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Synthesis and properties of phthalocyanine zinc(II) complexes replaced with oxygen and sulfur linked adamantane moieties

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ABSTRACT

Novel, zinc (II) phthalocyanines substituted with 2-adamantanol and 1-adamantanethiol moieties were prepared from the corresponding phthalonitriles employing commercially available 3- and 4-nitrophthalonitrile as the starting material. The Q-band of tetra-α-substituted phthalocyanines occurred at longer wavelengths than those of the corresponding, tetra-β-substituted phthalocyanines. Substituents at the β position increased Φ_F values; all phthalocyanines studied displayed excellent singlet oxygen generations ability, with α-substituted dyes showing higher Φ_Δ values than their β-isomers. The dyes exhibited good photo-stability, with α-substituted phthalocyanines proving to be of higher stability than the corresponding β-isomers.

1. Introduction

Phthalocyanines play a major role in modern photochemistry; their versatility enables their utilization in many fields of material science such as those related to dyes, catalysts, chemical sensors, liquid crystals and non-linear optics [1,2]. In medicine, phthalocyanines have been found to have applications as phototoxic drugs for photodynamic therapy [3–6]. In addition to their well-known chemical stability, phthalocyanines possess characteristic absorption spectra [1], with a Soret band at approximately 350 nm and a usually narrow but very strong Q-band around 675 nm, with a molar absorption coefficient of ca. of 10^5 M^{-1} cm^{-1}. In addition to being red shifted in comparison to porphyrins, light absorption of phthalocyanines is approximately two orders of magnitude stronger than the highest Q-band absorption of a porphyrin. Their photophysical properties are strongly influenced by the presence and nature of the coordinated central metal ion.

Closed shell, diamagnetic ions, such as Zn^{2+}, Al^{3+} and Ga^{3+} give phthalocyanine complexes with both high triplet yields and long lifetimes of the excited triplet state. Thus, these complexes are expected to exhibit strong photochemical and photodynamic activities due to a higher efficiency in generating reactive oxygen species than porphyrins [3].

Thiol–derivatized metallophthalocyanine complexes show excellent spectroscopic and photochemical properties, such as wavelength absorption over 700 nm [7]. A systematic comparison of oxygen and sulfur as covalent linkers on octasubstituted zinc(II) phthalocyaninates shows a bathochromic shift of 30 nm in the absorption and emission maxima, and of 60 nm in the triplet–triplet absorption spectra when alkylsulfanyl instead of alkyloxy moieties were present [8]. Highly hindered adamantane substituted magnesium, nickel and metal-free phthalocyanines showed interesting red shifts in their UV–vis spectra. As compared with the tetrasubstituted analog, the octaadamantylamine-substituted derivative exhibited a red shift of 80 nm [9].

On the basis of these results, further studies have been undertaken to investigate the synthesis, absorption and emission spectra, fluorescence quantum yields, quantum yield of singlet oxygen production and photo-stability of zinc(II) phthalocyaninates tetrasubstituted with oxygen and sulfur linked adamantane moieties.

2. Experimental

Melting points were determined on an Electrothermal 9100 capillary melting point apparatus. ^1H NMR was recorded on a Bruker MSL 300 spectrometer. The ^1H NMR of phthalocyanines was recorded on a Bruker AM 500. Mass spectra were obtained with a TRIO 2

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(electronic ionization 70 eV) spectrometer. Phthalocyanines ESI mass spectra were measured with a Q-TOF Premier micromass/ Waters Corporation spectrometer. Electronic absorption spectra were determined with a Shimadzu UV-3101 PC spectrophotometer. Fluorescence spectra were monitored with a QuantaMaster Model QM-1 PTI spectrofluorometer. Infrared spectra were recorded with a Perkin Elmer Spectrum One FT-IR spectrometer. Chromatography columns were prepared with tlc Kiesegel (Merck), and Aluminium Oxide 90 standardized (Merck). N,N-dimethylformamide was dried over 3 Å molecular sieves during 72 h, then filtered and freshly distilled before utilization [10]. Sodium hydride Riedel-de Haën 80% suspension in oil was employed. 1,3-Diphenylisobenzofuran (DPBF) as well as all reagents were provided by Sigma–Aldrich. Tetra-*t*-butylphthalocyaninatozinc(II) [11] and 2,3,9,10,16,17,23,24-octakis(decyloxi)-phthalocyaninatozinc(II) (ZnPc) [12] were synthesized in our laboratory.

2.1. Synthesis

2.1.1. 4-(Adamantan-2-yloxy)-phthalonitrile(*3*)

A mixture of 2-adamantanol [caution: irritant] (0.104 g, 0.68 mmol) and NaH (0.023 g, 0.76 mmol) in DMF (3 mL) was stirred for 2 h, 4-nitrophthalonitrile (**1**) (0.100 g, 0.58 mmol) was then added and the stirring continued at room temperature for another 96 h. The reaction mixture was poured into a 10% NaCl solution with stirring. After 1 h, the precipitate obtained was centrifuged and then dried. The solid residue was dissolved in a small volume of CH_2Cl_2–hexane (4:1) and filtered through a silica-gel column packed and pre-washed with the same solvent. After evaporation of the solvent, the residue was recrystallized from ethanol. Yield: 0.086 g (54%); mp 110–112 °C. IR (KBr, cm^{-1}): 2921, 2851, 2233, 1599, 1559, 1488, 1469, 1452, 1426, 1386, 1347, 1293, 1249, 1216, 1174, 1101, 1092, 1043, 999, 961, 916, 880, 839, 732, 651, 523. ^1H NMR (300 MHz, $CDCl_3$): δ 1.57–2.14 (m, 14H, adamantane), 4.52 (br, 1H, HCO), 7.18 (dd, 1H, $J = 8.98$, 2.57 Hz, Ar), 7.26 (d, 1H, Ar), 7.68 (d, 1H, $J = 8.98$ Hz, Ar). MS (EI, 70 eV): m/z (%) 278 (4.69) [M^+], 135 (100). Anal. calcd. for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.95; H, 6.58; N, 9.94.

2.1.2. 3-(Adamantan-2-yloxy)-phthalonitrile(*4*)

A mixture of 2-adamantanol (0.104 g, 0.68 mmol) and NaH (0.023 g, 0.76 mmol) in DMF (3 mL) and 3-nitrophthalonitrile (**2**) (0.100 g, 0.58 mmol) was reacted by applying the procedure described for **3**. Yield: 0.084 g (52%); mp 173–175 °C. IR (KBr, cm^{-1}): 2927, 2856, 2232, 1583, 1467, 1288, 1102, 1048, 1030, 962, 918, 797, 732. ^1H NMR (300 MHz, $CDCl_3$): δ 1.57–2.23 (m, 14H, adamantane), 4.62 (br, 1H, HCO), 7.22 (m, 1H, $J = 7.76$ Hz, Ar), 7.30 (m, 1H, Ar), 7.58 (m, 1H, $J = 7.63$ Hz, Ar). MS (EI, 70 eV): m/z (%) 278 (7.49) [M^+], 135 (100). Anal. calcd. for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.55; H, 6.60; N, 9.98.

2.1.3. 1-(3,4-Diisocyanophenylsulfanyl)-adamantane (*5*)

A mixture of 1-adamantanethiol [caution: irritant] (0.583 g, 3.47 mmol), K_2CO_3 (3.2 g, 23.2 mmol) and 4-nitrophthalonitrile (**1**) (0.100 g, 0.58 mmol) in DMF (3 mL) was stirred at room temperature under argon for 96 h. The mixture was poured into a 10% NaCl solution with stirring. After 1 h, the precipitate obtained was centrifuged and then dried. The solid residue was dissolved in a small volume of CH_2Cl_2–hexane (4:1) and filtered through a silica-gel column packed and pre-washed with the same solvent. After evaporation of the solvent, the residue was recrystallized from ethanol. Yield: 0.169 g (99%); mp 141–143 °C. IR (KBr, cm^{-1}): 2963, 2914, 2885, 2851, 2673, 2231, 1651, 1579, 1544, 1474, 1453, 1378, 1351, 1312, 1297, 1260, 1208, 1103, 1035, 976, 959, 906, 870, 843, 727, 684, 613, 526. ^1H NMR (300 MHz, $CDCl_3$): δ 1.52–2.07 (m, 15H, adamantane), 7.73 (d, 1H, $J = 8.22$ Hz, Ar), 7.82 (dd, 1H, $J = 7.92$, 1.46 Hz, Ar), 7.90 (d, 1H, Ar). ESI-TOF MS: m/z $[M+H]^+$ calcd. for $C_{18}H_{18}N_2S$: 295.1191; found $[M+H]^+$: 295.1269 (100). Anal. calcd. for $C_{18}H_{18}N_2S$: C, 73.43; H, 6.16; N, 9.51. Found: C, 73.59; H, 6.18; N, 9.48.

2.1.4. 1-(2,3-Diisocyanophenylsulphanyl)-adamantane (*6*)

A mixture of 1-adamantanethiol (0.583 g, 3.47 mmol), K_2CO_3 (3.2 g, 23.2 mmol) and 3-nitrophthalonitrile (**2**) (0.100 g, 0.58 mmol) in DMF (3 mL) was reacted by applying the procedure described for **5**. Yield: 0.157 g (92%); mp 155–157 °C. IR (KBr, cm^{-1}): 2901, 2849, 2677, 2655, 2230, 1993, 1933, 1873, 1743, 1621, 1570,1471, 1445, 1423, 1365, 1351, 1312, 1298, 1257, 1198, 1143, 1102, 998, 978, 959, 938, 889, 855, 808, 779, 768, 683, 643, 573, 553. ^1H NMR (300 MHz, $CDCl_3$): δ 1.55–2.05 (m, 15H, adamantane), 7.65 (m, 1H, $J = 7.95$ Hz, Ar), 7.79 (m, 1H, Ar), 7.87 (m, 1H, $J = 7.95$ Hz, Ar). ESI-TOF MS: m/z $[M+H]^+$calcd. for $C_{18}H_{18}N_2S$: 295.1191; found $[M+H]^+$: 295.1269 (100). Anal. calcd. for $C_{18}H_{18}N_2S$: C, 73.43; H, 6.16; N, 9.51. Found: C, 73.23; H, 6.17; N, 9.53.

2.1.5. 2,9(10),16(17),23(24)-Tetrakis(2-adamantoxy)phthalocyaninatozinc(II) (*7*)

A mixture of **3** (0.050 g, 0.18 mmol), anhydrous zinc acetate (0.050 g, 0.22 mmol), and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) [caution: corrosive; lachrymator] (0.2 mL, 1.34 mmol) [13] was stirred and heated at 150 °C under argon during 1 h. The mixture was cooled down and CH_2Cl_2 (5 mL) was added, washed with water (3 × 5 mL) and evaporated in vacuo. The blue-green solid residue was dissolved in a small volume of CH_2Cl_2 and filtered through a silica-gel column packed and pre-washed with the same solvent. The title compound was eluted with CH_2Cl_2–methanol (98:2). After evaporation in vacuo, the dye was recrystallized from CH_2Cl_2–hexane. Yield 0.032 g (60%). IR ((KBr, cm^{-1}): 2922, 1718, 1605, 1571, 1473, 1359, 1231, 1143, 1089, 1043, 1000, 827, 747, 686. ^1H NMR (500 MHz, $CDCl_3$): δ 1.57–2.14 (m, 56H, adamantane), 4.52 (br, 4H, HCO), 7.50–7.80 (m, 12H, Ar). ESI-TOF MS: m/z $[M+H]^+$ calcd. for $C_{72}H_{72}N_8O_4Zn$: 1179.8131; found: $[M+H]^+$ 1179.8125, and $[M+2H]^+/2$ 590.4099. Anal. calcd. for $C_{72}H_{72}N_8O_4Zn$: C, 73.36; H, 6.16; N, 9.51. Found: C, 72.92; H, 5.84; N, 9.23.

2.1.6. 1,8(11),15(18),22(25)-Tetrakis(2-adamantoxy)phthalocyaninatozinc(II) (*8*)

A mixture of **4** (0.050 g, 0.18 mmol), anhydrous zinc acetate (0.050 g, 0.22 mmol), and DBU (0.2 mL, 1.34 mmol) in anhydrous butanol (4 mL) [14,15] was stirred and heated at 130 °C under argon during 2 h. The mixture was cooled down, evaporated in vacuo and CH_2Cl_2 (5 mL) was added, and then centrifuged to eliminate the excess of zinc acetate. The methylene chloride solution was washed with water (3 × 5 mL) and evaporated in vacuo. The green solid residue was dissolved in a small volume of CH_2Cl_2 and filtered through a silica-gel column packed and pre-washed with the same solvent. The title compound was eluted with CH_2Cl_2–methanol (98:2). After evaporation the dye was recrystallized from CH_2Cl_2–hexane. Yield 0.016 g (30%). IR (KBr, cm^{-1}): 2922, 1731, 1646, 1485, 1262, 1091, 803. ^1H NMR (500 MHz, $CDCl_3$): δ 1.57–2.14 (m, 56H, adamantane), 4.60 (br, 4H, HCO), 7.00–7.80 (m, 12H, Ar). ESI-TOF MS: m/z $[M+H]^+$ calcd. for $C_{72}H_{72}N_8O_4Zn$: 1179.8131; found: $[M+H]^+$ 1179.8136, and $[M+2H]^+/2$ 590.4115. Anal. calcd. for $C_{72}H_{72}N_8O_4Zn$: C, 73.36; H, 6.16; N, 9.51. Found: C, 73.14; H, 5.84; N, 9.22.

2.1.7. 2,9(10),16(17),23(24)-Tetrakis(1-adamantylsulfanyl)phthalocyaninatozinc(II) (*9*)

A mixture of **5** (0.050 g, 0.17 mmol), anhydrous zinc acetate (0.050 g, 0.22 mmol), and DBU (0.2 mL, 1.34 mmol) in anhydrous butanol (4 mL) [14,15] was stirred and heated at 130 °C under argon during 1 h. The mixture was cooled down, evaporated in vacuo and CH_2Cl_2 (5 mL) was added, and then centrifuged to eliminate the excess of zinc acetate. The methylene chloride solution was washed with water (3 × 5 mL) and evaporated in vacuo. The green solid residue was dissolved in a small volume of CH_2Cl_2–methanol (99:1) and filtered through a silica-gel column packed and pre-washed with the same solvent. The title compound was eluted with CH_2Cl_2–methanol (99:1). After evaporation the dye was recrystallized from CH_2Cl_2–hexane. Yield 0.031 g (58%). IR (KBr, cm^{-1}): 2918, 2850, 1732, 1626, 1489, 1453, 1342, 1298, 1099, 1037, 976, 909, 799, 745, 685, 472. ^1H NMR (500 MHz, $CDCl_3$): δ 1.49–2.21 (m, 60H, adamantane), 7.79–8.00 (m, 12H, Ar). ESI-TOF MS: m/z [M^+] calcd. for $C_{72}H_{72}N_8S_4Zn$: 1243.4054; found: [M^+] 1243.4132. Anal. calcd. for $C_{72}H_{72}N_8S_4Zn$: C, 69.57; H, 5.84; N, 9.01. Found: C, 69.22; H, 5.82; N, 9.05.

2.1.8. *1,8(11),15(18),22(25)-Tetrakis(1-adamantylsulfanyl)phthalocyaninatozinc(II)* (**10**)

A mixture of **6** (0.050 g, 0.17 mmol), anhydrous zinc acetate (0.050 g, 0.22 mmol), and DBU (0.2 mL, 1.34 mmol) in anhydrous butanol (4 mL) was reacted by applying the procedure described for **9**. The dye was recrystallized from CH_2Cl_2–hexane. Yield 0.026 g (50%). IR (KBr, cm^{-1}): 2960, 2905, 2849, 1622, 1429, 1261, 1125, 1087, 1029, 843, 797, 734, 699, 481. ^1H NMR (500 MHz, $CDCl_3$): δ 1.35–2.15 (m, 60H, adamantane), 7.59–7.93 (m, 12H, Ar). ESI-TOF MS: m/z [M^+] calcd. for $C_{72}H_{72}N_8S_4Zn$: 1243.4054; found: [M^+] 1243.4132. Anal. calcd. for $C_{72}H_{72}N_8S_4Zn$: C, 69.57; H, 5.84; N, 9.01. Found: C, 69.86; H, 5.82; N, 8.97.

2.2. *Photophysical and photochemical parameters*

2.2.1. *Spectroscopic studies*

Absorption and emission spectra were recorded at different concentrations employing a 10 × 10 mm quartz cuvette. All experiments were performed at room temperature.

The emission spectra of **7**, **9**, **10** were collected at an excitation wavelength of 610 nm (Q-band) and recorded between 630 and 800 nm whereas **8** was collected at an excitation wavelength of 630 nm and recorded between 650 and 850 nm.

2.2.2. *Fluorescence quantum yields*

Fluorescence quantum yields (Φ_F) were determined by comparison with those of tetra-*t*-butyl phthalocyaninatozinc(II) ($\Phi_F = 0.30$ in toluene) [11] as reference at $\lambda_{exc} = 610$ nm for **7**, **9**, **10** and $\lambda_{exc} = 630$ nm for **8**. Calculation was performed by equation (1).

$$\Phi_F^S = \Phi_F^R \frac{I^S\left(1 - 10^{-A^R}\right)}{I^R\left(1 - 10^{-A^S}\right)} \left(\frac{n^S}{n^R}\right)^2 \tag{1}$$

where R and S superscripts refer to the reference and the sample respectively; *I* is the integrated area under the emission spectrum; *A* is the absorbance of solutions at the excitation wavelength and $(n^S/n^R)^2$ stands for the refractive index correction.

2.2.3. *Quantum yield of singlet oxygen production*

Standard chemical monitor bleaching rates were used to calculate the quantum yield of singlet oxygen generation rates [16]. For Φ_Δ studies, DPBF was used as a singlet oxygen chemical quencher. To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the absorbance of DPBF was under 1.9 employing a 10 × 10 mm quartz cuvette. DPBF decay at 410 nm was monitored. Polychromatic irradiation was performed using a projector lamp (Philips 7748SEHJ, 24 V-250 W) and a cut-off filter at 610 nm (Schott, RG 610) and a water filter were used to prevent ultraviolet and infrared radiation. Samples **7**–**10** and reference (ZnPc: $\Phi_\Delta = 0.70$ in THF) [12] were irradiated within the same wavelength interval λ_1–λ_2, and Φ_Δ was calculated according to equation (2).

$$\Phi_\Delta^S = \Phi_\Delta^R \frac{r^S}{r^R} \frac{\int_{\lambda_1}^{\lambda_2} I_0(\lambda)\left(1 - 10^{-A^R(\lambda)}\right) d\lambda}{\int_{\lambda_1}^{\lambda_2} I_0(\lambda)\left(1 - 10^{-A^S(\lambda)}\right) d\lambda} \tag{2}$$

where *r* is the singlet oxygen photogeneration rate and the superscripts S and R stand for the sample and reference respectively, *A* is the absorbance at the irradiation wavelength and $I_0(\lambda)$ is the incident spectral photon flow (mol s^{-1} nm^{-1}). When the irradiation wavelength range is narrow, the incident intensity varies smoothly with wavelength and the sample and reference have overlapping spectra I_0 may be approximated by a constant value which may be drawn out of the integrals and cancelled.

2.2.4. *Photo-oxidative stability*

The photo-stability of phthalocyanines **7**–**10** was determined by the decay of the Q-band intensity after exposure to red light [17]. The fluence rate was adjusted to 20 m Wcm^{-2}. Measurements were performed under air in THF. Photodegradation rate constants *k* were calculated by equation (3).

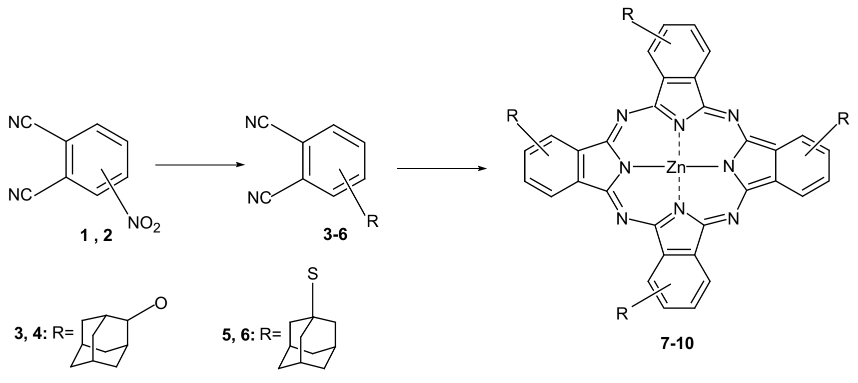
$$\ln\frac{A_0}{A_t} = k \cdot t \tag{3}$$

where t, A_0, A_t are the irradiation time, absorbance at $t = 0$, absorbance at different times, respectively.

3. Results and discussion

3.1. *Chemistry*

Novel bulky tetrasubstituted phthalocyanine compounds were designed and synthesized as depicted in Scheme 1. The sequence



Scheme. 1. Synthetic route of phthalocyanines **7**–**10**.

Table 1
Photophysical parameters obtained for phthalocyanines **7**–**10** in THF.

Compound	λ_{max},Q-band(nm)	λ_{max}, Emission (nm)	ε_{max} ($M^{-1}\,cm^{-1}$)	Φ_F	Φ_Δ	$k(10^{-3}\,min^{-1})$
7	678	686	$(1.6 \pm 0.1) \times 10^4$	0.33 ± 0.01	0.63 ± 0.02	0.5
8	706	712	$(7.2 \pm 0.2) \times 10^4$	0.14 ± 0.01	0.78 ± 0.02	0.3
9	680	687	$(1.0 \pm 0.1) \times 10^5$	0.31 ± 0.01	0.66 ± 0.01	0.7
10	682	689	$(1.2 \pm 0.1) \times 10^5$	0.17 ± 0.01	0.81 ± 0.01	0.6

begins with the reaction of 4- and 3-nitrophthalonitrile with the corresponding nucleophiles to achieve precursors **3**–**6** in good yields; in all cases DMF proves to be more effective than DMSO as the reaction solvent as it resulted in improved yields of pure products. The reaction of 2-adamantanol with 4- and 3-nitrophthalonitrile (**1**,**2**) was performed in the presence of a strong base, sodium hydride, in order to generate compounds **3** and **4**. As expected, precursors **5**–**6** were obtained employing potassium carbonate [13,18,19].

Phthalocyanine **7** was readily prepared by cyclotetramerization of phthalonitriles **3** employing 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and zinc acetate at 150 °C, whereas phthalocyanines **8**–**10** were prepared by reacting **4**–**6** respectively with DBU and zinc acetate in butanol. Intermediates **3**–**6** and dyes **7**–**10** were characterized by IR and ^{1}H NMR spectroscopy while EI-MS spectroscopy at 70 eV was performed for the characterization of **3**–**4**, o-dinitriles **5**–**6** were determined with ESI-TOF-MS spectroscopy since EI-MS at 70 eV or 40 eV only afforded decomposition fragments. ESI-TOF mass spectroscopy was employed for the characterization of phthalocyaninates **7**–**10**.

3.2. Absorption spectra

The absorption spectra of zinc (II) phthalocyanines in the 320–800 nm range in all the compounds studied are similar to those previously reported for other analogues in homogeneous media [11,20] (Fig. 1).

Q-bands of substituted 1, 8(11), 15(18), 22(25) (α) zinc (II) phthalocyanines appears at longer wavelengths than 2,9(10),16(17),23(24) (β) derivatives (Table 1). This red spectral shift is consistent with previous reports for substituted zinc(II) phthalocyaninates with electron-releasing groups [21,22], which can be reasonably explained by considering the magnitude of the atomic orbital coefficients of the carbon atoms derived from molecular orbital calculations. According to these studies the coefficient of the α carbon atoms is larger than that of β carbon atoms in the HOMO, the destabilization extent of this orbital by introducing electron-donating groups is larger when they are linked to the α-positions, which makes the HOMO–LUMO gap smaller and thereby results in the Q-band shifting to a longer wavelength [22]. The same behavior was observed in phthalocyanines studied in our laboratory, 2,3,9,10,16,17,23,24-octakis[(N,N-dimethylaminoethoxy)]phthalocyaninatozinc(II) [8], **7** and **8**, whose Q-bands appear at 672, 678 and 706 nm respectively thus indicating that λ_{max} values decrease in the following order: 4αZnPc > 4βZnPc > 8βZnPc. However, different behavior was observed when sulfanyl groups are involved; the 2,3,9,10,16,17,23,24-octakis[(N,N-dimethylaminoethylsulfanyl)]phthalocyaninatozinc (II) [8], **9** and **10** Q-band appears at 704, 680 and 682 nm respectively thus showing that λ_{max} values decrease in the following order: 8βZnPc > 4αZnPc > 4βZnPc. Further theoretical studies must be conducted to explain this phenomenon.

A higher bathochromic shift of 28 nm for the Q-band is observed for oxygen linked adamantane α-phthalocyanine in comparison

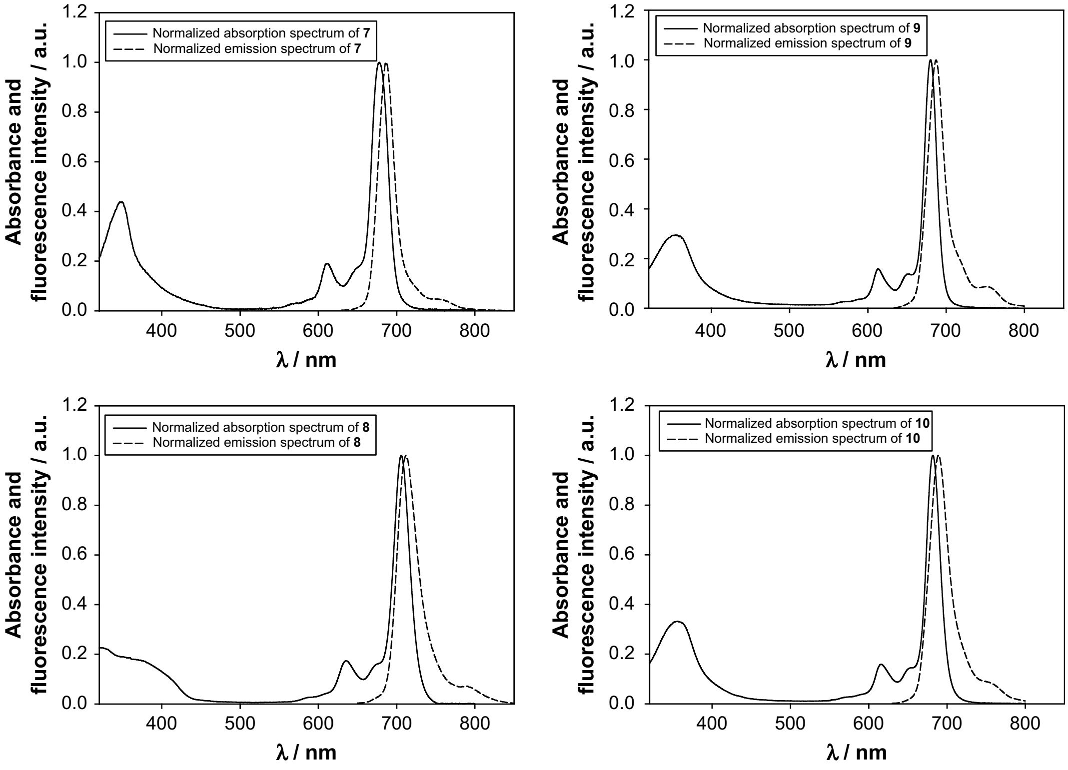


Fig. 1. Absorption and fluorescence spectra of **7**–**10** in THF.

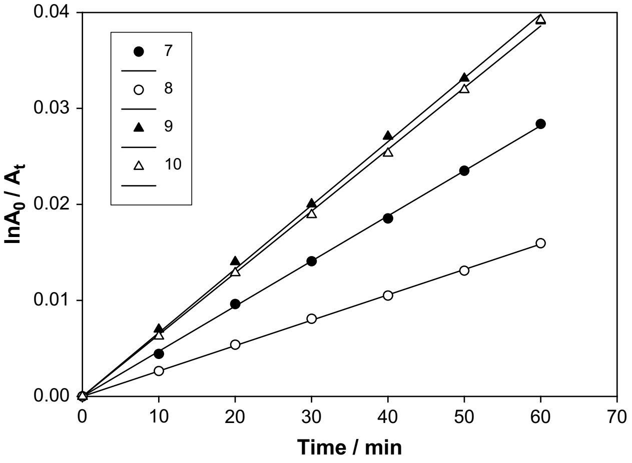


Fig. 2. First-order plots for the photodegradation of phthalocynines **7**–**10** in THF.

with β-isomer. The same effect but of lesser magnitude (2 nm) was observed for the sulfur linked adamantane α-phthalocyanine.

3.3. *Fluorescence*

Fig. 1 shows the fluorescence spectra of the zinc (II) tetrasubstituted phthalocyanines. The shapes of the spectra for all dyes are the same and maximum emission differs depending on the position of the peripheral substituents [21,22].

As previously reported [22], relative fluorescence quantum yields are similar for compounds **7**, **9** and present higher Φ_F values than compounds **8**, **10** whose Φ_F values are ca. 0.16 (Table 1). This observation implies that Φ_F becomes smaller with a decreasing energy gap between the HOMOs and LUMOs thus suggesting that excited states become unstable in systems showing a Q-band at lower energy, plausibly due to the ease of electron transfer.

3.4. *Quantum yield of singlet oxygen production*

The Φ_Δ values in THF obtained for dyes **7**–**10** are listed in Table 1. Sample absorbances were kept as low as possible to prevent aggregation, though enough to obtain measurable values of quantum yield of singlet molecular oxygen. The Φ_Δ in homogeneous solution are similar to those previously published [11,12] corresponding to zinc (II) phthalocyanine monomers at the concentration employed. As indicated in Table 1, phthalocyanines **7**–**10** are excellent singlet oxygen generators with a high value of Φ_Δ , 0.63–0.81. This is consistent with a conclusion that substituted zinc(II) phthalocyaninates bearing electron-donating substituents have higher Φ_Δ , as reported by Wöhrle and co-workers [23]. Phthalocyanines **8** and **10** (α-substituted) present higher values of Φ_Δ in comparison with **7**, **9**(β-substituted). This effect was also described elsewhere [24].

3.5. *Photo-oxidative stability*

The photo-stability of **7**–**10** was analyzed in THF by measuring the decrease in the intensity of the Q-band over time irradiation with red light under air. The time decay of the absorbance maxima of the Q-band for all the compounds obeyed first-order kinetics as shown in Fig. 2.

The corresponding photodegradation constants *k* are listed in Table 1. Smaller values of *k* infer a high photo-oxidative stability. As shown in Table 1, phthalocyanines bearing an adamantoxy group present the highest stability in THF. For all the substituents studied, tetra-α-substituted phthalocyanines are more stable as compared with their tetra-β-substituted counterparts. A similar trend has recently been reported by other authors [24,25]. Moreover, phthalocyanines **7**–**10** show low values of *k* thus indicating they are stable at the irradiation times of our experiments.

4. Conclusions

Novel zinc (II) phthalocyanines were synthesized from the corresponding o-phthalonitriles employing commercially available 3- and 4-nitrophthalonitrile as the starting material. These dyes were characterized by their photophysical properties; the Q-band of α-phthalocyanines **8** and **10** lies at a longer wavelengths than that of β-phthalocyanines **7** and **9**, showing that adamantoxy-substituted phthalocyanines offered the highest bathochromic shift progressing into the therapeutic window which could be useful for biomedical applications such as tissue imaging and photodynamic therapy. Substituents at the β-position increase Φ_F values.

Phthalocyanines **7**–**10** are excellent singlet oxygen generators, the α-substituted dyes showing higher values of Φ_Δ than those of β-isomers. Besides, **7**–**10** are photo-stable at the irradiation times studied. At the same time, the tetra-α-substituted phthalocyanines show a higher photo-stability as compared with their tetra-β-substituted counterparts.

The results demonstrate that substituents in positions 1,8(11), 15(18), 22(25) improve the photophysical properties and photo-stability of the tetrasubstituted zinc (II) phthalocyanines, these dyes appear promising as second-generation photosensitizers for biological purposes.

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