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The synthesis and photophysical properties of novel cationic tetra pyridiloxy substituted aluminium, silicon and titanium phthalocyanines in water

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ABSTRACT

This work reports on the synthesis, characterisation and photophysical properties of new unquaternized β-2,(3)-tetra-(2 pyridiloxy) aluminium(III) (**3a**), silicon(IV) (**3b**), titanium(IV) (**3c**) phthalocyanines and their water-soluble quaternized counterparts, **4a**, **4b** and **4c**, respectively. The water-soluble silicon(IV) (**4b**) and titanium(IV) (**4c**) phthalocyanine derivatives were found to be aggregated in aqueous media but were partially or fully disaggregated in the presence of a surfactant Cremophor® EL (CEL). The photophysical properties of aggregated complexes were investigated both in the presence of CEL and in pH 11 alone. Low triplet and fluorescence yield were obtained in pH 11 but an improvement was achieved upon addition of CEL for the aggregated complexes. The unquaternized silicon(IV) phthalocyanine complex (**3b**) gave the highest triplet quantum yield of 0.77 in DMF followed by its quaternized derivative (**4b**) with triplet yield of 0.73 in pH 11 plus CEL. The highest triplet lifetime of 220 μs was obtained for **4b** in the presence of CEL. Higher fluorescence yields of 0.23 were obtained for quaternized water-soluble aluminium(III) phthalocyanine derivative (**4a**) in the presence of CEL.

1. Introduction

The synthesis of metallopthalocyanine (MPc) complexes has attracted attention due to their technological importance. The structure of phthalocyanine complexes may be engineered for specific applications by introducing different metals and non-metals to its cavity [1]. The ease of varying the chemical properties of these molecules has promoted their applications in areas such as dye-sensitised solar cell [2,3], photodynamic therapy of cancer (PDT) [4–6], electrocatalysis [7,8], chemical sensors, liquid crystals, and in non-linear optical limiters devices [9–16]. The properties of MPc complexes cannot be fully exploited since they have low solubility in common organic solvents and they tend to aggregate. Recently much focus has been paid to modifying the metallophthalocyanine complexes by introducing substituents on the peripheral and non-peripheral positions of the ring in order to improve solubility and reduce aggregation [17–20]. In this work we report on the synthesis and photophysical behaviour of aluminium(III), silicon(IV) and titanium(IV) phthalocyanines tetrasubstituted with pyridiloxy substituents at the peripheral position and their quaternized water-soluble derivatives. Tetrasubstituted cationic MPc complexes (such as those containing pyridiloxy reported in this work) [21–24] are more prone to aggregation than eight or more substituted derivatives. For example, for a series of zinc and aluminium phthalocyanines substituted with pyridiniomethyl groups, as the number of cation substituents increased, the aggregation ability of phthalocyanines were found to decrease in aqueous media, and the quantum yields of fluorescence and singlet oxygen generation increased as well as the photodynamic inactivation of bacteria [25,26]. The reason for such monomeric state of these complexes was attributed to strong electrostatic repulsive force of eight charges thereby preventing the formation of the aggregates [25]. However, it has been documented that tetrasubstituted phthalocyanines are more soluble than their octa-substituted counterparts due to formation of constitutional isomers and that they possess high dipole moments [21], hence they are studied in this work.

We have recently reported the synthesis and photophysical properties of cationic water-soluble phthalocyanines complexes of indium, zinc, and gallium substituted with the pyridyloxy groups at the periphery which readily formed aggregates in aqueous solutions [24]. Cationic AlPc complexes containing pyridiloxy substituents have been reported [25], but no photophysical data is available on these complexes. Also quaternized TiPc complexes containing pyridiloxy groups are reported in this work. Unquaternized pyridiloxy substituted SiPc complex has been reported [27] however, its quaternization is reported in this work. We show in this work that the tetrasubstituted quaternized pyridiloxy AlPc is monomeric, contradicting the observation that terasubstitution results in aggregation in these complexes. For those MPc complexes that are aggregated, the photophysical behaviour is studied in the presence of a surfactant Cremophor® EL.

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2. Experimental and method

2.1. Materials

Potassium carbonate, Cremophor® EL [CEL, registered trade mark of Badische Anilin Soda Fabric (BASF)], 2-hydroxypyridine, D_2O, DMSO-d_6, K_2CO_3, dimethyl sulphate (DMS), aluminium(III) chloride, titanium(IV) butoxide and silicon(IV) chloride were obtained from Aldrich. Quinoline, dimethylsulphoxide (DMSO), methanol, *n*-hexane, chloroform ($CHCl_3$), dichloromethane (DCM), tetrahydrofuran (THF), acetone, ethanol and dimethylformamide (DMF) were dried according to reported procedures [28] before use. Zinc phthalocyanine was purchased from Aldrich and Zn tetrasulfonated phthalocyanine (ZnTSPc) was synthesised and purified according to well-known procedures [29]. Phosphate-buffered pH 11 solution was prepared using appropriate amounts of Na_2HPO_4 (0.005 mol) and NaOH (8.2×10^{-4} mol) in 100 mL distilled water.

2.2. Equipment

UV–visible spectra were recorded on a Varian 500 UV–vis/NIR spectrophotometer. ^{1}H NMR spectra were recorded using a Bruker EMX 400 MHz NMR spectrometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluoremeter. IR spectra (KBr pellets) were recorded on a Perkin-Elmer spectrum 2000 FTIR spectrometer. Laser flash photolysis experiments were performed with light pulses produced by a Quanta-Ray Nd: YAG laser providing 400 mJ, 9 ns pulses of laser light at 10 Hz, pumping a Lambda-Physik FL3002 dye (Pyridin 1 dye in methanol). Single pulse energy ranged from 2 to 7 mJ. The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as a detector. Signals were recorded with a digital real-time oscilloscope (Tektronix TDS 360). The solutions (absorbance ~ 1.5 at the Q band) for triplet quantum yields and lifetimes were introduced into a 1 cm pathlength UV/visible spectrophotometric cell, deaerated using argon (bubbled for 30 min) and irradiated at the Q band maxima with laser flash photolysis equipment described above.

The triplet lifetimes were then determined by exponential fitting of the kinetic curves using the program OriginPro 7.5.

2.3. Synthesis

The synthesis of 4-(2-pyridyloxy) phthalonitrile (**2**) has been reported before [30]

2.3.1. β-2,(3)-(tetra-2-pyridyloxyphthalocyaninato) aluminium(III) chloride (Scheme 1, (ClAlT-2-PyPc, *3a*))

A mixture of excess anhydrous aluminium(III) chloride (0.60 g, 3.4 mmol), 2-pyridyloxyphthalonitrile (**2**) (1.50 g, 6.8 mmol) and quinoline (5 mL, doubly distilled over CaH_2) was stirred at 180 °C for 24 h under nitrogen atmosphere. The solution was then cooled and dropped in *n*-hexane. The green solid product was precipitated and collected by centrifugation and washed with *n*-hexane. The crude product was dissolved in DMF. After concentrating, the dark green waxy product was precipitated with hot ethanol and washed with ethanol, acetone, THF, $CHCl_3$, *n*-hexane and diethylether in a Soxhlet extraction apparatus.

Yield: (57%). IR (KBr, cm^{-1}): 3442(O–H), 3114(C–H), 1560(C=C), 1450, 1341, 1100(C–O–C), 843, 748, 610, 543. ^{1}H NMR (DMSO-d_6): δ, ppm 8.74–9.02 (4 H, m, Pc-H), 9.16–9.19 (4 H, d, Pc-H), 9.53–9.60 (4 H, m, Pc-H), 8.19–8.21 (4 H, br, pyridyl-H), 8.10–8.16 (8 H, m, pyridyl-H), 7.94–7.99 (4 H, br, pyridyl-H). UV/Vis (DMF) λ_{max} nm (log ε): 354 (3.87), 676 (5.12). Calc. for C_{52} $N_{12}H_{28}O_4ClAl$: C 65.98, H 2.96, N 17.76; Found: C 65.59, H 3.46 N 17.58.

2.3.2. β-2,(3)-(tetra-2-pyridyloxyphthalocyaninato) silicon(IV) dichloride (Scheme 1, $(Cl)_2$SiT-2-PyPc, *3b*))

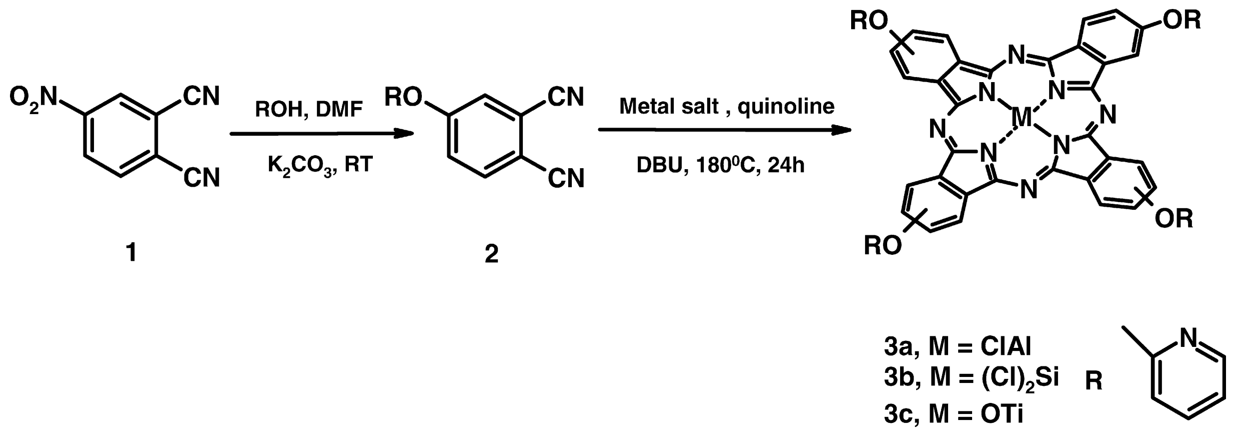
The synthesis and purification of the silicon(IV) phthalocyanine complex **3b** is as outlined for the aluminium(III) phthalocyanine complex (**3a**), except that about 1 mL of the $SiCl_4$ was employed instead of aluminium(III) chloride. Purification procedure and the amounts of the rest of the reagents were as outlined for **3a**.

Yield: (42%). IR (KBr, cm^{-1}): 3437(O–H), 3110(C–H), 1569(C=C), 1500, 1226, 1089(C–O–C), 837, 753, 639, 582, 524, 482(Si–Cl), 448. ^{1}H NMR (DMSO-d_6): δ, ppm 8.99–9.09 (4 H, m, Pc-H), 9.22–9.37 (4 H, d, Pc-H), 9.56–9.61 (4 H, m, Pc-H), 8.14–8.19 (4 H, br, pyridyl-H), 7.97–8.11 (8 H, m, pyridyl-H), 7.83–7.90 (4 H, br, pyridyl-H). UV/Vis (DMF) λ_{max} nm (log ε): 347 (3.52), 674 (5.03). Calc. for C_{52} $N_{12}H_{28}O_4Cl_2Si$: C 68.41, H 2.85, N 17.10; Found: C 67.95, H 3.2, N 16.98.

2.3.3. β-2,(3)-(tetra-2-pyridyloxyphthalocyaninato) oxotitinium (IV) (Scheme 1, (OTiT-2-PyPc, *3c*))

The synthesis and purification of (**3c**) is as outline for the aluminium(III) phthalocyanine complex (**3a**) except Ti(IV) butoxide was employed instead of aluminium(III) chloride. Purification procedure and the amounts of the rest of the reagents were as outlined for **3a**.

Yield: (64%). IR (KBr, cm^{-1}): 3438 (O–H), 3116(C–H), 1557(C=C), 1384, 1223, 1096(C–O–C), 981(T=O),826, 757, 645, 589, 543. ^{1}H NMR (DMSO-d_6): δ, ppm 8.86–8.99 (4 H, m, Pc-H), 9.22–9.34 (4 H, d, Pc-H), 9.53–9.58 (4 H, m, Pc-H), 8.10–8.19 (4 H, br, pyridyl-H),



Scheme 1. The synthesis of chloro-aluminium(III) (**4a**), dichloro-silicon(IV) (**4b**), and oxo-titanium(IV) (**4c**) phthalocyanines tetrasubstituted with 2-pyridyloxy groups.