



Synthesis and physicochemical behavior of new low symmetry Ge, Ti and Sn phthalocyanines: Effect of central metal

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ABSTRACT

The synthesis and photophysical properties of new low symmetrically Ge, Sn and Ti phthalocyanines substituted with one carboxy containing group are reported. Broadening and splitting in the absorption spectra were observed for some of the complexes in particular for both the titanium Pcs due to loss of symmetry. Higher fluorescence quantum yields and lifetimes were obtained for the Pcs substituted with three benzyloxy (**5–7**) compared to their corresponding counterparts substituted with six 2-diethylaminoethylthiol groups (**9–11**). The germanium Pc complexes gave the highest triplet and singlet oxygen quantum yields compared to all the other complexes studied in DMF. All the complexes showed reasonable ability to generate singlet oxygen with quantum yields ranging from 0.54 to 0.69.

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1. Introduction

Numerous methods for the synthesis of phthalocyanines (Pcs) have been reported since their discovery in the early 1900s [1]. Because of their flexibility and fine-tuneable properties, phthalocyanines have been used for a wide range of industrial applications, hence they are vital in the modern society. Their applications range from their use as drugs in medicine [2–4], in the clothing industry [1,5,6] and in electronic devices [7,8]. The main advantage of using phthalocyanines over other dyes is that their photophysical, electrochemical and photochemical properties are readily altered by changing the substitution pattern or the metal in their cavity [9–12]. Phthalocyanine are good photosensitizers for photodynamic therapy (PDT) due to their a high molar absorption coefficient ($\epsilon \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) in the visible region; long lifetime of the triplet excited state and high singlet oxygen quantum yields [3–6,9]. Symmetrically substituted Pcs have been extensively researched [5,6,9]. A disadvantage of symmetrically substituted Pcs is their lack of selective binding to various biological materials and nanomaterials. Focus on asymmetrically substituted Pcs has increased in recent years [6,12–17], due to their selectivity when conjugated to other molecules. Low symmetrically substituted Pcs have been reported to selectively conjugate to biomolecules [18,19] and nanostructured materials resulting in covalent bond formation for drug delivery purposes [20–23]. However purification and separation of these complexes is known to be tedious and

challenging, hence relatively low yields are obtained [15,16]. We have recently reported on asymmetrically phthalocyanines mono substituted with a mono-cystenyl or mono-phenoxy carboxy groups at the periphery, but containing Zn as a central metal [24]. The current work uses Ge, Sn and Ti as central metal and compares the photophysical properties of these complexes with those of the Zn counterparts. The singlet oxygen behavior of the Zn phthalocyanine derivatives is reported here for the first time. Singlet oxygen is crucial for the application of phthalocyanines as photosensitizers. The cystenyl substituent is chosen in this work since it contains both carboxyl and amino groups hence has two sites for future binding studies. The mono-phenoxy carboxy group has one binding site. The rest of the substituents are chosen to increase solubility and/or red shifting the Q band, another requirement for PDT.

2. Experimental and methods

2.1. Materials

Potassium carbonate, deuterated dimethyl sulfoxide (DMSO- d_6), zinc acetate, 2-(diethylaminoethanethiol) hydrochloride, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,3-diphenylisobenzofuran (DPBF), silica gel 60, zinc phthalocyanine and aluminum oxide (WN-3: neutral) for column chromatography were purchased from Sigma–Aldrich. Bio-Beads S-X1 were obtained from Bio-Rad. Dimethylformamide (DMF), dichloromethane (DCM), dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc), methanol (MeOH), n-hexane, chloroform, dichloromethane (DCM), tetrahydrofuran (THF), acetone, and ethanol were obtained from Merck and were dried according to reported procedures [25] before use.

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2.2. Experimental

UV-vis spectra were recorded on a Shimadzu 2550 UV-vis spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer. IR spectra (KBr pellets) were recorded on a Perkin-Elmer spectrum 2000 FTIR spectrometer. Fluorescence lifetimes were measured using a time correlated single photon counting setup (TCSPC) (FluoTime 200, Picoquant GmbH) with a diode laser (LDH-P-670 with PDL 800-B, Picoquant GmbH, 670 nm, 20 MHz repetition rate, 44 ps pulse width) as described in detail before [20]. The support plane approach [26] was used to estimate the errors of the decay times. Mass spectral data were collected with a Bruker AutoFLEX III Smartbeam TOF/TOF Mass spectrometer. The instrument was operated in either negative or positive ion modes using a m/z range of 400–3000 amu. The voltage of the ion sources were set at 19 and 16.7 kV for ion sources 1 and 2 respectively, while the lens was set at 8.50 kV. The reflector 1 and 2 voltages were set at 21 and 9.7 kV respectively. The spectra were acquired using alpha-cyano-4-hydroxycinnamic acid as the MALDI matrix, and a 354 nm nitrogen laser as the ionizing source.

Laser flash photolysis experiments were performed as described before [20]. The solutions (absorbance ~ 1.5 at the Q band) for triplet quantum yields and lifetimes were introduced into a 1 cm path length UV-vis spectrophotometric cell, de-aerated using argon (bubbled for 30 min) and irradiated at the Q band maxima with laser flash photolysis equipment. The triplet life times were then determined by exponential fitting of the kinetic curves using the program OriginPro 8.0.

Photo-irradiations for singlet oxygen determination were performed using the set up described in literature [27]. Light intensity was measured with a POWER MAX5100 (Molelectron detector incorporated) power meter and was found to be 1.78×10^{16} photons $s^{-1} cm^{-2}$ for singlet oxygen studies.

2.3. Synthesis

1,2-Bis-(diethylaminoethylthiol)-4,5 dicyanobenzene (**3**) [28,29], 4-phenoxy phthalonitrile (**2**) [30,31] and 4-(3,4-dicyanophenoxy)benzoic acid (**4**) [32] were synthesized as reported before. Syntheses of complexes **8** and **12** have been reported before [24].

2.3.1. Tris {9 (10), 16 (17), 23 (24)}-(4-phenoxy)-2-(4-cysteiny) phthalocyanine} (OH)₂Ge (**5**), OTi (**6**) and (OH)₂Sn (**7**) (Scheme 1)

A mixture of 4-cysteiny phthalonitrile (**1**) (0.64 g, 2.6 mmol) and 4-phenoxy phthalonitrile (**2**) (1.72 g, 7.8 mmol) was firstly finely ground, homogenized and placed in a round bottom flask that contained pre-heated DMAc (15 mL). The mixture was then stirred under reflux at 130 °C for 7 h under an argon atmosphere in the presence of excess metal salt (germanium (IV) chloride for complex **5**, titanium (IV) butoxide for complex **6** and tin (IV) chloride for complex **7**) and DBU (0.25 mL) as a catalyst. Thereafter, the mixture was cooled to room temperature and dropped in (1:1) water: acetone. The green solid product which precipitated was collected by centrifugation, washed with n-hexane and dried in air. Purification was achieved using column chromatography with silica gel as column material and MeOH:THF (2:10) as eluent followed by the addition of (2:1) THF:DMF to elute the second fraction which was our desired product. The product was dried in air and further washed with ethanol, acetone, n-hexane and diethyl ether.

Complex **5** yield: (9%) (0.22 g). IR (KBr, cm^{-1}): 3441 (O–H), 3125 (C–H), 2986 (carboxylic acid OH), 1621 (C=O), 1525 (C=C), 1433, 1339, 1317, 1237 (C–O–C) 978, 858, 716 (C–S–C), 701 (Ge–O), 637, 547. NMR (DMSO- d_6): δ , ppm 9.35–9.21 (12H, m, Pc-H), 8.46–8.32 (12H, m, aromatic-H), 7.67–7.51 (3H, dd, aromatic-H), 6.26–6.21

(1H, d, C–H), 4.37–4.32 (1H, br, OH) 3.57–3.43 (2H, d, S–CH₂), 2.63–2.56 (2H, broad, NH₂). UV-vis (DMF) λ_{max} nm (log ϵ): 691 (5.04). Calc. for C₅₃H₃₅N₉SO₇Ge + H₂O: C 61.64, H 3.58, N 12.21, S 3.11 Found: C 61.93, H 3.67, N 12.01, S 2.96 MALDI TOF MS m/z : Calcd: 1014.61 Found: [M+H]⁺ 1015.62

Complex **6** yield: (11%) (0.26 g). IR (KBr, cm^{-1}): 3444 (O–H), 3136 (C–H), 2972 (carboxylic acid OH), 1607 (C=O), 1543 (C=C), 1519, 1469, 1385, 1332, 1238 (C–O–C) 1077, 988 (Ti=O), 864, 717 (C–S–C), 704, 633, 569. NMR (DMSO- d_6): δ , ppm 9.67–9.61 (12H, m, Pc-H), 8.75–8.65 (12H, m, aromatic-H), 7.46–7.39 (3H, dd, aromatic-H), 6.33–6.28 (1H, d, C–H), 4.51–4.47 (1H, br, OH) 3.78–3.70 (2H, d, S–CH₂), 2.62–2.53 (2H, broad, NH₂). UV-vis (DMF) λ_{max} nm (log ϵ): 680 (4.98). Calc. for C₅₃H₃₃N₉SO₆Ti: C 65.49, H 3.39, N 12.97, S 3.29 Found: C 65.52, H 3.42, N 13.12, S 3.44 MALDI TOF MS m/z : Calcd: 971.85 Found: [M–H][–] 970.86

Complex **7** yield: (15%) (0.34 g). IR (KBr, cm^{-1}): 3447 (O–H), 3121 (C–H), 2980 (carboxylic acid OH), 1616 (C=O), 1540 (C=C), 1468, 1358, 1335, 1234 (C–O–C) 1099, 885, 717 (C–S–C), 694, 624, 563 (Sn–O). NMR (DMSO- d_6): δ , ppm 9.37–9.25 (12H, m, Pc-H), 8.67–8.52 (12H, m, aromatic-H), 7.72–7.64 (3H, dd, aromatic-H), 6.37–6.25 (1H, d, C–H), 4.44–4.37 (1H, br, OH) 3.51–3.43 (2H, d, S–CH₂), 2.63–2.57 (2H, broad, NH₂). UV-vis (DMF) λ_{max} nm (log ϵ): 671 (4.84). Calc. for C₅₃H₃₅N₉SO₇Sn + H₂O: C 59.01, H 3.43, N 11.69, S 2.97 Found: C 58.97, H 3.10, N 12.01, S 3.15 MALDI TOF MS m/z : Calcd: 1060.67 Found: [M+2H]⁺ 1062.70.

2.3.2. Hexakis {9; 10, 16; 17, 23; 24 –

(1,2-bis-(diethylaminoethylthiol))-2-(4-phenoxy-carboxy) phthalocyanine} (OH)₂Ge (**9**), OTi (**10**) and (OH)₂Sn (**11**) (Scheme 2)

Synthesis for **9–11** was as outlined for **5–7** except that 4-(3,4-dicyanophenoxy)benzoic acid (**4**) (0.68 g, 2.6 mmol) and 1,2-bis-(diethylaminoethanethiol)-4, 5-dicyanobenzene phthalonitrile (**3**) (3.04 g, 7.8 mmol) were employed instead of **1** and **2**. Purification was achieved using column chromatography with neutral alumina as column material and DCM:MeOH:THF (10:5:5) as eluent, followed by drying. The desired product was further washed with ethanol, acetone, n-hexane and diethylether.

Complex **9** yield: (16%) (0.61 g). IR (KBr, cm^{-1}): 3410 (O–H), 3131 (C–H), 2970 (carboxylic acid OH), 1612 (C=O), 1550 (C=C), 1435, 1328, 1116, 947, 750 (C–S–C), 700 (Ge–O), 634, 544. ¹H NMR (DMSO- d_6): δ , ppm 10.33–10.26 (6H, m, Pc-H), 9.47–9.40 (3H, br, Pc-H), 7.62–7.56 (4H, m, aromatic), 4.48–4.41 (1H, br, OH), 3.52–3.43 (12H, m, S–CH₂), 3.10–2.89 (12H, m, N–CH₂), 2.51–2.38 (24H, m, CH₂-methyl), 1.97–1.81 (36H, q, CH₃). UV-vis (DMF) λ_{max} nm (log ϵ): 614 (5.00). Calc. for C₇₅H₁₀₀N₁₄S₆O₅Ge: C 68.15, H 6.49, N 12.72, S 12.48 Found: C 67.85, H 6.55, N 12.61, S 12.72. MALDI TOF MS m/z : Calcd: 1541.75 Found: [M+]⁺ 1541.74.

Complex **10** yield: (15%) (0.54 g). IR (KBr, cm^{-1}): 3415 (O–H), 3128 (C–H), 2973 (carboxylic acid OH), 1617 (C=O), 1549 (C=C), 1500, 1428, 1342, 1120, 1038, 985 (Ti=O), 754 (C–S–C), 621, 565. ¹H NMR (DMSO- d_6): δ , ppm 10.30–10.25 (6H, m, Pc-H), 9.50–9.43 (3H, br, Pc-H), 7.61–7.56 (4H, m, aromatic), 4.44–4.37 (1H, br, OH), 3.58–3.49 (12H, m, S–CH₂), 3.21–2.43 (12H, m, N–CH₂), 2.28–2.16 (24H, m, CH₂-methyl), 1.95–1.77 (36H, q, CH₃). UV-vis (DMF) λ_{max} nm (log ϵ): 727 (4.93). Calc. for C₇₅H₉₈N₁₄S₆O₄Ti: C 60.09, H 6.54, N 13.08, S 12.84 Found: C 59.66, H 5.82, N 12.85, S 12.53. MALDI TOF MS m/z : Calcd: 1498.99 Found: [M+2H]⁺ 1500.98.

Complex **11** yield: (11%) (0.40 g). IR (KBr, cm^{-1}): 3420 (O–H), 3130 (C–H), 2969 (carboxylic acid OH), 1614 (C=O), 1553 (C=C), 1513, 1422, 1316, 1094, 997, 759 (C–S–C), 631, 614, 560 (Sn–O), 543. ¹H NMR (DMSO- d_6): δ , ppm 10.13–10.02 (6H, m, Pc-H), 9.42–9.34 (3H, br, Pc-H), 7.57–7.46 (4H, m, aromatic), 4.55–4.47 (1H, br, OH), 3.63–3.58 (12H, m, S–CH₂), 3.39–2.31 (12H, m, N–CH₂), 2.26–2.17 (24H, m, CH₂-methyl), 2.01–1.96 (36H, q, CH₃). UV-vis (DMF) λ_{max} nm (log ϵ): 726 (4.90). Calc. for C₇₅H₁₀₀N₁₄S₆O₅Sn: C

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