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Novel, soluble, FluXoro functional substituted zinc phthalocyanines; synthesis, characterization and photophysicochemical properties

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ABSTRACT

Three novel phthalonitriles and the respective, peripheral tetrakis zinc phthalocyanines were synthesized and characterized using elemental analysis, IR, ^{1}H NMR, mass spectra and electronic spectroscopy. The phthalocyanines displayed good solubility in organic solvents such as $CHCl_3$, DCM, DMSO, DMF, THF and toluene. The presence of a long chain fluorine substitituent was found to result in reduced aggregation. The singlet oxygen, photodegradation, fluorescence quantum yield, triplet quantum yield and triplet life time of the complexes in toluene were determined. The effect of fluoro-functional groups on the photophysical and photochemical parameters of the zinc(II) phthalocyanines are also reported. Fluorescence quantum yields for the complexes ranged from 0.021 to 0.041

1. Introduction

Metallophthalocyanines (MPcs) have potential applications in many areas such as in medicinal and material science [1–3]. MPcs enjoy usage in printing inks, catalysis, display devices, data storage, chemical sensors, gas sensors, solar cells, organic light emitting devices (OLED) and photonic devices [4–6]. Owing to their strong and long-wavelength absorption, highly efficient reactive oxygen specie generation (ROS) and ease of chemical modification, phthalocyanines have emerged as a promising class of second-generation photosensitizers for photodynamic therapy (PDT), [7–16]. Over the last decade, a substantial number of phthalocyanine-based photosensitizers have been prepared and evaluated for their photodynamic activity, with the focus being on silicon, zinc and aluminium analogues as a result of their desirable photophysical properties.

Unsubstituted phthalocyanines are generally insoluble in organic solvents. The introduction of different types of substituents such as alkyl, alkoxyl, phenoxyl and macrocyclic groups into the peripheral of the Pc ring enhances solubility [17,18]. Recently, fluorinated MPcs are receiving a great deal of attention [19–23].

Fluorinated phthalocyanines have been reported to show improved photosensitizer activity for PDT compared to non-fluorinated derivatives [24,25]. However, the study of photochemical and photophysical properties of fluorinated MPc complexes is still very limited. Our previous papers have described synthesis, photophysical and photochemical properties of zinc phthalocyanines carrying various substituents [26–28]. In this work, we describe the photophysical and photochemical properties of the three novel zinc-phtalocyanines peripherally tetra substituted with fluoro groups (Scheme 1, complexes **4**–**6**), which show good solubility in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran (THF), dimethylformamide (DMF) and toluene. The effect of different fluoro groups on the photophysical and photochemical properties of ZnPc will be evaluated in toluene. Fluorine substituted MPc complexes are of interest since conjugation (or its lack) with the Pc ring influences photophysical properties [29] therby enabling the design of MPc complexes with optimal photophysical properties. The novel zinc phthalocyanines described herein displayed good photophysical and photochemical properties with high singlet oxygen quantum yield in toluene. The presence of sulfur in the complexes is expected to result in red shifting of the Q band.

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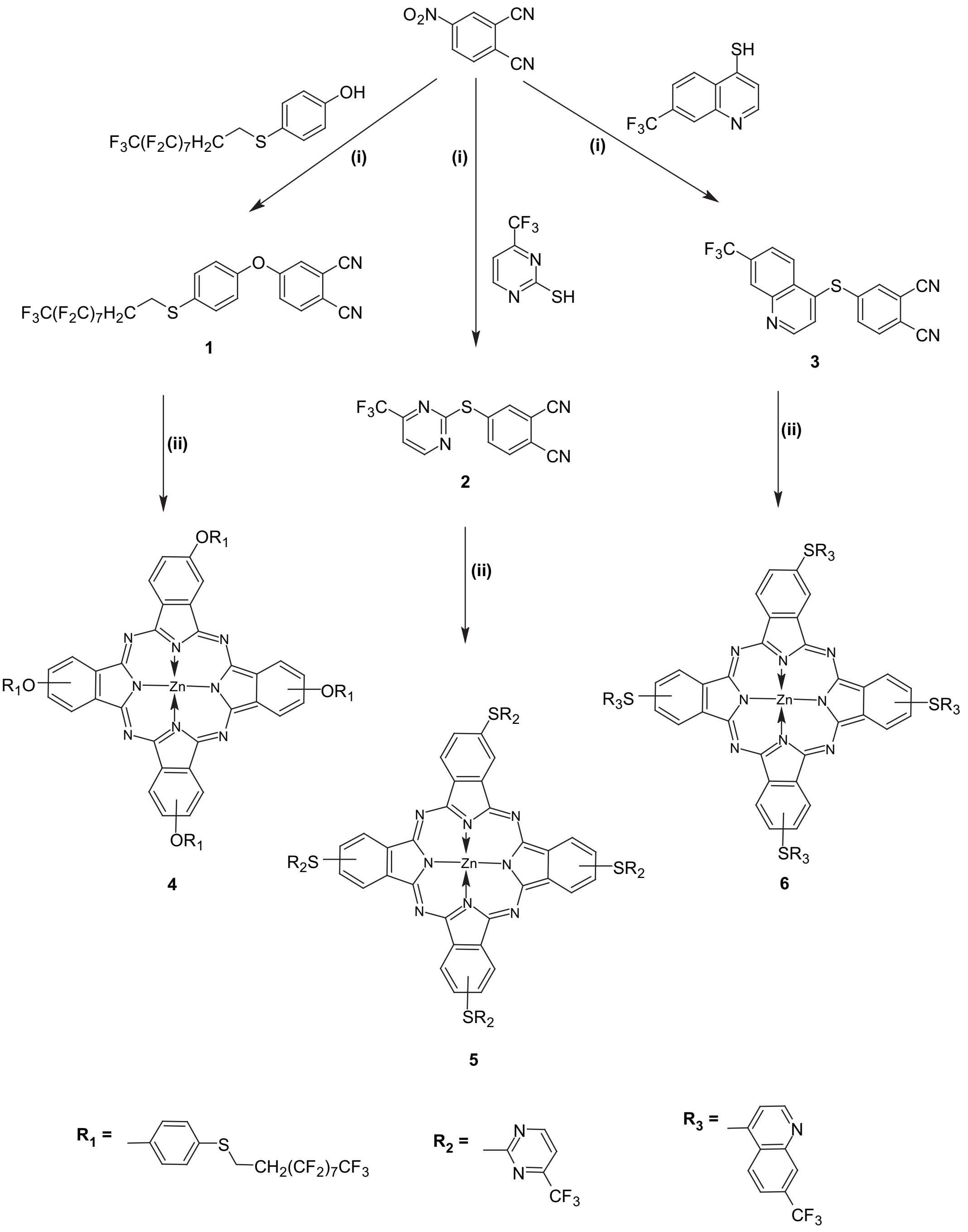

Scheme 1. Synthetic route of three phthalonitriles (**1**, **2** and **3**), (i) DMF, K_2CO_3, 24h; and their zinc phthalocyanines derivatives (**4**, **5** and **6**) (ii) anhydrous $Zn(Ac)_2$, pentanol, 15h, DBU, argon atm.

2. Experimental

2.1. Materials and equipment

Dimethyl sulfoxide (DMSO), *N,N′*-dimethylformamide (DMF), chloroform ($CHCl_3$), tetrahydrofuran (THF), methanol (MeOH), dicholoromethane (DCM), 1-pentanol, n-hexane, acetone and toluene were purchased from SAARCHEM; zinc phthalocyanine (ZnPc), 1,2-diphenyi*so*benzofuran (DPBF), 4-nitrophthalonitrile, 7-(trifluoromethyl)quinoline-4-thiol, 4-(trifluoromethyl)pyrimidine-2-thiol, 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylthio)phenol, 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU), potassium carbonate, and zinc acetate were purchased from Aldrich.

FTIR spectra (KBr pellets) were recorded on a Perkin–Elmer spectrum 2000 FTIR spectrometer. UV/Vis spectra were recorded on a Cary 500 UV/Vis/NIR spectrophotometer. ^1H and spectra were obtained in $CDCl_3$ using a Bruker EMX 400 NMR spectrometer. Elemental analyses were done on Vario Elementar EL III. Fluorescence spectra were recorded on the Varian Eclipse spectrofluoremeter. Triplet absorption and decay kinetics were recorded on a laser flash photolysis system, the excitation pulses were produced by a Nd: YAG laser (Quanta-Ray, 1.5 J/90 ns) pumping a dye laser (Lambda Physic FL 3002, Pyridin 1 in methanol).

The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as detector. Signals were recorded with a two-channel digital real-time oscilloscope (Tektronix TDS 360); the kinetic curves were averaged over 256 laser pulses. 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. MALDI-TOF mass spectra were recorded using an Applied Biosystems Voyager-DE STR at the University of Stellenbosch in Cape Town, with 2,5-dihydroxy benzoic acid as matrix. The mass spectra for phthalonitriles (**1**–**3**) were acquired on a Bruker Daltonics, MicrOTOF mass spectrometer equipped with an electronspray ionization (ESI) source.

2.2. Synthesis

*2.2.1. 4-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylthio)phenoxy]-phthalonitrile (**1**)*

4-Nitrophthalonitrile (0.30 g 1.75 mmol) was dissolved in dry DMF (15 mL) under argon and 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylthio)phenol (1.00 g 1.75 mmol) was added. After stirring for 30 min at room temperature, finely ground anhydrous potassium carbonate (0.73 g 5.25 mmol) was added in portions during 2 h with efficient stirring. The reaction mixture was stirred under argon atmosphere at room temperature for 24 h after which time, the ensuing mixture was poured into 100 mL iced water and the precipitate filtered off, washed with water and methanol and then dried. The crude product was chromatographed over a silica gel column using a mixture of $CHCl_3$:MeOH (100:5 (v:v)) as eluent, giving a powder of 4-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylthio)phenoxy]-phthalonitrile (**1**). Finally, the pure powder was dried in a vacuum. Yield: 0.78 g (65%). IR spectrum (cm^{-1}): 3075 (Ar-CH), 2234 (C≡N), 1602 (C=C), 1584, 1486, 1370 (C–F), 1314, 1249, 1083 (C–O–C), 1036, 954, 778, 664 (C–S–C). ^{1}H NMR ($CDCl_3$): $\delta = 7.77$ (d, $J = 8.70$ Hz, 1H, Ar-H), 7.50 (d, $J = 8.76$ Hz, 2H, Ar-H), 7.34–7.10(m, 4H, Ar-H), 3.18 (t, 2H, CH_2), 2.54–2.40 (m, 2H, CH_2). Calcd for $C_{24}H_{11}F_{17}N_2OS$: C, 41.21; H, 1.73; N, 4.01; S, 4.58%. Found: C, 41.34; H, 1.79; N, 3.97; S, 4.65%. MS (ESI-MS) *m/z*: Calc. 698.4; Found: 721.1 $[M + Na]^+$.

*2.2.2. 4 [4-(Trifluoromethyl)pyrimidine-2-thio]-phthalonitrile (**2**)*

The synthesis of **2** was similar to that of **1**, except 4-(trifluoromethyl)pyrimidine-2-thiol (1.00 g 5.55 mmol) was employed instead of -(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylthio) phenol. The amounts of the other reagents were: 4-nitrophthalonitrile, 0.96 g (5.55 mmol) and anhydrous potassium carbonate, 1.92 g (13.88 mmol).

Yied: 0.40 g (23%). IR spectrum (cm^{-1}): 3081, 3021 (Ar-CH), 2227 (C≡N), 1572 (C=C), 14 377, 1386 (C–F), 1232, 1034, 990, 866, 799, 719, 661 (C–S–C). ^{1}H NMR ($CDCl_3$): $\delta = 8.41$ (s, 1H, Ar-H), 7.76 (d, $J = 4.83$ Hz, 1H, Ar-H), 7.49–7.06 (m, 3H, Ar-H). Calcd for $C_{13}F_3H_5N_4S$: C, 50.98; H, 1.65; N, 18.29; S, 10.47%. Found: C, 50.93; H, 1.71; N, 18.23; S, 10.53%. MS (ESI-MS) *m/z*: Calc. 306.3; Found: 329.1 $[M + Na]^+$.

*2.2.3. 4-[7-(Trifluoromethyl)quinoline-4-thio]-phthalonitrile (**3**)*

The synthesis of **3** was similar to that of **1**, except 7-(trifluoromethyl)quinoline-4-thiol (1.00 g 4.40 mmol) was employed instead of 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylthio) phenol. The amounts of the other reagents were: 4-nitrophthalonitrile, 0.76 g (5.55 mmol) and anhydrous potassium carbonate, 1.52 g (11.00 mmol). Yied: 0.60 g (38%). IR spectrum (cm^{-1}): 3090, 3047 (Ar-CH), 2235 (C≡N), 1582 (C=C), 1454, 1353 (C–F), 1288, 1065, 974, 884, 778, 679 (C–S–C). ^{1}H NMR ($CDCl_3$): $\delta = 9.03$–8.89 (m, 1H, Ar-H), 8.69-8-53 (m, 2H, Ar-H), 8.43–8.11 (m, 2H, Ar-H), 7.85–7.53 (m, 3H, Ar-H). Calcd for $C_{18}H_8F_3N_3S$ C, 60.84; H, 2.27; N, 11.83; S, 9.02%. Found: C, 60.91; H, 2.32; N, 11.78; S, 8.95%. MS (ESI-MS) *m/z*: Calc. 355.3; Found: 378.1 $[M + Na]^+$.

*2.2.4. (4)-tetra[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylthio)phenoxy]-phthalocyaninato zinc(II) (**4**)*

Compound **1** (0.50 g, 0.72 mmol), anhydrous zinc acetate (0.16 g, 0.72 mmol) and 2 mL of dry 1-pentanol were placed in a standard Schlenk tube in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.45 mL, 0.29 mmol) under a nitrogen atmosphere and held at reflux temperature for 15 h. After cooling to room temperature, the reaction mixture was precipitated by adding it drop-wise into water. The crude product was precipitated, collected by filtration and washed with water, hexane, ethanol and methanol and then dried. The crude green product was further purified by chromatography over a silica gel column using THF, $CHCl_3$ and a mixture of THF and CH_2Cl_2 (1:50 by volume), as eluent respectively. Yield: 45 mg (10%). UV–Vis (toluene): λ_{max} nm (log ε) 355 (4.66), 613 (4.39), 679 (5.11). IR spectrum (cm^{-1}): 3073 (Ar-CH), 2935, 2856 (CH), 1589 (C=C), 1487, 1398, 1334 (C–F), 1237, 1088 (C–O–C), 952, 815, 745, 731, 617 (C–S–C). ^{1}H NMR ($CDCl_3$): $\delta = 8.42$–7.26 (28H, m, Ar-H), 3.32–3.21 (m, 8H, CH_2), 2.61–2.49 (m, 8H, CH_2). Calcd for $C_{96}H_{44}F_{68}N_8O_4S_4Zn$: C, 41.33; H, 1.85; N, 3.92; S, 4.49%. Found: C, 42.39; H, 2.00; N, 4.09; S, 4.37%. MS (ES^+), (*m/z*): Calc. 2858; Found: 2849 [M − 9H].

*2.2.5. (4)-tetra-[4-(Trifluoromethyl)pyrimidine-2-thio] phthalocyaninato zinc(II) (**5**)*

The synthesis and purification of **5** was as outlined for **4**, except compound **2** (0.30 g, 0.10 mmol) was employed instead of complex **1**. The amounts of the other reagents were anhydrous zinc acetate (0.21 g, 0.10 mmol), dry 1-pentanol (2 mL) and DBU (0.23 mL, 0.15 mmol). Yield: 35 mg (12%). UV–Vis (toluene): λ_{max} nm (log ε) 368 (4.70), 622 (4.42), 684 (5.12). IR spectrum (cm^{-1}): 3066 (Ar-CH), 1618 (C=C), 1431, 1392, 1363 (C-F), 1231, 1026, 930, 862, 812, 772, 619 (C–S–C). ^{1}H NMR ($CDCl_3$): $\delta = 8.79$–7.11 (20H, m, Ar-H). Calcd for $C_{52}H_{20}F_{12}N_{16}S_4Zn$: C, 48.40; H, 1.56; N, 17.37; S, 9.94%. Found: C, 49.15; H, 1.67; N, 17.79; S, 10.32%. MS (ES^+), (*m/z*): Calc. 1290.5; Found: 1291.6 $[MH^+]$.

*2.2.6. (4)-tetra-[7-(trifluoromethyl)quinoline-4-thio] phthalocyaninato zinc(II) (**6**)*

The synthesis and purification of **6** was as outlined for **4**, except compound **3** (0.50 g, 1.41 mmol) was employed instead of complex **1**. The amounts of the other reagents were anhydrous zinc acetate (0.30 g, 1.41 mmol), dry 1-pentanol (3 mL) and DBU (0.45 mL, 0.29 mmol). Yield: 35 g (7%). UV–Vis (toluene): λ_{max} nm (log ε) 360 (4.76), 619 (4.49), 689 (5.17). IR spectrum (cm^{-1}): 3079 (Ar-CH), 1617 (C=C), 1463, 1385, 1364 (C–F), 1233, 1069, 980, 907, 853, 833, 741, 618 (C–S–C). ^{1}H NMR ($CDCl_3$): $\delta = 8.92$–7.18 (32H, m, Ar-H). Calcd for $C_{72}H_{32}F_{12}N_{12}S_4Zn$: C, 58.16; H, 2.17; N, 11.31; S, 8.63%. Found: C, 59.11; H, 2.32; N, 12.04; S, 8.79%. MS (ES^+), (*m/z*): Calc. 1468.8; Found: 1489.6 $[MH^+]$.

2.3. Photophysical studies

2.3.1. Fluorescence quantum yields

Fluorescence quantum yields (Φ_F) were determined by the comparative method [30,31], (Eq. (1)):

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

where F and F_{Std} are the areas under the fluorescence emission curves of **4** to **6** and the standard, respectively. A and A_{Std} are the respective absorbances of the sample and standard at the excitation wavelengths (which was ~0.05 in the solvent used), and n and n_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc in toluene ($\Phi_F = 0.07$) [32], was employed as the standard.

2.3.2. Triplet quantum yields and lifetimes

The solutions for triplet quantum yields and lifetimes were introduced into a 1.0 mm pathlength UV/visible spectrophotometric cell, deaerated using nitrogen and irradiated at the Q band maxima. Triplet state quantum yields (Φ_T) of **4** to **6** were determined by the triplet absorption method [33], using zinc phthalocyanine (ZnPc) as a standard, Eq. (2):

$$\Phi_T = \Phi_T^{Std} \cdot \frac{\Delta A_T \cdot \varepsilon_T^{Std}}{\Delta A_T^{Std} \cdot \varepsilon_T} \quad (2)$$

where ΔA_T and ΔA_T^{Std} are the changes in the triplet state absorbances of **4** to **6** and the standard, respectively. ε_T and ε_T^{Std} are the triplet state molar extinction coefficients for **4** to **6** and the standard, respectively. Φ_T^{Std} is the triplet quantum yield for the standard, ZnPc ($\Phi_T = 0.65$ in toluene [34]). ε_T and ε_T^{Std} were determined from the molar extinction coefficients of their respective ground singlet state (ε_S and ε_S^{Std}) and the changes in absorbances of the ground singlet states (ΔA_S and ΔA_S^{Std}), according to Eq. (3):

$$\varepsilon_T = \varepsilon_S \cdot \frac{\Delta A_T}{\Delta A_S} \quad (3)$$

Quantum yields of internal conversion (Φ_{IC}) were obtained from Eq. (4), which assumes that only three processes (fluorescence, intersystem crossing and internal conversion), jointly deactivate the excited singlet state of the **4** to **6** molecules.

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T) \quad (4)$$

2.4. Photochemical studies

2.4.1. Singlet oxygen quantum yields

Quantum yields of singlet oxygen photogeneration were determined as previously explained in detail [32,35–37] in air (no oxygen bubbled) using the relative method with ZnPc as reference and DPBF as chemical quencher for singlet oxygen, using Eq. (5):

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

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard, ZnPc ($\Phi_\Delta = 0.58$ in toluene [32]). R_{DPBF} and R_{DPBF}^{Std} are the DPBF photobleaching rates in the presence of **4** to **6** and the standard respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by **4** to **6** and the standard respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [38], the concentration of DPBF was ~3 × 10^{-5} mol L^{-1}. Solutions of sensitizer (absorbance = 1.1 at the irradiation wavelength) containing DPBF were prepared in the dark and irradiated in the Q band region using the setup described above. DPBF degradation at 417 nm was monitored. The light intensity used for singlet oxygen studies was 2 × 10^{15} photons s^{-1} cm^{-2}. The error in the determination of Φ_Δ was ~10% (determined from several Φ_Δ values).

2.4.2. Photodegradation quantum yields

For determination of photodegradation quantum yields, Eq. (6) was employed [32,35–37]:

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

where C_0 and C_t in mol dm^{-3} are the concentrations of **4** to **6** before and after irradiation respectively; V is the reaction volume; S, the irradiated cell area (2.0 cm^2); t, the irradiation time; N_A, the Avogadro's number and I_{abs}, the overlap integral of the radiation source intensity and the absorption of **4** to **6** (the action spectrum) in the region of the interference filter transmittance. The light intensity for photodegradation studies was 5 × 10^{16} photons s^{-1} cm^{-2}.

3. Results and discussion

3.1. Syntheses and characterization

The synthetic routes to novel phthalocyanines (**4** to **6**) are showed in Scheme 1. These complexes were prepared by the template cyclotetramerization of 4-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylthio)phenooxy]-phthalonitrile **(1)**, 4-[4-(trifluoromethyl)pyrimidine-2-thio]-phthalonitrile **(2)**, 4-[7-(trifluoromethyl)quinoline-4-thio]-phthalonitrile **(3)** and anhydrous $Zn(OAc)_2$ in the presence of 1-pentanol and DBU (as a strong base) at reflux temperature under argon atmosphere. 2(3),9(10),16(17),23(24)-Tetra-substituted phthalocyanines can be synthesized from 4-substituted phthalonitriles [1]. A mixture of four possible structural isomers is obtained. The four probable isomers can be designed by their molecular symmetry as C_{4h}, C_{2v}, C_s and D_{2h}. The 2(3)-substituted compounds always occur in the expected statistical mixture of 12.5% C_{4h}–, 25%C_{2v}–, 50%C_s– and 12.5%D_{2h}– isomer [39]. In this study, synthesized tetra-(triethyleneoxythia) substituted phthalocyanine compounds are obtained as isomer mixtures as expected. No attempt was made to separate the isomers of complexes **4** to **6**. All of these new zinc phthalocyanines were purified by column chromatography. They were obtained in a low yield (10% for **4**, 12% for **5**, and 7% for **6**) and were characterized by elemental analysis together with the spectral data (^{1}H NMR, FTIR, mass and UV–visible spectroscopies). The characterization data of the new compounds are consistent with the assigned formula.

Generally, phthalocyanine complexes are insoluble in most organic solvents; however introduction of substituents on the ring increases the solubility. All phthalocyanine complexes (**4** to **6**) exhibited excellent solubility in organic solvents such as dichloromethane, chloroform, THF, toluene, DMF, DMSO. Complex **4**, in particular, showed high solubility in these solvents (except DMSO) due to long fluoro chain.

The characteristic vibrations corresponding to CN were observed at 2234, 2227 and 2235 cm^{-1} for **1**, **2** and **3** respectively. The C–O–C vibration for **1** was observed at 1083cm^{-1}, the thio ethers (C–S–C) for **1**, **2** and **3** at 664 and, 661, 679 cm^{-1}, respectively. Aromatic C–H peaks occurred above 3050 cm^{-1} for all the phthalonitriles. The ^{1}H NMR spectrum of the compounds **1**, **2** and **3** showed signals with δ ranging from 7.06 to 9.03, belonging to aromatic protons and 2.40–3.18 ppm belonging to aliphatic H for just compound **1** integrating for a total of 11 protons for **1**, 5 protons for **2**, and 8 protons for **3** as expected.

In the mass spectra of phthalonitriles obtained by the relatively soft ESI-MS technique, the molecular ion peaks were observed at *m/z* 721.1 $[M + Na]^+$ for **1**, 329.1 $[M + Na]^+$ for **2** and 378.1 $[M + Na]^+$ for **3** with Na ion.

After conversion into zinc phthalocyanine derivations, the characteristic CN stretch at ~2230 cm^{-1} of phthalonitriles **1**, **2** and

3 disappeared in the FTIR spectra, indicative of metallophthalocyanine formation. The characteristic vibrations corresponding to C–O–C group were observed at 1088 (for **4**). Thio ether groups (C–S–C) were observed at 617 cm^{-1} (for **4**), 619 cm^{-1} (for **5**) and 618 cm^{-1} (for **6**).

The ZnPc derivatives were found to be pure by ^{1}H NMR with both the substituents and ring protons observed in their respective regions. The ^{1}H NMR spectra of tetra substituted phthalocyanine derivatives (**4** to **6**) were almost identical with that of the starting compounds **1**, **2** and **3** except for broadening and small shift. It is likely that broadness is due to both chemical exchange caused by aggregation–disaggregation equilibrium in $CDCl_3$ and the fact that the product obtained in this reaction is a mixture of four positional isomers which are expected to show chemical shifts which slightly differ from each other. In the ^{1}H NMR spectrum of **4** to **6** the aromatic and Pc protons appear between 7.26 and 8.42 ppm (for **4**, integrating for 28H), 7.11 and 8.79 ppm (for **5**, integrating for 20H), and 7.18 and 8.92 ppm (for **6**, integrating for 32H). For complex **4** aliphatic protons, were observed between at 2.49 and 3.32 ppm, integrating for a total of 16 protons. In the mass spectrum of Zn phthalocyanines (**4**–**6**), the presence of molecular ion peaks at *m*/*z* 2849 [M – 9H], 1291.6 [MH]$^{+}$ and 1489.6 [MH]$^{+}$ respectively, confirmed the proposed structures. MPc complexes have been observed to degrade with molecular ion peaks [M]$^{+}$, [M + nH]$^{+}$ or [M–nH]+ ($n = 1$–3) [40]. The matrix employed in this work is 2,5-dihydroxy benzoic acid, which is known [40] to intensify the fragmentation process hence the observed patterns, hence the observed mass spectral data.

Elemental analysis results also were consistent with the proposed structures of all compounds **1** to **6**.

3.2. Ground state electronic absorption spectra

The UV–Vis spectra of the phthalocyanine complexes exhibit characteristic Q and B bands. Two principle π–π^* transitions are seen for phthalocyanines: a Q-band which is a π–π^* transition from the highest occupied molecular orbital (HOMO, a_{1u}) to the lowest unoccupied molecular orbital (LUMO, e_g) of the complexes. The B bands (B1 and B2), were observed in the 300–350 nm region [41,42]. The Q band absorptions in the UV–Vis absorption spectra of the phthalocyanines (**4**, **5** and **6**) were observed as a single high intensity band due to a π–π^* transition at 679, 684 and 689 nm in toluene. Table 1 and Fig. 1. The Q band maxima are red shifted compared to ZnPc in toluene alone, 670 nm [32], showing the electron donating effects of the presence of sulfur. Complex **4** showed less red shifting, this is consistent with the notion that aromatic fluorine groups in complexes **5** and **6** are part of the phthalocyanine π system while aliphatic fluorine groups in complex **4** are not conjugated with the phthalocyanine π system, hence less red shifted for the latter [29].

The Q bands for complex **5** and **6** are broader compared to that of **4**, suggesting some aggregation, Fig. 1a. This was also observed in THF, Fig. 1b. Some aggregation for **5** and **6** was also observed in other solvents (DMSO and DMF). The fact that there is less aggregation in **4**, suggests that the long chain group is more effective at preventing the stacking of the Pc rings.

Table 1
Spectral parameters of **4**, **5** and **6** in toluene.

Compound	Q band, λ_{max} (nm)	(log ε)	Excitation, λ_{max} (nm)	Emission, λ_{max} (nm)	Stokes shift, δ_{Stokes} (nm)
4	679	5.11	679	689	10
5	684	5.12	683	695	12
6	689	5.17	686	704	18

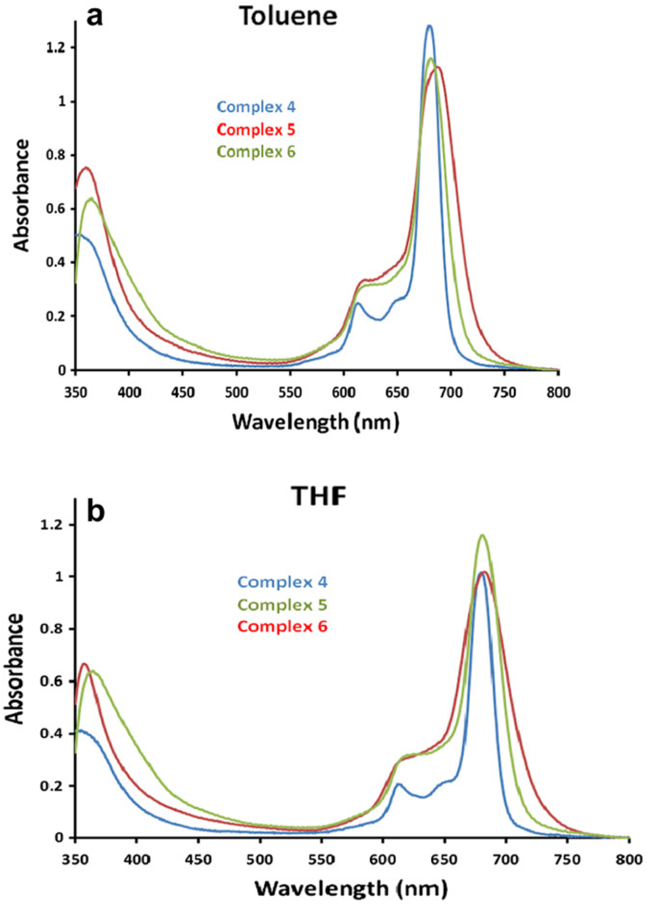

Fig. 1. UV–vis absorption spectra of **4**, **5** and **6** in toluene (a), concentration = 1×10^{-5} mol dm^{-3}; THF (b), concentration = 6×10^{-6} mol dm^{-3} for 4 and 5, 8×10^{-6} mol dm^{-3} for **6**.

Aggregation behavior of Pc is depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes and it is dependent on concentration, nature of solvent and substituents, metal ions and temperature [43]. In this study, the aggregation behavior of the ZnPc derivatives (**4**, **5** and **6**) were investigated in toluene at different concentrations. For all complexes, as the concentration was increased, the intensity of the Q band also increased and there was no new bands due to the aggregated species [44] observed, Fig. 2. Lambert–Beer law was obeyed for all complexes in the concentrations ranging from 2.0×10^{-6} to 1.2×10^{-5} mol dm^{-3} as given for 4 in toluene as an example, Fig. 2, showing that the complexes are not significantly aggregated within this concentration range.

3.3. Fluorescence spectra and quantum yields

Fig. 3 shows the absorption, fluorescence excitation and emission spectra of **4**, **5** and **6** in toluene. For complex **4**, the excitation spectra showed broadening compared to absorption spectra, suggesting slight change in symmetry upon excitation. For complexes **5** and **6**, the excitation spectra show less absorption in the region between 500 and 600 nm. Absorbance in this area is due to aggregation and aggregates do not fluorescence.

The fluorescence spectra were mirror images of the excitation spectra for **4** to **6**. The proximity of the wavelength of each component of the Q band absorption to the Q band maxima of the excitation spectra for all complexes suggest that the nuclear

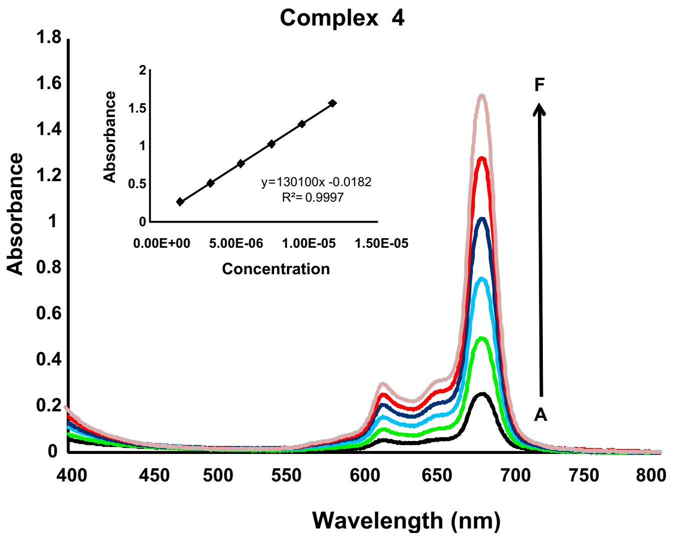

Fig. 2. Absorption spectra of **4** in toluene at different concentration: (A) 2 × 10^{-6}, (B) 4 × 10^{-6}, (C) 6 × 10^{-6}, (D) 8 × 10^{-6}, (E) 10 × 10^{-6}, (F) 12 × 10^{-6} mol dm^{-3}.

configurations of the ground and excited states are similar and not affected by excitation in toluene [45]. Fluorescence emission peaks were observed at: 689 nm for **4**, 695 nm for **5**, 704 nm for **6** in toluene (Table 1). The Stokes' shifts range from 10 to 18 nm, which is usual for ZnPc derivatives [46]. As has been observed before [29], there is a decrease Φ_F on going from ZnPc (Φ_F = 0.07 [32] in toluene) to fluorinated derivatives (Φ_F = 0.041 (**4**), = 0.035 (**5**) and 0.021 (**6**)) with complex **4** showing the largest value. This observation is again consistent with the fact that aromatic fluorine groups in complexes **5** and **6** are part of the phthalocyanine π system and thus increase the intersystem crossing. Aliphatic fluorine groups in complex **4** are not conjugated with the phthalocyanine π system, resulting in larger fluorescence quantum yield compared to **5** and **6**. The decrease for all complexes compared to ZnPc alone is due to the heavy atom effect of the halogen. The lower Φ_F values for **5** and **6** (compared to **4**) may also be explained by the aggregation tendencies of these molecules in this solvent. Aggregation reduces the likelihood of radiative deactivation (fluorescence) through dissipation of energy by the aggregates. Complex **4** showed larger quantum yield for internal conversion (Φ_{IC}, Table 2) in toluene when compared to complexes **5** and **6**.

Table 2
Photophysical and photochemical properties of **4**, **5** and **6** in toluene.

Compound	Solvent	Φ_F	τ_T	Φ_T	Φ_{IC}	Φ_d (10^6)	Φ_Δ	S_Δ
4	Toluene	0.041	110	0.65	0.31	8.11	0.52	0.80
5	Toluene	0.035	90	0.69	0.28	1.39	0.60	0.87
6	Toluene	0.021	100	0.71	0.27	4.22	0.56	0.79

3.4. *Triplet quantum, yields and lifetimes*

Triplet quantum yield (Φ_T) represents the fraction of absorbing molecules that undergo intersystem crossing to the metastable triplet excited state. Therefore, factors which induce spin-orbit coupling will certainly populate the triplet excited state. Fig. 4 displays the triplet decay curves of the complexes (using complex **6** in toluene as an example). The triplet life time for **4** (110 μs), **5** (90 μs) and **6** (100 μs) in toluene are lower than for unsubstituted ZnPc (330 μs) in toluene [46]. This suggests that the fluoro-functional substituents quench the triplet state.

The triplet quantum yields (Φ_T) for substituted complexes (**4**, **5** and **6**) in toluene are higher or comparable to ZnPc standard in toluene (Φ_T = 0.65 for ZnPc). The high values of Φ_T values suggest more efficient intersystem crossing (ISC) in the presence of the

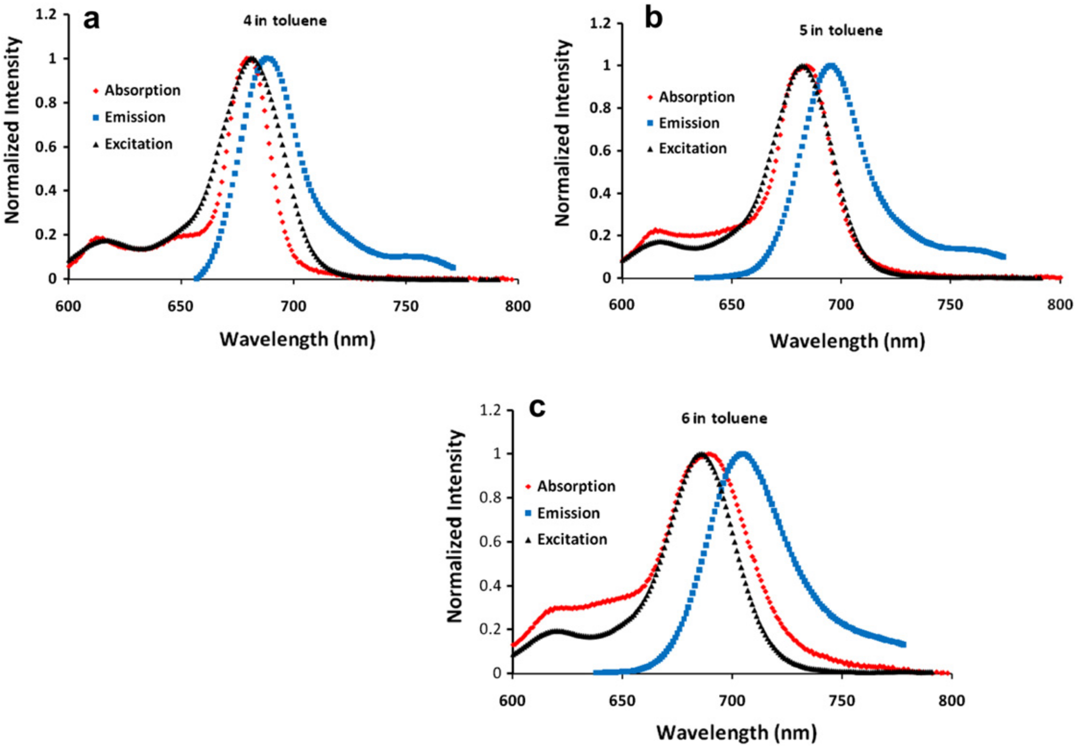

Fig. 3. Absorption (i), excitation (ii) and emission (iii) spectra of the compounds **4**(a), **5**(b), and **6**(c) in toluene. Excitation wavelength = 679nm for (**4**) 683 nm for (**5**) and 686 nm for (**6**) in toluene.

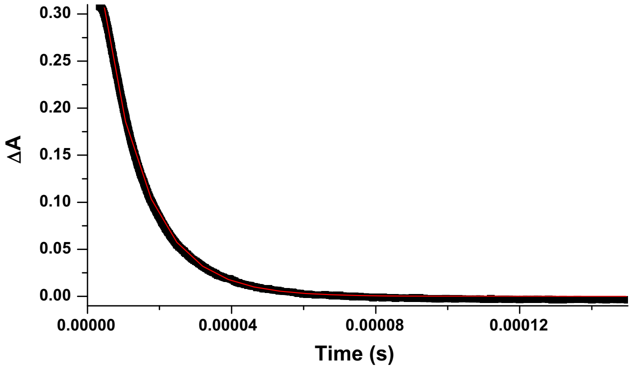

Fig. 4. Mono-exponential triplet decay profile for complex **6** in toluene. Excitation wavelength = 689 nm.

fluorine substituents for substituted complexes **5** ($\Phi_T = 0.69$) and **6** ($\Phi_T = 0.71$), corresponding to low Φ_F values discussed above.

3.5. Photochemical properties

3.5.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield Φ_Δ is a measure of singlet oxygen generation and the Φ_Δ values were obtained using eq. (5). Singlet oxygen quantum yields were studied in toluene using a chemical method (1,3-diphenylisobenzofuran, DPBF). Fig. 5 shows spectral changes observed during photolysis of complex **4** in toluene in the presence of DPBF. The disappearance of DPBF was monitored using UV–vis spectroscopy. There were no changes in the Q band intensities during the Φ_Δ determinations, confirming that complexes are not degraded during singlet oxygen studies [47]. The Φ_Δ values of three complexes are high in toluene, corresponding to high Φ_T values in this solvent. The Φ_Δ values for **4** and **6** ($\Phi_\Delta = 0.52$ and 0.56 in toluene, respectively) are lower and for **5** ($\Phi_\Delta = 0.60$) is higher when compared to unsubstituted ZnPc in toluene (0.58 [32]). The magnitude of the $S_\Delta = (\Phi_\Delta/\Phi_T)$ represents the efficiency of quenching of the triplet excited state by singlet oxygen. Compound **4**, **5** and **6** displayed S_Δ of near unity in toluene Table 2.

3.5.2. Photodegradation (photobleaching) quantum yields

Photodegradation is a process where a phthalocyanine is degraded under light irradiation due to singlet oxygen attack. It can be used to determinate MPcs stability and this is especially important for those molecules intended for use as photocatalysts. The photobleaching stabilities of complexes **4**, **5** and **6** were determined in toluene by monitoring the decrease in the intensity of the Q band under irradiation with increasing time. The photodegradation quantum yield (Φ_d) values for the complexes are listed in Table 2 are of the order of 10^{-6}. These values show that the molecules are of high stability in the solvent used. Stable ZnPc molecules show values as low as 10^{-6} and for unstable molecules, values of the order 10^{-3} have been reported [48]. The order of stability among the substituted complexes was **5** > **6** > **4** in toluene.

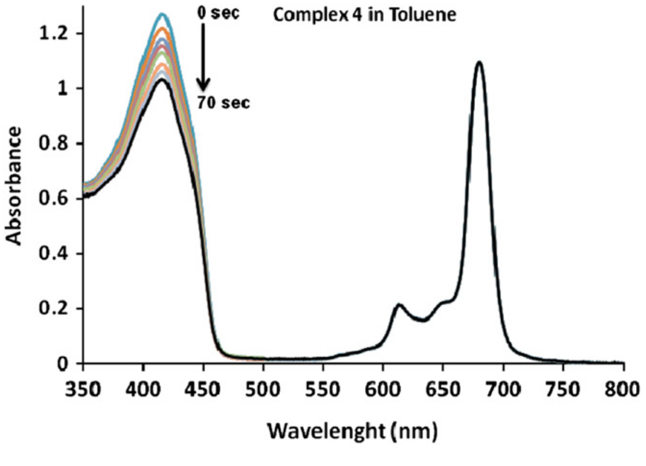

Fig. 5. A typical spectrum for the determination of singlet oxygen quantum yield. This figure was for complex **4** in toluene at a concentration 6×10^{-6} mol dm^{-3}.

4. Conclusion

In this study, the syntheses, spectral and photophysicochemical properties of soluble peripheral fluoro-functional substituted zinc phthalocyanines (**4**, **5** and **6**) are discussed. The complexes have good solubility and are mainly monomeric in solution. The introduction of different fluoro-functional groups on the ring results in high triplet quantum yields (ranging from 0.65 to 0.71 in toluene). All complexes showed similar and typical fluorescence quantum yields for MPcs in the solvent used. While Complex **4** has the lowest triplet quantum yield (0.65) and singlet quantum yield values (0.52), complexes **5** and **6** have higher triplet quantum yields and singlet quantum yield values in toluene. The singlet oxygen quantum yields, which give indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism) ranged from 0.52 to 0.60. Thus, these complexes show potential as Type II photosensitizers and can be used in photodynamic therapy.

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