



Novel soluble octa-substituted phthalocyanines bearing chloro and long alkyl chain containing fluorine: Synthesis, characterization and photophysical and photochemical properties



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ABSTRACT

The synthesis of a new phthalonitrile (**1**), together with photophysical, photochemical and spectral properties of the resulting peripherally octakis zinc, magnesium and oxotitanium phthalocyanines (**2**, **3** and **4**) are described for the first time. New compounds **1–4** have been synthesized and characterized by elemental analysis, IR, ¹H NMR, mass spectra and electronic spectroscopy. Complexes **2**, **3** and **4** have good solubility in organic solvents such as CHCl₃, DCM, THF and toluene. In this study, fluorescence quantum yield (photophysical), fluorescence behavior, singlet oxygen quantum and photodegradation quantum yields (photochemistry) and spectral properties of these new complexes were studied in THF. Aggregation was not observed in the presence of a long alkyl chain containing fluorine in the complexes. The effects of metal and the fluoro-functional groups on new peripherally octa-substituted metallo-phthalocyanines on the photophysical parameters of the phthalocyanines (**2**, **3** and **4**) were also investigated.

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1. Introduction

The researches on phthalocyanines (Pcs) and metallophthalocyanines (MPcs) have been increased due to their various application areas such as chemical sensors, catalysts, non-linear optics, liquid crystals, Langmuir–Blodgett films and electrochromic displays [1–5]. Moreover, recently, Pcs and MPcs have been used in photodynamic therapy (PDT) as a photosensitizer because of their strong and long-wavelength absorptions [6–8]. Solubility is the major problem on above application areas. Unsubstituted phthalocyanines (Pcs) are generally insoluble in a solvent, but they can become soluble in many kinds of organic solvent by attaching appropriate substituents such as hydrophilic groups. The properties of Pcs and MPcs can be tuned by depending on the substituents at peripheral or non-peripheral positions onto the macrocycle ring [9]. A new generation of phthalocyanines with fluorinated, electron withdrawing substituents has been developed [10–13]. These Pcs

have been of much interest due to their high solubilities in polar solvents such as acetone or THF. The electronic properties are significantly affected by introducing electron donor or acceptor groups, as well. Moreover, fluorinated phthalocyanines show improved photosensitizer activity for PDT when compared to non-fluorinated derivatives [14–16]. Metal phthalocyanines bearing fluorine atoms are currently receiving a great deal of attention due to their high thermal and chemical stability; they also possess interesting electron-transporting characteristics [15,17,18]. Fluoro-substituted phthalocyanines are known with their high solubilities, even in polar, aprotic solvents. The increased solubility may be due to fluorine which has the highest electronegativity of all elements [19]. In our previous studies, we reported the synthesis, photophysics, photochemistry, spectroscopic, fluorescence, electrochemical and spectroelectrochemical properties of symmetric and asymmetric phthalocyanines [20–27]. During the last few years, we have focused on the preparation of fluorine-containing phthalocyanines [6,28]. In this work, the syntheses and characterizations of three novel metallophthalocyanines (metal: Zn, Mg, TiO) peripherally octa-substituted with four chloro and four long chain fluoro groups were carried out and the photophysical properties of these metallophthalocyanines were studied.

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2. Experimental

2.1. Materials and equipment

All chemicals and solvents used were analytical grade and commercially purchased and were used as received without further purification. Column chromatography was performed on silica gel 60 (0.04–0.063).

Photo-irradiations were carried out using a General Electric quartz line lamp (300 W). 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, 700 nm with a band width of 40 nm) was additionally placed in the light path before the sample. The FT-IR spectra were recorded on a Perkin-Elmer spectrum 2000 FT-IR spectrometer in the range of 400–4000 cm^{-1} . Elemental analyses for C, H, N and S were carried out on a Thermo Flash EA 105 1112 Series. $^1\text{H-NMR}$ spectra of the synthesized compounds were obtained using a Bruker EMX 400 NMR spectrometer in CDCl_3 . GC-MS spectra were acquired on a Agilent Technologies including 6890 N network GC system and 5973 inert Mass selective detector. Mass spectra were acquired on a Bruker Daltonics Microflex mass spectrometer (Bremen, Germany) equipped with a nitrogen UV-Laser operating at 337 nm. UV/vis and fluorescence spectra were recorded on a Cary 500 UV/Vis/NIR spectrophotometer and Varian Eclipse spectrofluorometer, respectively.

2.2. Synthesis

2.2.1. 1-Chloro-3,4-dicyano-6-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylthio)phenoxy]-benzene (**1**)

The 4,5-dichloro-phthalonitrile (0.52 g 2.62 mmol) was dissolved in 20 ml dry DMF under nitrogen and 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylthio)phenol (3.00 g 5.24 mmol) was added at room temperature. After stirring for 30 min at room temperature, finely ground anhydrous K_2CO_3 (3.62 g 13.10 mmol) was added portion wise for 2 h and the reaction mixture was stirred at room temperature for 48 h. Then, the mixture was poured into 250 ml ice-water and the precipitate was filtered off, washed with water and methanol and then dried. The crude product was further purified by chromatography over a silica gel column using a mixture of CHCl_3 :MeOH (20:1 v/v) as eluents, giving a powder of 1-chloro-3,4-dicyano-6-[(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylthio)phenoxy]-benzene (**1**). Yield: 0.84 g (44%). IR spectrum (cm^{-1}): 3095, 3063 (Ar-CH), 2932 (aliphatic-CH), 2238 (C≡N), 1601, 1589 (C=C), 1494, 1430, 1370 (C-F), 1344, 1197, 1143, 1082 (C-O-C), 960, 820, 705 (C-S-C). $^1\text{H NMR}$ (CDCl_3): δ = 7.89–7.68 (m, 2H, Ar-H), 7.48–7.26 (m, 4H, Ar-H), 3.26 (t, 2H, CH_2), 2.68–2.54 (m, 2H, CH_2). Calcd for $\text{C}_{24}\text{H}_{10}\text{ClF}_{17}\text{N}_2\text{OS}$: C, 39.33; H, 1.38; N, 3.82; S, 4.38%. Found: C, 40.02; H, 1.59; N, 3.74; S, 4.65%. MS (ESI-MS) m/z : Calc. 732.84; Found: 759 [M + Na] $^+$.

2.2.2. 2,9,16,23-Tetrakis-[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylthio)phenoxy]-3,10,17,24 tetrachlorophthalocyaninato-zinc(II) (**2**)

Compound **1** (0.20 g, 0.273 mmol), anhydrous $\text{Zn}(\text{OAc})_2$ (0.250 g, 0.136 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) (0.115 ml, 0.77 mmol) under a nitrogen atmosphere and held at reflux temperature for 18 h. After cooling to room temperature, the reaction mixture was precipitated by adding it drop-wise into *n*-hexane. 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 CHCl_3 and a mixture of THF and CH_2Cl_2 (1:50 by

volume), as eluent, respectively. Yield: 40 mg (48%). UV-vis (THF): λ_{max} nm (log ϵ) 603 (4.99), 636 (4.79), 675 (6.00). IR spectrum (cm^{-1}): 3071 (Ar-CH), 2944, 2857 (aliphatic-CH), 1589 (C=C), 1487, 1435, 1392, 1333 (C-F), 1237, 1197, 1144 (C-O-C), 994, 953, 826, 788, 741, 703 (C-S-C). $^1\text{H NMR}$ (CDCl_3): δ = 8.56–7.32 (24H, m, Ar-H), 3.44–3.32 (m, 8H, CH_2), 2.74–2.56 (m, 8H, CH_2). Calcd for $\text{C}_{96}\text{H}_{40}\text{Cl}_4\text{F}_{68}\text{N}_8\text{O}_4\text{S}_4\text{Zn}$: C, 38.48; H, 1.35; N, 3.74; S, 4.28%. Found: C, 39.37; H, 1.52; N, 3.63; S, 4.37%. MS (ESI-MS) m/z : Calc. 2996.76; Found: 3000.30 [M + 4H] $^+$.

2.2.3. 2,9,16,23-Tetrakis-[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylthio)phenoxy]-3,10,17,24 tetrachlorophthalocyaninato-magnesium(II) (**3**)

The procedure for the synthesis of **3** was similar to that used for **2**, except anhydrous $\text{Mg}(\text{OAc})_2$ (0.013 g, 0.136 mmol) was used instead of anhydrous $\text{Zn}(\text{OAc})_2$. Compound **3** was purified with column chromatography using a mixture of CHCl_3 :THF (10:1 by volume) as eluent. Yield: 32 mg (39%). UV-vis (THF): λ_{max} nm (log ϵ) 607 (4.79), 642 (4.78), 677 (5.34). IR spectrum (cm^{-1}): 3099 (Ar-CH), 2972, 2873 (aliphatic-CH), 1615, 1589 (C=C), 1487, 1432, 1390 (C-F), 1236, 1200, 1144, 1081 (C-O-C), 992, 954, 827, 746, 704 (C-S-C). $^1\text{H NMR}$ (CDCl_3): δ = 8.64–7.41 (24H, m, Ar-H), 3.52–3.44 (m, 8H, CH_2), 2.69–2.52 (m, 8H, CH_2). Calcd for $\text{C}_{96}\text{H}_{40}\text{Cl}_4\text{F}_{68}\text{N}_8\text{O}_4\text{S}_4\text{Mg}$: C, 39.01; H, 1.36; N, 3.79; S, 4.34%. Found: C, 40.13; H, 1.27; N, 3.16; S, 4.38%. MS (ES^+), (m/z): Calc. 2955.66; Found: 2945.39 [M – 10H] $^+$.

2.2.4. 2,9,16,23-Tetrakis-[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decylthio)phenoxy]-3,10,17,24 tetrachlorophthalocyaninato-oxotitanium(IV) (**4**)

The synthesis of **4** was as outlined for **2**, except $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ (0.046 ml, 0.136 mmol) was used instead of anhydrous $\text{Zn}(\text{OAc})_2$. The crude product was purified by column chromatography using a mixture of CHCl_3 :MeOH (20:1 v/v) as eluent. Yield: 26 g (32%). UV-vis (THF): λ_{max} nm (log ϵ) 628 (4.88), 665 (4.99), 697 (5.37). IR spectrum (cm^{-1}): 3067 (Ar-CH), 2952, 2865 (aliphatic-CH), 1610, 1588 (C=C), 1488, 1440, 1389 (C-F), 1235, 1198, 1144, 1114, 1083 (C-O-C), 1012 (Ti=O), 953, 880, 829, 739, 704 (C-S-C). $^1\text{H NMR}$ (CDCl_3): δ = 8.72–7.43 (24H, m, Ar-H), 3.64–3.44 (m, 8H, CH_2), 2.79–2.59 (m, 8H, CH_2). Calcd for $\text{C}_{96}\text{H}_{40}\text{Cl}_4\text{F}_{68}\text{N}_8\text{O}_5\text{S}_4\text{Ti}$: C, 38.50; H, 1.35; N, 3.74; S, 4.28%. Found: C, 39.21; H, 1.76; N, 3.59; S, 4.43%. MS (ES^+), (m/z): Calc. 2995.22; Found: 2996.6 [M + H] $^+$.

2.3. Photophysical and photochemical studies

2.3.1. Fluorescence quantum yields

Fluorescence quantum yields (Φ_F) were determined by the comparative method [29,30], (Eq. (1)):

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

where, F and F_{Std} are the areas under the fluorescence emission curves of **2** to **4** 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 zinc phthalocyanine (**ZnPc**) in THF ($\Phi_F = 0.25$) was used as the standard [30].

2.3.2. Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_{Δ}) determinations were carried out using the experimental setup described in literature [31–33]. Quantum yields of singlet oxygen photogeneration were determined using the relative method with **ZnPc** as reference

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