides, an often laborious and time-consuming process. A one-step synthesis of a highly soluble Pc compound containing one or more substituents on the non-peripheral carbon atoms has been reported [8]. If the substituents were trialkylsilyl groups, the resultant soluble Pcs would be more suitable for use in PDT, since silicon is non-toxic. If trialkylsilyl substituted Pcs were found to degrade into species that could be metabolized in the human body, it is anticipated that such compounds could be prepared by the one-step method and used as photosensitizers for PDT.

Electrophilic substitutions of Pcs have been accomplished in prior studies [9,10]. In the cases where regioselectivity was observed, β-substitution was the preferred process. It is unclear whether this preference can be attributed to steric or electronic effects. It is known, however, that substitution at the α-position is preferable to β-substitution in order to produce soluble Pcs.

In the present paper, several trimethylsilyl-substituted metal Pcs have been prepared via a one-step method that utilized a sterically hindered metallic reagent, such as lithium 2,2,6,6-tetramethyl piperidine. The photolysis of the resultant Pcs was investigated in various solvents, and degradation products were characterized by GC–MS. A mechanism for the photodegradation of these compounds was developed and indirect evidence for the mechanism was obtained from MO calculations.

2. Experimental

2.1. Synthesis

H_2Pc, ZnPc, CuPc, PdPc, TiOPc and 2,2,6,6-tetramethylpiperidine (TEMP) were obtained from commercial sources. Tetra-(alpha-2,4-dimethyl-3-pentoxy) PdPc was synthesized by a previously described method [11]. Trimethylsilyl substituted Pc and MPc compounds were synthesized by a one-step procedure that employed Pc or MPc as the substrate. In a typical procedure, the Pc compound (1.3 mmol) was added at −78°C to a tetrahydrofuran (THF, 35 ml) solution containing Me_4SiCl (41.6 mmol) and lithium 2,2,6,6-tetramethylpiperidine (20.8 mmol), the latter prepared from *n*-BuLi (13.5 ml, 1.5 M in hexane) and TMP (3.6 ml, 21.3 mmol) in THF (40 ml). The solution was held at −78°C for 1 h and then was allowed to slowly warm to room temperature. The solvent was removed by rotary evaporation and the solid residue was extracted with CH_2C1_2 (100 ml). The extract was stirred with dilute HCl (1 M, 50 ml) and the CH_2C1_2 solution was dried ($MgSO_4$) and concentrated to yield trimethylsilyl substituted Pc compounds (>50%). The structures of $PdPc(SiMe_3)_x$ and $ZnPc(SiMe_3)_x$ ($x=2$ or 3) were confirmed by time-of-flight (TOF) mass spectrometry (Mariner API-TOF, TIS ion source, PE Co.). $PdPc(SiMe_3)_2$: *m/e* 786 ($M^+ + Na$), $PdPc(SiMe_3)_3$: *m/e* 858 ($M^+ + Na$) $ZnPc(SiMe_3)_2$: *m/e* 745 ($M^+ + Na$), $ZnPc(SiMe_3)_3$: *m/e* 817($M^+ + Na$).

2.2. Photochemical reactions

The photolysis of Pc compounds was carried out in a photochemical reaction apparatus (British Applied Photophys Limited) equipped with a 200-W Hg lamp. The effects of photolysis were examined by measuring the absorption spectra of irradiated solutions on a Shimadzu UV-260 spectrophotometer. In general, the solutions of Pc compounds used in these experiments were diluted with different solvents to a concentration that afforded an absorbance value of 1.8 at λ_{max}. This gave a linear relationship between Pc concentration and absorbance.

2.3. GC–MS analysis

After irradiation, the photodegradation products of trimethylsilyl substituted ZnPc were separated and characterized by GC–MS with the aid of an HP 1800B GCD detector. The chromatography employed an HP-5 (30 m×0.25 mm×0.25 μm) column. MS analysis was performed using a vacuum of 52 mtorr, a detector temperature of 167°C, and a voltage of 1507 V.

3. Results and discussion

3.1. Synthesis of trimethylsilyl substituted ZnPc

The general reaction scheme used in this study is shown in Fig. 1. The direct trimethylsilylation of Pcs was a facile one-step process, and in our case the introduction of trimethylsilyl groups occurred only in the α-positions. The observed process probably occurs because only one trimethylsilyl group may occupy the various pockets between two adjacent isoindole moieties, due to the bulkiness of the TMS group [8].

In our study, the aromatic region of a 400 MHz ^{1}H NMR spectrum of $ZnPc(SiMe_3)_4$ showed only half as many α-protons (δ 9.34–9.41) as β-protons (δ 7.98–8.05). This indicates that the lithiation and silylation steps were very selectively. With this in mind, there are four $MPc(SiMe_3)_4$ isomers, giving a statistical distribution of 1:2:2:4 [8]. The effects of reaction conditions on the yields of $ZnPc(SiMe_3)_x$ are summarized in Table 1.

Increasing the mol ratio of Me_3SiCl to LiTMP (e.g. from 1:1 to 2:1) increased the yield of product $ZnPc(SiMe_3)_x$, where $x=4$. The reaction yields were established by column chromatography on basic alumina, eluting first with CCl_4 and then with $CHCl_3$. Reaction temperature also influenced the product yield. When LiTMP was added to the reaction mixture at −30 and −5°C, the yield decreased, presumably because the reaction of LiTMP with Me_3SiCl competes with the deprotonation of ZnPc. Conducting the reaction at −78°C, favored the interaction of Me_3SiCl with ZnPc, and the yield of $ZnPc(SiMe_3)_x$ was high.

3.2. Photochemical properties of $ZnPc(SiMe_3)_x$

As seen in Table 2, all of the Me_3Si-substituted and alkyoxy-substituted Pcs have a strong absorption in the 680–700 nm wavelength range in $CHCl_3$. In order to determine the influence of solvents on the photolysis of $ZnPc(SiMe_3)_x$, we recorded changes in the absorbance values of $ZnPc(SiMe_3)_x$

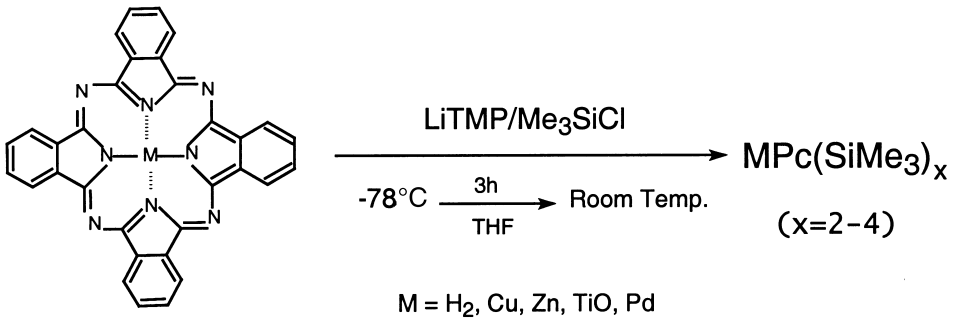


Fig. 1. Synthesis of trimethylsilyl substituted Pc compounds.

Table 1
Reaction conditions and yields in the formation of $ZnPc(SiMe_3)_x$

Equivalent of Me_3SiCl	Equivalent of LiTMP	Reaction temperature (°C)[a]	Total reaction time (h)	Yield (%)[b]
4	4	−78, then R.T.	2.5	66
12	8	−78, then R.T.	3.0	70
30	15	−78, then R.T.	3.2	76
3	15	−30	5	47
30	15	−78, then R.T.	10	77
30	15	−5	5	22

[a] When two temperatures are given, the first is the temperature for the addition of LiTMP to the $ZnPc/Me_3SiCl$ mixture and the second is the final reaction temperature.

[b] Based on $\frac{\text{g product}\,(x=2\text{–}4)}{\text{g ZnPc}}$.

as a function of exposure time in ethanol, dichloromethane, acetone and 2-ethoxyethanol. Since the photodegradation products of $ZnPc(SiMe_3)_x$ do not have an absorption in the visible region, the dependence of $ZnPc(SiMe_3)_x$ concentration on irradiation time was determined by recording the absorption spectrum at various irradiation times. The results were used to determine the rate constant for the photolysis process.

In this investigation, the relationships between $ZnPc(SiMe_3)_x$ concentration and absorbance in different solvents were assessed. The experimental results are summarized in Fig. 2. The linear relationship between $\ln(A_0/A_t)$ and irradiation time indicates that the photolysis of $ZnPc(SiMe_3)_x$ is a quasi-first order kinetic process. Accordingly, the reaction rate can be expressed as shown in Eq. (1).

$$-\mathrm{d}[\mathrm{ZnPc(SiMe_3)}_x]/\mathrm{d}t = k'[\mathrm{ZnPc(SiMe_3)}_x][\mathrm{O_2}] \qquad (1)$$

Since the $[O_2]$ in an air-saturated solution is $\sim 3\times10^{-4}$ M [12], the rate constant can also be expressed as Eq. (2). From Table 3, it is clear that the rate constants for the photodegradation of $ZnPc(SiMe_3)_x$ in different solvents correlate with the solvents' solubility parameter. As the solubility parameter decreases, the solubility of $ZnPc(SiMe_3)_x$ compounds increases, and the greater the solubility, the faster the fading. These results were

Table 2
Absorption maxima for trimethylsilyl substituted and alkoxy substituted Pcs in $CHCl_3$

Pcs	$H_2Pc(SiMe_3)_x$	$CuPc(SiMe_3)_x$	$ZnPc(SiMe_3)_x$	$TiOPc(SiMe_3)_x$	$PdPc(SiMe_3)_x$	$PdPc(RO)_4$
λ_{max} (nm)	689	691.5	694.2	688.1	693.4	685.1

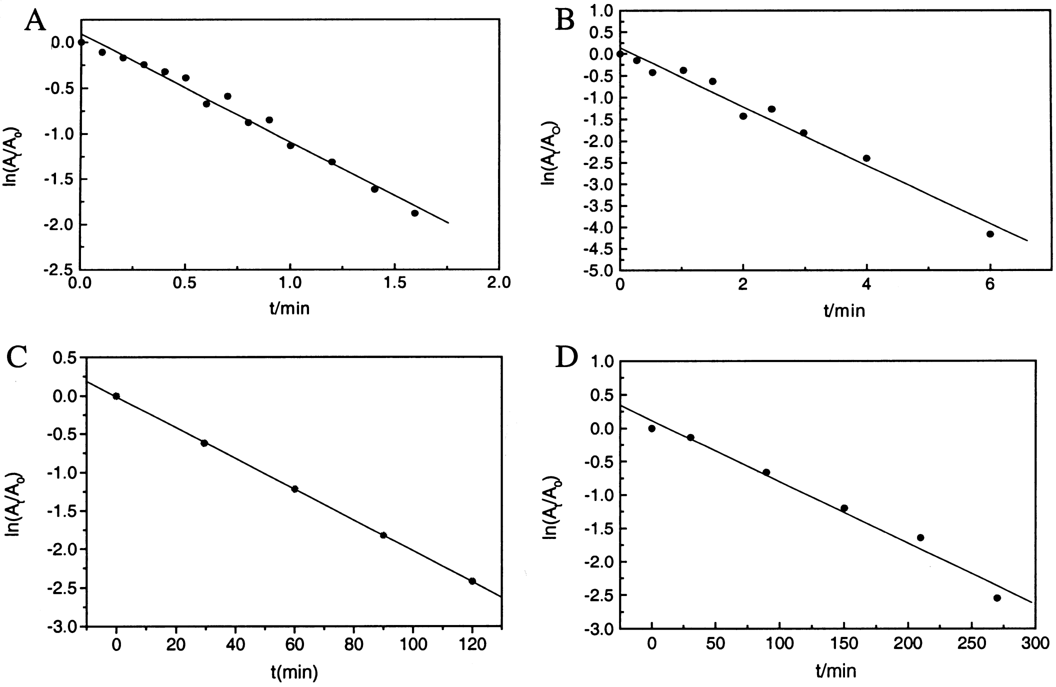


Fig. 2. The rate for $ZnPc(SiMe_3)_x$ photodegradation (A) at 694.2 nm in $CHCl_3$; (B) at 669.2 nm in CH_3COCH_3; (C) at 671 nm in $HOCH_2CH_2OC_2H_5$; and (D) at 669 nm in C_2H_5OH.

Table 3
Rate constants for the photodegradation of $ZnPc(SiMe_3)_x$ in different solvents

Solvent	$CHCl_3$	CH_3COCH_3	$HOCH_2CH_2OC_2H_5$	C_2H_5OH
Solubility parameter[a]	19.0	20.4	21.5	26.0
k (min^{-1})	1.18	0.675	0.020	0.0092

[a] $(J/cm^3)^{1/2}$ [16].

confirmed using computational experiments. We also found that the photolysis of tetra-(alpha-2,4-dimethyl-3-pentoxy) PdPc in $CHCl_3$ caused a color change from blue to colorless in several minutes.

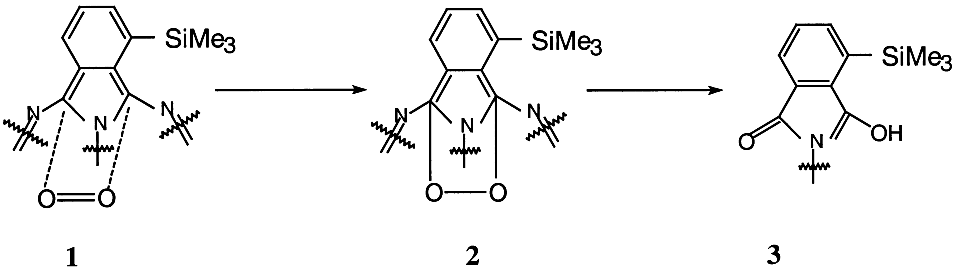
$$\ln\frac{[ZnPc(SiMe_3)_x]_t}{[ZnPc(SiMe_3)_x]_0} = \ln\frac{A_t}{A_0} = -kt \tag{2}$$

3.3. GC–MS analysis

The goal of this aspect of our study was to determine the mechanism of photodegradation. After decolorizing a CH_2Cl_2 solution of $ZnPc(SiMe_3)_x$ with a 200-W Hg lamp at ambient temperature, the solution was analyzed by GC–MS. The gas chromatogram showed one major peak and the M± of this product was *m*/*e* 219. A schematic representation of the product forming process is shown in Fig. 3. As indicated, the photo degradation of $ZnPc(SiMe_3)_x$ is a combination of oxidation and fragmentation steps, leading to structure **3**.

3.4. Computational section

To further investigate the photodegradation mechanism for the substituted metal Pcs, molecular mechanics (MM) and semi-empirical molecular orbital MO calculations were performed on ZnPc and its Me_3Si-substituted derivatives. The molecular interactions between ZnPc and its derivatives ($(ZnPc(SiMe_3)_x$, $x = 1$–4) with $CHCl_3$, CH_3COCH_3, $HOCH_2CH_2OC_2H_5$ and C_2H_5OH have been calculated, and the resultant binding energies were analyzed. In this regard, the steric energies between ZnPcs and solvent molecules were calculated using the MM method in the HyperChem program [13] and these values were used to generate the corresponding binding energies. It can be seen from Table 4 that the binding energies for solvent molecules (from −2.02 to −0.55 kJ/mol) are close to the values for ZnPcs and $CHCl_3$ (from −8.46 to −0.68 kJ/mol). However, the binding energy between ZnPc molecules (−264.21 kJ/mol) was much larger than the values for substituted ZnPc molecules (−15.96 to −62.86 kJ/mol). This indicates that the incorporation of Me_3Si groups into ZnPc decreases intermolecular interactions, as would be anticipated. The interaction between the Me_3Si-substituted ZnPc molecules, especially the tetra-substituted derivative ($(ZnPc(SiMe_3)_4$, BE = −15.96 kJ/mol), is quite close to that between solvent molecules and between substituted ZnPcs and solvents. Based on differences in polarity, it would also be expected that Me_3Si-substituted ZnPcs



1 **2** **3**

Fig. 3. Schematic representation for singlet-oxygen initiated degradation of $ZnPc(SiMe_3)_x$.

would dissolve in organic solvents much more readily than ZnPc itself, as observed in our experiments.

The semi-empirical PM3 method [14] was employed to calculate the electronic structures of the ZnPc compounds. The calculated heats of formation (ΔH_f) were used to estimate binding energies, and the results are summarized in Table 5. The values obtained were comparable to those from MM calculations. The results also indicate that ZnPc is a planar molecule and has C_{2v} symmetry. Therefore, ZnPc has a large dipole moment (4.05 D) giving strong dipole–dipole interactions between ZnPc molecules. The introduction of Me_3Si into ZnPc at different positions leads to isomeric structures. The energy differences between various isomers of $ZnPc(SiMe_3)_x$ were less than 3 kJ/mol when $x = 1$, and no more than 9 kJ/mol when $x = 2$. The backbones of all Me_3Si-substituted ZnPcs were essentially planar.

The results of prior studies indicate that the photodegradation of organic dyes was increased by electrophilic attack of singlet oxygen ($^1O_2$) [15]. According to frontier MO theory, this reaction takes place only if the energy difference between the HOMO of electron donor and LUMO of electron acceptor is less than ~6 eV. Calculated energies for the frontier MOs of ZnPcs and $^1O_2$ are shown in Table 6. We found that the energy difference between the LUMO of $^1O_2$ and the HOMO of ZnPcs was always less than 1.51 eV. Upon increasing the number of the Me_3Si groups from 0 to 4, the energy difference decreases from 1.51 to 1.26 eV, indicating that the reaction between $^1O_2$ and ZnPcs is somewhat easier when ZnPcs have more Me_3Si groups, but the difference is not statistically significant.

The data provided in Table 7 show that the coefficients for the HOMOs of ZnPcs are larger than 0.05. The HOMOs of ZnPcs are mainly formed by the 2Pz atomic orbital of carbon atoms. In all ZnPcs, there is a pair of carbon atoms located in the same five-member ring having comparable coefficients. They are C11 and C15 in ZnPc, C8 and C10 in $ZnPc(SiMe_3)_1$, $ZnPc(SiMe_3)_3$ and $ZnPc(SiMe_3)_4$, and C22 and C36 in $ZnPc(SiMe_3)_2$ (see numbering in Fig. 4). The coefficients for these pairs were almost identical in magnitude but different in sign. For example, in ZnPc C11 and C15 have coefficients −0.43 and 0.43 respectively. The incorporation of Me_3Si groups had little effect on the coefficient of these atoms and their symmetry

Table 4
MM calculated steric (SE) and the binding (BE) energies (kJ/mol)

Cpd	SE	Cpd	SE	BE
S1	0.04	$(S1)_2$	−1.95	−2.02
S2	−0.10	$(S2)_2$	−1.78	−1.58
S3	4.07	$(S3)_2$	6.59	−1.55
S4	1.11	$(S4)_2$	1.68	−0.55
ZnPc	291.40	$(ZnPc)_2$	318.58	−264.21
$ZnPc(SiMe_3)_1$	181.59	$(ZnPc(SiMe_3)_1)_2$	319.09	−44.10
$ZnPc(SiMe_3)_2$	181.44	$(ZnPc(SiMe_3)_2)_2$	300.02	−62.86
$ZnPc(SiMe_3)_3$	190.17	$(ZnPc(SiMe_3)_3)_2$	349.25	−31.09
$ZnPc(SiMe_3)_4$	182.39	$(ZnPc(SiMe_3)_4)_2$	348.81	−15.96
		ZnPc + S1	282.97	−8.46
		$ZnPc(SiMe_3)_1$ + S1	180.13	−1.50
		$ZnPc(SiMe_3)_2$ + S1	180.79	−0.68
		$ZnPc(SiMe_3)_3$ + S1	187.94	−2.27
		$ZnPc(SiMe_3)_4$ + S1	177.88	−4.54

Table 5
Heats of formation (ΔH_f) and BE values obtained by PM3 method (in kJ/mol)

Cpd	ΔH_f	Cpd	ΔH_f	BE
S1	−87.34	$(S1)_2$	−179.80	−5.12
S2	−223.08	$(S2)_2$	−451.43	−5.27
S3	−400.34	$(S3)_2$	−810.58	−9.90
S4	−237.88	$(S4)_2$	−474.77	0.99
ZnPc	1192.89	ZnPc + S1	1102.18	−3.37
$ZnPc(SiMe_3)_1$	1012.25	$ZnPc(SiMe_3)_1$ + S1	922.18	−2.73
$ZnPc(SiMe_3)_2$	827.77	$ZnPc(SiMe_3)_2$ + S1	739.62	−0.81
$ZnPc(SiMe_3)_3$	671.08	$ZnPc(SiMe_3)_3$ + S1	581.62	−2.12
$ZnPc(SiMe_3)_4$	496.32	$ZnPc(SiMe_3)_4$ + S1	404.06	−4.92

matched that of the LUMO of $^1O_2$. The coefficients of 2Pz orbitals of the oxygen atoms in the LUMO were −0.61 and 0.61, indicating that $^1O_2$ will attack C11 and C15 to begin the decomposition process (cf. Fig. 3).

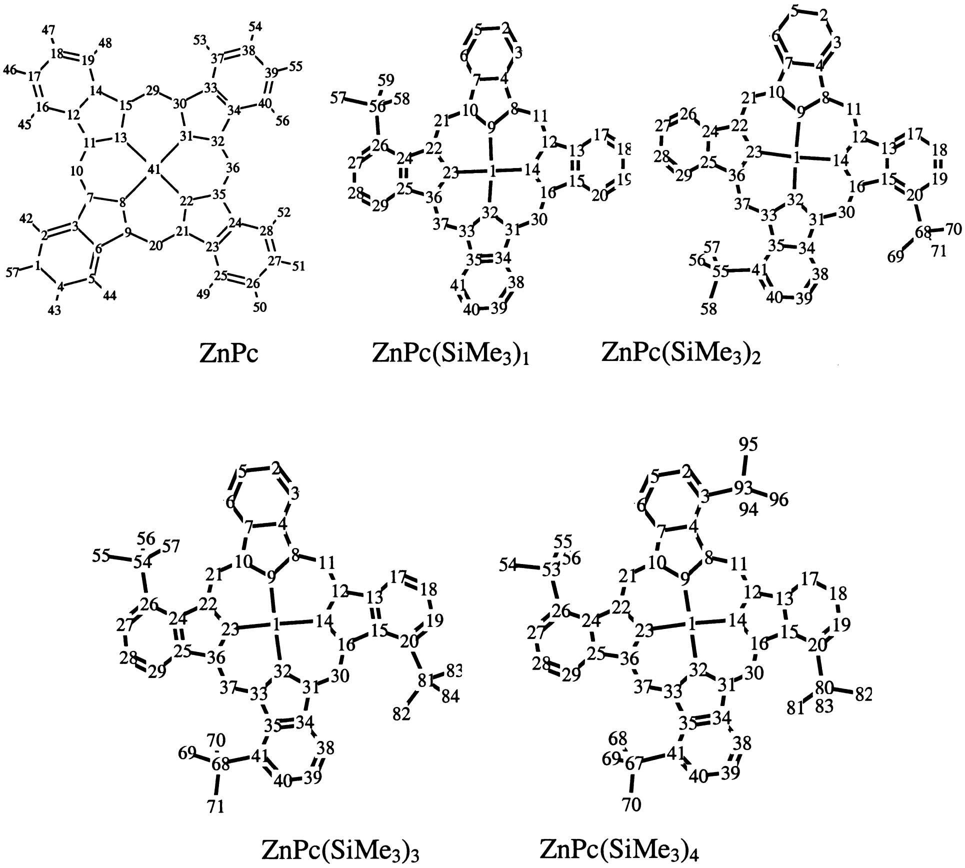
The results of these calculations confirm that the stability of ZnPc arises from strong intermolecular interactions, leading also to extremely low solubility. While the substitution of ZnPc with Me_3Si groups decreases intermolecular interactions and increases solubility in organic solvents, it also enhances photodegradation. Theoretically, molecular ZnPc should have the same reactivity as its TMS derivatives. If it were possible to prepare an isolated ZnPc molecule (non-aggregate form), it

Table 6
The energies (eV) of frontier MOs

	$^1O_2$	ZnPc	ZnPC($SiMe_3$)$_x$			
			$x=1$	$x=2$	$x=3$	$x=4$
HOMO	−5.86	−7.37	−7.32	−7.26	−7.20	−7.12
LUMO	−5.86	−2.28	−2.21	−2.12	−2.08	−2.02

Table 7
The MO coefficients of HOMOs of ZnPcs

	ZnPc		ZnPc($SiMe_3$)$_x$							
			$x=1$		$x=2$		$x=3$		$x=4$	
2Pz	C1	−0.06	C2	0.15	C2	−0.10	C2	0.17	C2	−0.16
	C2	−0.14	C3	0.22	C3	−0.09	C3	0.21	C3	−0.22
	C4	0.10	C4	−0.08	C4	0.06	C4	−0.10	C4	0.09
	C5	0.10	C5	−0.16	C5	0.05	C5	−0.15	C5	0.14
	C6	−0.06	C6	−0.21	C6	0.13	C6	−0.22	C6	0.21
	C7	0.33	C7	0.10	C8	0.19	C7	0.08	C7	−0.08
	C9	−0.21	C8	−0.43	C10	−0.31	C8	−0.41	C8	0.40
	C11	−0.43	C10	0.41	C12	−0.15	C10	0.44	C10	−0.40
	C12	−0.08	C12	0.34	C16	0.15	C12	0.30	C12	−0.31
	C14	0.08	C15	−0.07	C17	0.07	C15	−0.05	C15	0.06
	C15	0.43	C16	−0.22	C20	−0.07	C16	−0.19	C16	0.20
	C16	0.22	C17	−0.14	C22	0.41	C17	−0.13	C17	0.13
	C17	0.16	C18	−0.06	C24	0.09	C19	0.10	C18	0.05
	C18	−0.16	C19	0.11	C25	−0.08	C20	0.09	C19	−0.10
	C19	−0.22	C20	0.11	C26	−0.20	C22	−0.34	C20	−0.10
	C21	0.16	C22	−0.29	C27	−0.16	C25	0.06	C22	0.28
	C25	−0.07	C26	0.13	C28	0.15	C26	0.15	C25	−0.05
	C28	0.07	C27	0.06	C29	0.21	C27	0.07	C26	−0.11
	C30	−0.33	C28	−0.09	C31	−0.21	C28	−0.11	C27	−0.06
	C32	0.21	C29	−0.10	C33	0.33	C29	−0.11	C28	0.08
	C34	0.06	C31	0.16	C34	−0.06	C31	0.15	C29	0.09
	C35	−0.16	C33	−0.14	C36	−0.42	C33	−0.16	C31	−0.15
	C37	0.14	C36	0.18	C38	0.11	C36	0.22	C33	0.15
	C38	0.06	C38	−0.07	C39	0.10	C38	−0.07	C36	−0.19
	C39	−0.10	C41	0.06	C40	−0.07	C41	0.07	C38	0.06
	C40	−0.10			C41	−0.14	C41	−0.06		
2P			C8	−0.10	C22	0.12	C10	0.06	C6	0.05
			C10	0.09	C26	−0.07	C22	−0.07	C8	0.11
			C12	0.08	C27	−0.06			C10	−0.16
			C22	−0.09	C28	0.05			C12	−0.08
			C36	0.18	C29	0.07			C22	0.18
					C36	−0.11			C26	−0.09
									C28	0.06
									C29	0.06
									C33	0.07
									C36	−0.12



ZnPc ZnPc(SiMe$_3$)$_1$ ZnPc(SiMe$_3$)$_2$

ZnPc(SiMe$_3$)$_3$ ZnPc(SiMe$_3$)$_4$

Fig. 4. The structures and atomic numbering of ZnPcs.

would decompose quickly upon exposure to light in the presence of oxygen. This illustrates that solubility is the key factor in the photodegradation of ZnPcs, meaning that the greater the solubility the faster the fading.

4. Conclusions

The synthesis of trimethylsilyl substituted Pcs by reacting lithiated Pcs with chlorotrimethylsilane is a facile low cost method for producing soluble Pcs. It is also clear that the photodegradation of trimethylsilyl-substituted ZnPc follows quasi-first order kinetic decay and that the degradation rates in various organic solvents have differences that are influenced by the solvents' solubility parameters. The nature of the product resulting from the photodegradation process can be determined using GC/MS, and a mechanism for this process was proposed. The proposed mechanism is supported by MO calculations. Finally, it is clear that the substitution of ZnPc with trimethylsilyl groups decreases intermolecular interactions, increasing solubility in organic solvents and causing faster photodegradation.

Acknowledgements

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