Research Article

Synthesis, Characterization and Photostability Studies on Aluminium Phthalocyanine Chloride

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Abstract The synthesis, characterization and photostability studies of aluminium phthalocyanine chloride are hereby presented. Aluminium phthalocyanine chloride was synthesized by a solvent-free procedure involving microwave irradiation of a mixture of hydrated zinc chloride and 1,2-dicyanobenzene (phthalonitrile); the product was thoroughly purified and dried. The percentage yield was 83.4 %. The characterization of the blue product was done via Fourier Transform Infrared Spectroscopy (FTIR) and UV-Visible spectrophotometry, and the results were satisfactory. In the FTIR spectrum, the formation of zinc phthalocyanine was confirmed by the band due to $C\equiv N$ vibrations (around 2100 cm^{-1}) which was present in the phthalonitrile (starting material), but absent in the product (aluminium phthalocyanine chloride). The UV-Visible absorption spectrum showed an intense signal at 672 nm and a weaker one around 350 nm. These bands are taken to be due to $\pi \rightarrow \pi^*$ transitions within the phthalocyanine molecule. The Beer-Lambert's plot for the product resulted in a molar extinction coefficient value of 202,118 M^{-1} cm^{-1}. Photodegradation studies showed that zinc phthalocyanine is very stable towards photoirradiation, with a rather small photodegradation value of 2.73 x10^{-8}.

Introduction

The popularity of phthalocyanine chemistry has been sustained over decades as a result of the wide-ranging relevance of these compounds in the industry and academia [1,2]. The free unmetallated phthalocyanines (Pc) molecule has a two-dimensional geometry and a ring structure consisting of 18 π-electrons, which results in an extensive delocalization of the π-electrons. This delocalization makes the molecule useful as materials for dyes and pigments. The chemistry of phthalocyanines is also exploited in their use as electrocatalysts [3] and photocatalysts [4]. The cavity of a phthalocyanine molecule can play host to most metals to form a metallophthalocyanine (MPc), which are even more useful as electro- and photocatalysts. The literature is very robust on the synthesis of Pcs and MPcs [5-8]; but the mostly used method for the synthesis of MPcs was the one reported by Linstead and co-workers [9-11], which involves heating a metallic salt with phthalodinitrile in a high-boiling solvent. However, the products of these reactions usually lack purity, which calls for a vigorous purification procedure. In this work, by the reaction of phthalonitrile with hydrated metal salt without solvent and under microwave irradiation [12,13] is employed for MPc synthesis. Photostability measurements are required in many industries to characterize the effects of light on the degradation (photo-degradation) and efficacy of their products.

The aim of this work is to synthesize and characterize aluminium phthalocyanine chloride (AlPcCl, Figure 1), which has potential applications in research, industry and medicine. Also, the photostability (estimated in terms of photodegradation quantum yield) of the complex is investigated.
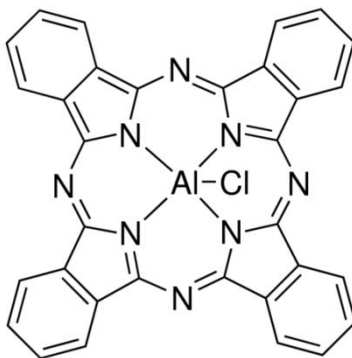

Figure 1: Structure of Aluminium phthalocyanine chloride (AlPcCl)

Materials and Methods

Phthalonitrile and Aluminium chloride hexahydrate (Aldrich) were used as received. Solvents: acetone, dichloromethane, acetonitrile and *N,N'*-Dimethyl formamide were used without further purification.

Equipment: FT-IR spectra (KBr pellets) were recorded on a Perkin-Elmer spectrum 2000 FT-IR spectrometer. UV/Vis spectra were recorded on a Cary 500 UV/Vis/NIR spectrophotometer. Photo-irradiations were done using a General electric Quartz line lamp (300W). 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 20 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.

Synthesis of aluminium phthalocyanine chloride: Irradiation with a microwave oven (Phthalonitrile + AlCl$_3$.6H$_2$O)
A mixture of phthalonitrile (10 mmol, 1.28 g) and finely ground aluminium chloride hexahydrate (2.5 mmol, 0.604 g) was placed in a 25 mL flask. The solid was then irradiated under microwaves for ten minutes. The solid was washed successively with water (15 mL), acetone (15 mL) and dichloromethane (15 mL) and then was dried in air. The solid was extracted by Soxhlet extraction for eight hours with acetonitrile as solvent. After drying at 110 °C, the pure phthalocyanine was analyzed.

Infra-red spectroscopy: The intra-red spectra of phthalonitrile and the synthesized aluminium phthalocyanine chloride were run at Rhodes University, Grahamstown, South Africa (Prof. T. Nyokong's laboratory).

UV-Vis spectrophotometry: A very dilute solution of AlPc ($\sim 3 \times 10^{-6}$ M) was prepared by dissolving 0.038 mg in 20 ml of solvent (DMF). 4 ml of which was introduced into the cuvette. (Molar mass of AlPcCl = 574.96 g mol^{-1})

Photodegradation quantum yield: This was determined using the standard equation employed before [14,15]

$$\Phi_d = \frac{(C_0 - C_t)V.N_A}{I_{abs}.S.t}$$

Where C_0 and C_t are the AlPcCl concentrations before and after irradiation respectively, V is the reaction volume, N_A the Avogadro's constant, S the irradiated cell area and t the irradiation time. I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the AlPcCl. The light intensity (using the power meter described above) of 4.82×10^{16} photons s^{-1} cm^{-2} for Φ_d determination was employed.

Results and Discussion

Synthesis of AlPcCl from phthalonitrile and aluminium chloride: In this work, a solvent-free synthesis of AlPcCl was carried out in a commercial microwave oven (Scheme 1).
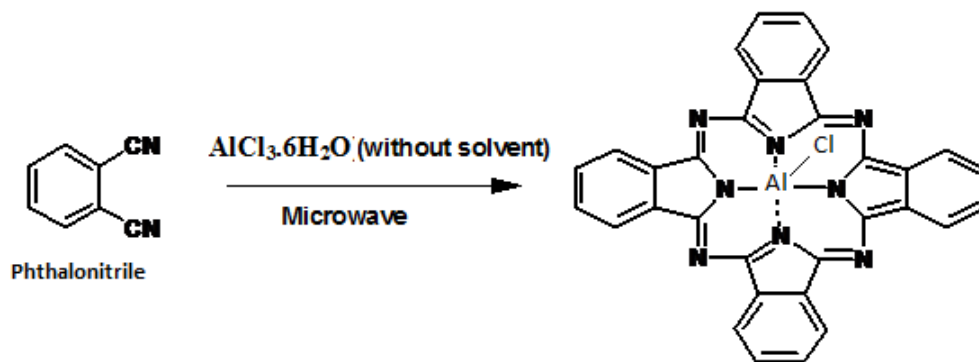
Scheme 1: Microwave-assisted synthesis od aluminium phthalocyanine chloride from phthalonitride and aluminium chloride

The formation of phthalocyanines needs powerful activation (high temperature), but this fact is not a limitation because metallophthalocyanines are thermally very stable. It is not really a dry reaction because water is necessary to obtain a strong coupling with microwave at the beginning of the reaction. The water molecules present in the $AlCl_3.6H_2O$ should provide the required water for microwave absorption. The excess of phthalonitrile and the free phthalocyanine formed were extracted after reaction by washing the product with acetonitrile.

Mass of AlPcCl obtained = 1.199 g

Mass of AlPcCl expected (2.5 mmol) = 1.437 g

$$\% \text{ yield} = \frac{\text{Experimental \ yield}}{\text{Theoretical \ yield}} \text{ x } 100\%$$

$$\% \text{ yield} = \frac{1.199 \text{ g}}{1.437 \text{ g}} \text{ x } 100\% = 83.4\%$$

Characterization of AlPcCl: Infra-red spectra: Infrared spectra of the product showed no characteristic infrared bands corresponding to free phthalocyanine (H_2Pc) (no band at 1336, 1322, 750 and 700 cm^{-1}). Also, the notable band in phthalonitrile around 2200 cm^{-1} was not found in the spectrum of AlPcCl (there is no C≡N bond in AlPcCl); hence the disappearance of the phthalonitrile C≡N signal is taken as being confirmatory for AlPcCl formation. Infra red signals due to the azomethine (C=N) bonds (in the region 160 – 1680 cm^{-1}) in AlPcCl could not be used as confirmatory for AlPcCl formation because these signals could also have arisen from C=C vibrations. Figures 2 – 4 show the FTIR spectra of phthalonitrile, AlPcCl and the overlayed spectra of both compounds.
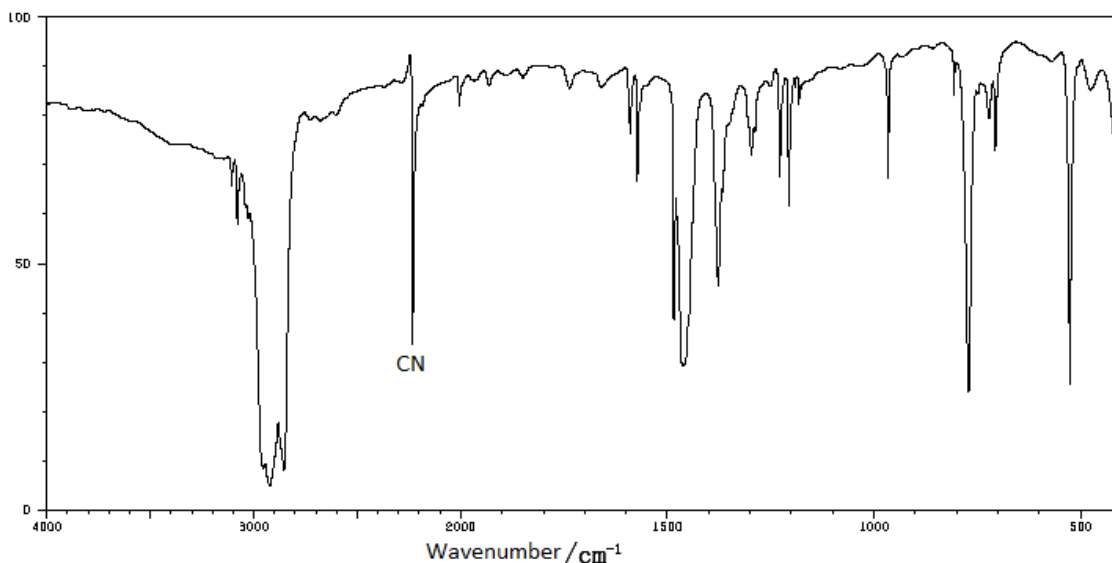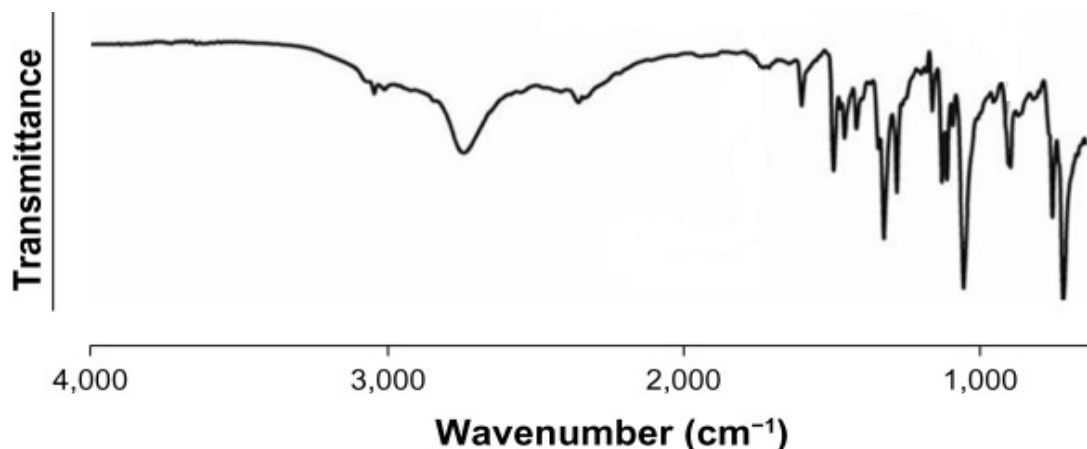

Figure 2: FTIR spectrum of phthalonitrile

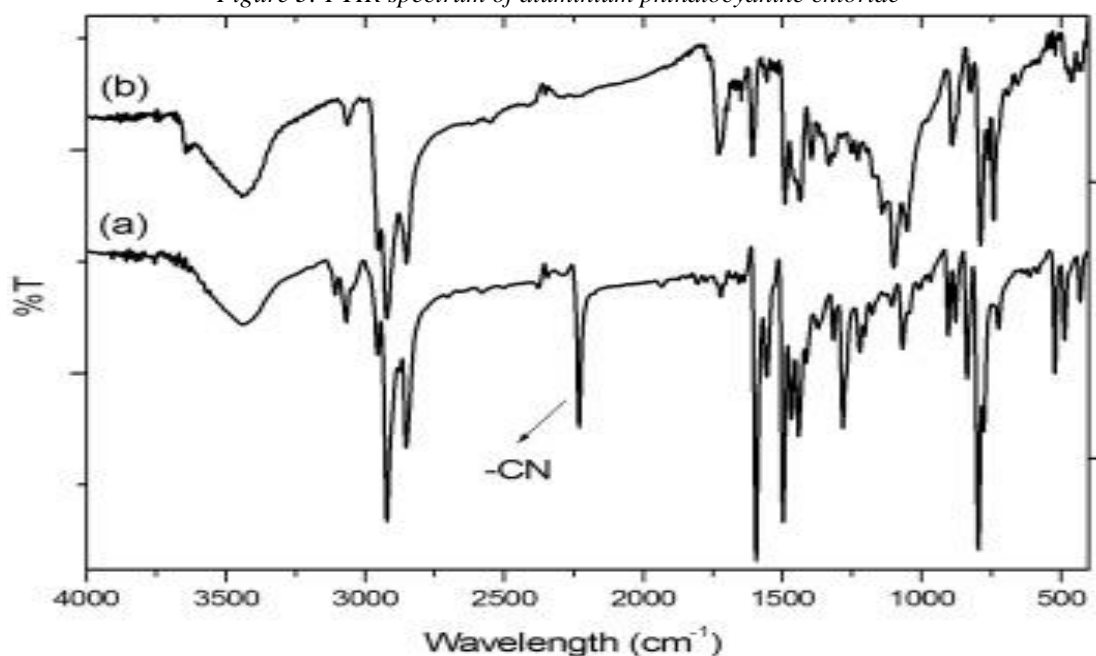*Figure 3: FTIR spectrum of aluminium phthalocyanine chloride*

Figure 4: Overlayed spectra of phthalonitrile and aluminium phthalocyanine chloride showing the disappearance of the C≡N band in the phthalocyanine (around 2200 cm^{-1})

UV-Visible spectrophotometry: Figure 5 shows the UV-Vis absorption spectrum of AlPcCl in DMF. The strong colour of the MPc arise from the strong band in the far red of the visible spectrum (Q band, 672 nm). The more energetic set of transitions are less intense, lying to the blue of the electromagnetic spectrum near 350 nm (B or Soret band). The intense features are due to transitions from bonding to anti-bonding orbitals, $\pi \rightarrow \pi^*$ states. Similar electron transitions are observed in macromolecules like porhyrins. In phthalocyanines the highest occupied molecular orbital (HOMO) of the phthalocyanine ring is $a_{1u}(\pi)$ and the next low-lying orbital is $a_{2u}(\pi)$ [16]. The lowest unoccupied molecular orbital (LUMO) is doubly degenerate $eg(\pi^*)$ and the one after it is $b_{1u}(\pi^*)$ [16]. The π-π^* transition involves a_{1u} to e_g transition which results in the intense Q-band at 672 nm. The π-π^* transitions involving a_{2u} and/or b_{2u} to e_g transition yield the less intense B-band or Soret band which lies near 350 nm,
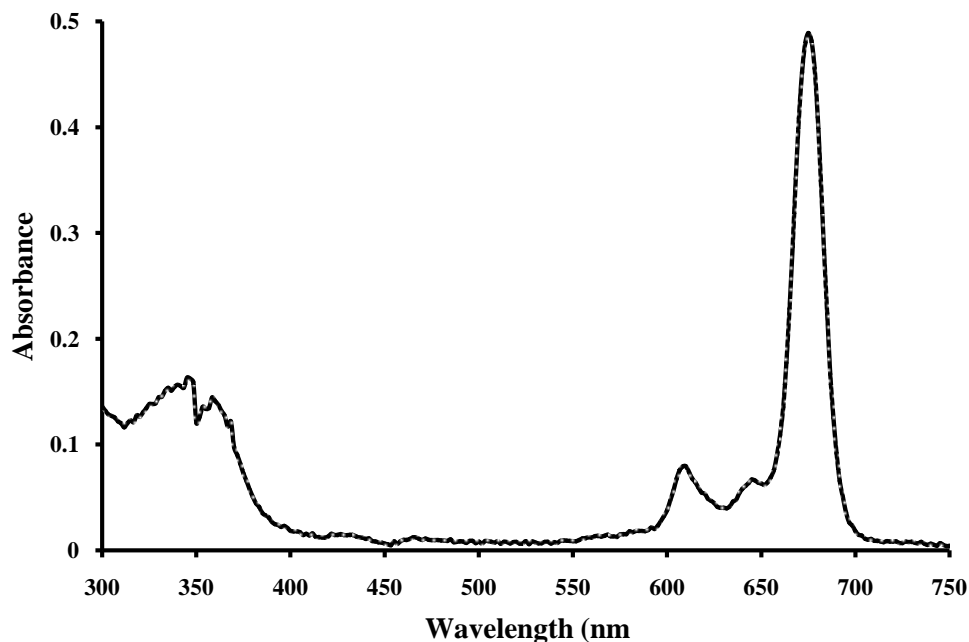
Figure 5: UV-Vis spectrum of Aluminium phthalocyanine chloride in DMF

Molar extinction coefficient of AlPcCl at 672 nm in DMF: The Beer-Lambert's plot for AlPcCl in DMF is shown in Figure 6.
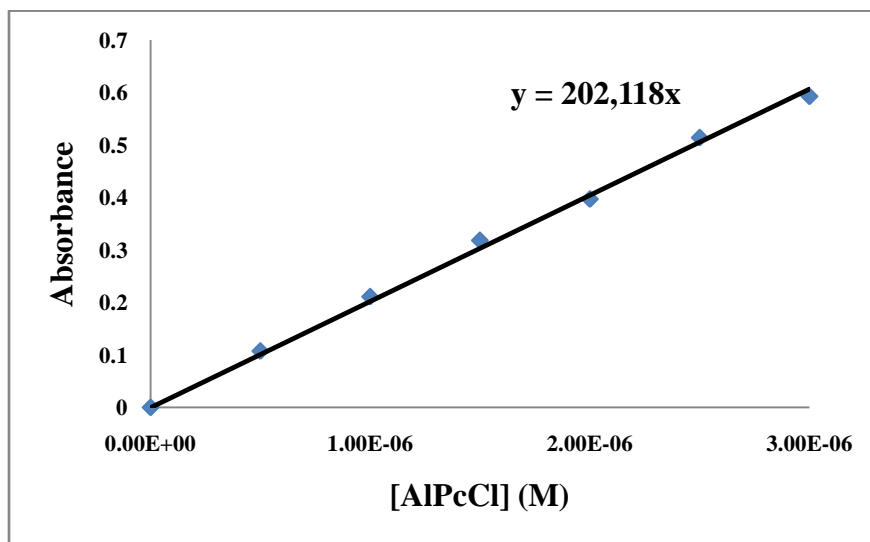

Figure 6: Beer-Lambert's plot for AlPcCl in DMF

The Beer-Lambert's plot (plot of A vs. C) should therefore have a slope of ε.l.

The slope = 202,118; and with the cuvette path length being 1 cm, it follows that the molar extinction coefficient of AlPc (ε) = 202,118 M^{-1} cm^{-1}.

Photodegradation quantum yield of aluminium phthalocyanine chloride: The ability of singlet oxygen to react with macrocyclic metal complexes has been documented [17-20]. Singlet oxygen reacts with tetra-azaporphyrin derivatives in a Diels-Alder [4+2]-cycloaddition, with the MPc ring acting as a diene and singlet oxygen as the dienophile. For metaallophthalocyanines, phthalimide was found to be the photo-oxidation product [18] (Scheme 2).
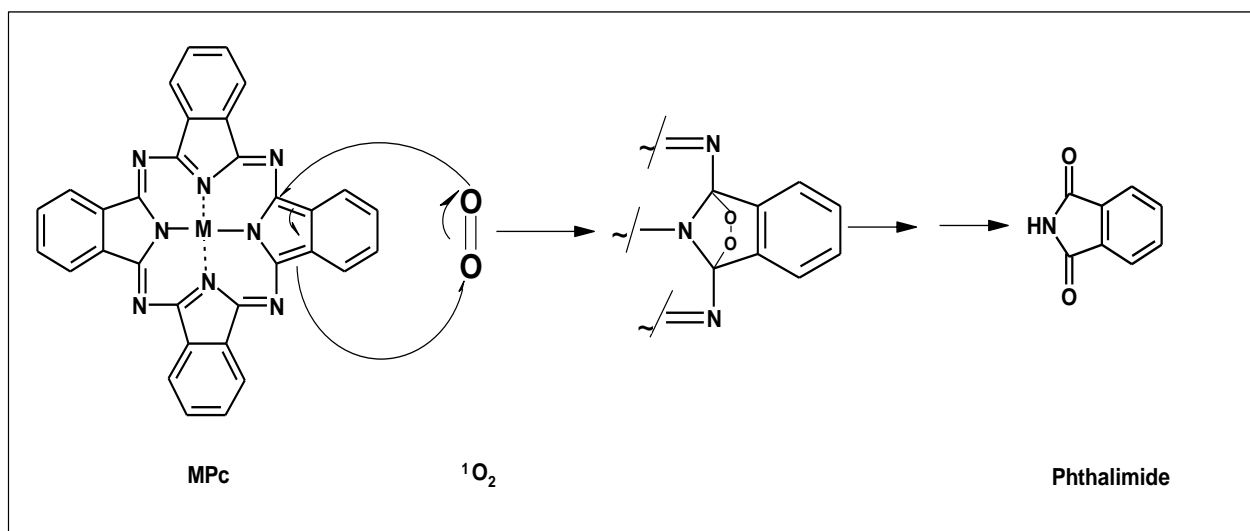
Scheme 2: [4+2] cycloaddition reaction of MPc with singlet oxygen

Photodegradation of is characterised by a decrease in spectral intensities due to the degradation of the phthalocyanine ring in the presence of light.

Table 1 summarizes the result and analysis of data obtained from the AlPcCl photodegradation experiment.

Table 1: Photodegradation data for AlPcCl in DMF

	Before irradiation	After irradiation
Absorbance	0.705	0.577
Concentration (M). $C = \frac{A}{\varepsilon.l}$	3.49×10^{-6}	2.86×10^{-6}
No. of moles (moles) $n = C.V$	1.40×10^{-8}	1.14×10^{-8}

$A = \varepsilon cl$; $\varepsilon = 202,118$ M^{-1} cm^{-1}; $l = 1$ cm; Volume of solution = 4 ml (0.004 L)

$n(AlPcCl)_{Pd} = \Delta n =$ no. of moles of AlPcCl before irradiation - no. of moles of AlPcCl after irradiation

$= (1.40 \times 10^{-8} - 1.14 \times 10^{-8})$ moles $= 2.60 \times 10^{-9}$ moles

Therefore, $\Phi_{Pd} = \dfrac{\text{No.of moles of AlPc degraded}}{\text{No.of moles of photons absorbed}} = \dfrac{n(AlPc)_{Pd}}{n(Photons)_{Abs}} = \dfrac{2.60 \times 10^{-9} \text{ moles}}{0.095 \text{ moles}}$

$\Phi_{Pd} = 2.73 \times 10^{-8}$

Conclusion

The solvent-free microwave-assisted procedure makes a simple, straight-forward and convenient synthetic route to aluminium phthalocyanine chloride. The method is void of troubles associated with choice and handling of solvents; and the yield is quantitative.

AlPcCl exhibits an intense absorption in the red portion of the visible region of the electromagnetic radiation. The molar extinction coefficient for the most intense absorption (at 672 nm) was 202,118 M^{-1} cm^{-1}, implying that only a very small quantity of the substance is needed for strong colouration in solution.

Photodegradation of metallophthalocyanines is characterised by the disappearance of the UV/Visible spectra due to the degradation of the Pc ring in the presence of light. Photostability is important both to the shelf life of the sensitizers, as well as their behaviour inside living tissue. Upon localization in tissues cells, a small fraction of the sensitizer may locate in the neighbouring healthy cells. If irradiated with light, photodegradation of the sensitizer at low concentration may occur before damage is done to the healthy cells; hence a prior knowledge of the photodegradability of a sensitizer meant for medical applications is highly desirable. AlPcCl's photodegradation quantum yield is very low (2.73×10^{-8}), implying that the compound is highly photostable. It is therefore expected

that the shelf life of the compound is very long, and it can withstand long exposures to light without any significant loss of material. However, caution has to be applied if this compound is to be used as a drug, as it is bound to be retained in the patient's system even after treatment.

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