# CONTENTS

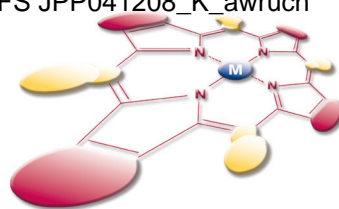*Journal of Porphyrins & Phthalocyanines*
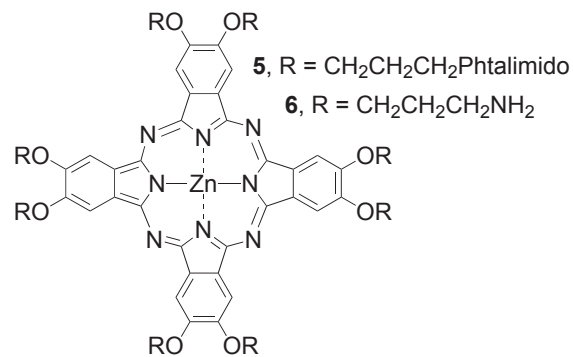
http://www.u-bourgogne.fr/jpp/

### ###

## A synthetic approach towards novel octa-substituted zinc(II) phthalocyanines with different solubility and photophysical properties

Cristian A. Strassert, Myriam E. Rodriguez, Lelia E. Dicelio and Josefina Awruch*

The synthesis and behavior in homogeneous solutions of 2,3,9,10,16,17,23,24-octakis(3-phthalimidopropyloxy)phthalocyaninatozinc(II) (**5**) and 2,3,9,10,16,17,23,24-octakis(3-aminopropyloxy)phthalocyaninatozinc(II) (**6**) are reported.

**5**, R = $CH_2CH_2CH_2$Phtalimido
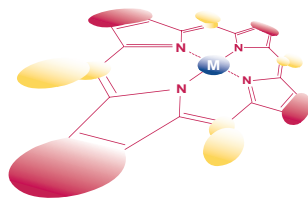
**6**, R = $CH_2CH_2CH_2NH_2$

# A synthetic approach towards novel octa-substituted zinc(II) phthalocyanines with different solubility and photophysical properties

## Cristian A. Strassert[a,b], Myriam E. Rodriguez[a,b], Lelia E. Dicelio[b] and Josefina Awruch*[a◇]

[a] *Departamento de Química Orgánica, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Junín 956, 1113 Buenos Aires, Argentina*

[b] *INQUIMAE. Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, 1428 Buenos Aires, Argentina*

**ABSTRACT:** The synthesis and behavior in homogeneous solutions of 2,3,9,10,16,17,23,24-octakis(3-phthalimidopropyloxy)phthalocyaninatozinc(II) (**5**) and 2,3,9,10,16,17,23,24-octakis(3-aminopropyloxy)phthalocyaninatozinc(II) (**6**) are reported. Copyright © 2005 Society of Porphyrins & Phthalocyanines.

**KEYWORDS:** zinc(II) phthalocyanine, photophysics, solubility.

## INTRODUCTION

Phthalocyanines play a major role in modern photochemistry. Complexation of phthalocyanines with metal ions has an influence on their photophysical properties. These compounds are used as catalysts as well as photoreceptors in electrographic printing [1]. In medicine these dyes have been found to have applications as phototoxic drugs for photodynamic therapy [2, 3]. All of these applications require compounds of various solubility and high degree of purity in order to prevent byproducts from harming their photoconducting and optical characteristics.

Additionally, utilization of phthalocyanines for inks requires these dyes to be dissolved in water or in organic solvents miscible with water.

Since phthalocyanines are highly insoluble, many efforts were made to prepare lipophilic compounds through the introduction of peripheral alkyl chains [4-7]. In addition, phthalocyanine amphiphilicity was improved by employing sulfonated zinc(II) [2, 8] and sulfonated aluminium phthalocyanines [9, 10]. Also, zinc(II) phthalocyanines with peripheral substituents such as hydroxy and alkylhydroxy [11, 12], alkylamino [13-15] and quaternary alkyl ammonium salts [16, 17] have been synthesized.

The great interest in the development of these macromolecules has led us to investigate the synthesis and properties of phthalocyanines substituted with amphiphilic groups in order to evaluate their influence on the solubility and photophysical properties.

In a recent paper [15] we stated that zinc phthalocyanine derivatives functionalized with both methyl and phthalimidomethyl as well as methyl and aminomethyl units on the benzenoid rings are moderately soluble in organic solvents and insoluble in water. Incorporation of functional moieties such as 3-phthalimidopropyloxy to one phthalocyanine and of 3-aminopropyloxy to another, allowed us to prepare two novel octa-substituted dyes which differ as regards solubility and photophysical properties, and these were thoroughly investigated in homogeneous solution.

◇SPP full member in good standing

*Correspondence to: Josefina Awruch, email: jawruch@ffyb.uba.ar, fax: +54 11-4508-3645

## General

All reagents for organic synthesis were purchased from Merck or Aldrich and used without further purification.

TLC Kiesegel (Merck) was the silica gel used in column chromatography. N,N-dimethylformamide was dried over 3 Å molecular sieves during 72 h, filtered and freshly distilled before utilization [18].

Tetra-*t*-butylphthalocyaninatozinc(II) [19], hydroxyaluminium tricarboxymonoamidephthalocyanine [20], and 2,3,9,10,16,17,23,24-octakis(decyloxy)-phthalocyaninatozinc(II) [21] were synthesized in our lab.

Tetrahydrofuran (THF) was obtained from Mallinckrodt Chemical Works. Toluene was provided by Dorwil (Buenos Aires, Argentina). Methylene Blue (Fluka p.a.) and $D_2O$ (Merck Uvasol 99.8%) were used as supplied.

If not otherwise specified, all chemicals were reagent grade and used without further purification. Distilled water treated in a Milli-Q system (Millipore) was used.

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. The ^{1}H NMR were recorded on a Bruker MSL 300 spectrometer. The ^{1}H NMR of phthalocyanines **5** and **6** were recorded on a Bruker AM 500. Mass Spectra were obtained with a TRIO 2 (electronic ionisation 70 eV) spectrometer. Phthalocyanine HRFAB-MS spectra were measured with a VG AutoSpec spectrometer. Microanalyses were performed using a Carlo Erba EA 1108 elemental analyser. Infrared spectra were performed with an FT-IR Nicolet 510P spectrometer. Electronic absorption spectra were determined using a Shimadzu UV-3101 PC spectrophotometer. Fluorescence spectra were monitored with a QuantaMaster Model QM-1 PTI spectrofluorometer.

## Synthesis

**1,2-di(3-phthalimidopropyloxy)benzene 2.** A mixture of pyrocatechol 1.1 g (10 mmol), N-(3-bromopropyl)phthalymide 5.36 g (20 mmol) and potassium carbonate 2.76 g (20 mmol) in dry N,N-dimethylformamide (50 mL) was stirred and heated at 60 °C for 65 h under nitrogen and then poured into water (100 mL) and extracted with methylene chloride (3 × 30 mL) [4]. The combined extracts were washed with water (2 × 50 mL), dried (sodium sulphate) and evaporated to dryness *in vacuum*. The solid residue was dissolved in a small volume of methylene chloride-methanol (99:1) and filtered through a TLC silica gel column. After evaporation of the solvent, the solid residue was recrystallized from toluene-hexane, 3 g (62%) mp 137 °C. MS: *m/z* 484 ([M]+, 2.51%), 188 (100%), 160 (62.40%). Anal. calcd. for

$C_{28}H_{24}N_2O_6$: C, 69.41; H, 4.99; N, 5.78. Found: C, 69.48; H, 5.03; N, 5.72. ^{1}H NMR (CDCl_3): δ, ppm 2.17-2.20 (m, 4H, CH_2); 3.90 (t, 4H, OCH_2); 4.02 (t, 4H, CH_2N); 6.87 (s, 2H, Ar); 7.65-7.80 (m, 8H, phthalimide). IR (KBr): ν, cm[-1] 3084; 3061; 2957; 2930; 2866; 1776; 1767; 1709; 1504; 1466; 1439; 1396; 1373; 1342; 1251; 1215; 1145; 1124; 1047; 1035; 943; 898; 748; 721.

**1,2-dibromo-4,5-di(3-phthalimidopropyloxy)-benzene 3.** Bromine (0.19 mL, 3.6 mmol) dissolved in 6 mL of methylene chloride was added dropwise to an ice cold solution of **2** (0.830 g, 1.7 mmol) dissolved in 8.5 mL of methylene chloride. After addition stirring was continued for 1 h. Methylene chloride (100 mL) was added, the solution washed with 10% sodium thiosulphate (2 × 50 mL) followed by water (2 × 100 mL), 10% sodium carbonate (2 × 100 mL), and water (2 × 100 mL). The organic phase was dried (sodium sulphate) and evaporated to dryness *in vacuum*. The solid residue was recrystallized from toluene-hexane, 0.582 g (83%) mp 205 °C. MS: *m/z* 644 ([M]+ 2, 0.17%), 640 (M+- 2, 0.17%), 642 (M+, 0.33%), 188 (100%). Anal. calcd. for $C_{28}H_{22}N_2O_6Br_2$: C, 52.36; H, 3.45; N, 4.36. Found: C, 52.28; H, 3.55; N, 4.27. ^{1}H NMR (CDCl_3): δ, ppm 2.08-2.21 (m, 4H, CH_2); 3.88 (t, 4H, OCH_2); 3.95 (t, 4H, CH_2N); 7.02 (s, 2H, Ar); 7.63-7.85 (m, 8H, phthalimide). IR (KBr): ν, cm[-1] 3053; 2949; 2885; 1773; 1709; 1499; 1488; 1448; 1408; 1393; 1379; 1354; 1335; 1316; 1250; 1204; 1156; 1142; 1051; 1043; 852; 723; 710.

**1,2-dicyano-4,5-di(3-phthalimidopropyloxy)-benzene 4.** A solution of 0.500 g (0.77 mmol) of **3** and 0.250 g cuprous cyanide in N,N-dimethylformamide (17 mL) was heated at 145 °C during 15 h under argon [14, 15]. The solution acquired a brown colour. After cooling, it was poured into a concentrated ammonia solution (35 mL) and stirred during 4 h. Water (40 mL) was added and left in the refrigerator overnight. The solid precipitate obtained was separated by centrifugation, washed twice with cold water and then dried. The residue was dissolved in methylene chloride-methanol (99:1) and filtered through a TLC silica gel column. After evaporation of the solvent, the solid residue R_f 0.4 was rechromatographed using TLC followed by recrystallization from methylene chloride-hexane, 0.0915 g (22%), mp 237-241 °C. MS: *m/z* 534 ([M]+, 0.16%); 188 (100%). Anal. calcd. for $C_{30}H_{22}N_4O_6$: C, 67.41; H, 4.15; N, 10.48. Found: C, 67.38; H, 4.25; N, 10.37. ^{1}H NMR (CDCl_3): δ, ppm 2.03-2.17 (m, 4H, CH_2); 3.91 (t, 4H, OCH_2); 4.05 (t, 4H, CH_2N); 7.07 (s, 2H, Ar); 7.68-7.82 (m, 8H, phthalimide). IR (KBr): ν, cm[-1] 3459; 2946; 2230; 1771; 1709; 1590; 1518; 1468; 1447; 1408; 1381; 1358; 1337; 1285; 1227; 1215; 1175; 1156; 1140; 1096; 1051; 916; 723.

**2,3,9,10,16,17,23,24-octakis(3-phthalimidopropyloxy)phthalocyaninatozinc(II) 5.** A mixture of

0.100 g (0.181 mmol) of **4** and 0.040 g of powdered zinc [14, 15] was heated at 238 °C in a closed vessel during 2 h. It was allowed to cool, methylene chloride (100 mL) was added and the remaining zinc filtered under suction. The solution was evaporated *in vacuum*, leaving a green solid. This residue was dissolved in methylene chloride-methanol (97:3) and filtered through a TLC silica gel column packed and pre-washed with the same solvent. After evaporation of the solvent, the green residue was recrystallized from methylene chloride-hexane: 0.035 g (34%). HRFAB-MS: observed 2203.552 (M$^+$), required 2203.556. Anal. calcd. for $C_{120}H_{88}N_{16}O_{24}Zn$: C, 65.41; H, 4.03; N, 10.17. Found: C, 65.30; H, 3.99; N, 10.20. $^1$H NMR (CDCl$_3$): δ, ppm 2.14-2.17 (m, 16H, CH$_2$); 3.91 (t, 16H, OCH$_2$); 4.06 (t, 16H, CH$_2$N); 7.20(s, 8H, Ar); 7.66-7.81 (m, 32H, phthalimide). IR (KBr): ν, cm$^{-1}$ 3415, 2924, 1771, 1709, 1638, 1617, 1497, 1466, 1397, 1281, 1190, 1043, 721, 622.

**2,3,9,10,16,17,23,24-octakis(3-aminopropyl-oxy)phthalocyaninatozinc(II) 6.** Hydrazine (0.16 mL) was added to a solution of **5** in 2 mL of N,N-dimethylformamide and 8 mL of tetrahydrofuran, and stirred during 16 h [14, 15]. After evaporation of the solvent, the residue was dissolved in a 0.1 M hydrochloric acid solution and 2 mL of methanol. After cooling during 18 h, the phthalazide was filtered. The methanol was evaporated and then the acid solution was adjusted to pH 7 with a 0.1 M sodium hydroxide solution, freeze-dried, washed with methanol and dried to give **6** in quantitative yield. HRFAB-MS: observed 1161.508875 (M$^+$), required 1161.508500. Anal. calcd. for $C_{56}H_{72}N_{16}O_8Zn$: C, 57.85; H, 6.24; N, 19.28. Found: C, 57.74; H, 6.30; N, 19.35. $^1$H NMR (D$_2$O): δ, ppm 2.22-2.38 (m,16H,CH$_2$); 3.21-3.26 (m, 16H, OCH$_2$); 3.57-3.60 (m, 16H, CH$_2$N); 7.50 (s, 8H, Ar). IR (nujol): ν, cm$^{-1}$ 3448, 1662, 1559, 1496, 1082, 954, 827, 792, 683, 628.

## Spectroscopic and photophysical characterization

*Aggregation equilibrium.* Absorption spectra were recorded at different concentrations by using a 100 mm quartz cuvette. Depending on the dye concentration, phthalocyanines may present different degrees of aggregation (dimers, trimers and higher oligomers) in solution. Solutions of phthalocyanine **5** in THF and phthalocyanine **6** in water were investigated. Concentrations employed ranged from $1 \times 10^{-9}$ M to $1 \times 10^{-6}$ M. In order to obtain monomer and aggregate concentrations and their corresponding spectra, the aggregation constant of **6** was calculated upon deconvolution of the Q-band of the experimental absorption spectra as an apparent dimerization constant, $K_{dapp} = c_D/c_M^2$, where M stands for the monomer and D for the dimer [22].

*Emission and excitation spectrum experiments.* Excitation and emission spectra of **5** in THF and **6** in water were obtained at concentrations of $1 \times 10^{-7}$ M. Emission spectra were recorded between 600 and 800 nm exciting at 580 nm in order to collect a wide range of wavelengths. Excitation spectra were acquired between 550 and 750 nm, setting the detector at 770 nm.

*Fluorescence quantum yields.* Relative fluorescence quantum yields of **5** in THF and **6** in water at concentrations ranging from $1 \times 10^{-7}$ M to $1 \times 10^{-6}$ M were determined by comparison with hydroxyaluminium tricarboxymonoamidephthalocyanine ($\Phi_F = 0.42$ in DMSO) [20]. In all cases the excitation wavelength was 610 nm and the emission spectra were registered between 630 and 800 nm. The quantum yield was calculated as described elsewhere [23].

As the aggregation effect is important in the case of **6**, even for the highly diluted solutions employed for fluorescence measurements, the dimer concentration is not negligible with reference to that of the monomer. Thus, an additional correction was included, replacing (1-10$^{-A}$), the total absorbed light, with the fraction of light absorbed by the monomer $\gamma_m = (1-10^{-A})A_m/A$ [16].

In order to evaluate $\gamma_m$, it was necessary to determine the monomer absorbance $A_m$ at 610 nm for each concentration of phthalocyanine. This was achieved by calculating the corresponding monomer concentrations (according to the dimerization constant obtained). The absorption coefficient of the monomer, calculated by deconvolution, allowed then the evaluation of $A_m$ for each concentration.

*Flash photolysis.* All experiments were performed at room temperature. A solution $1 \times 10^{-6}$ M of **5** in THF, deareated in an evacuable 10 × 10 mm pathlength fluorescence quartz cuvette by several freeze-pump (10$^{-2}$ Pa)-thaw cycles, was excited with different laser intensities whereas a solution of **6**, $1 \times 10^{-6}$ M in water, was deareated with bubbling argon for 1 h. The triplet quantum yield of **5** was calculated as described elsewhere [21]. Samples were excited with a Spectron SL 4000 Pyridine 1 (690 nm) dye laser pumped by a doubled Q-switched Spectron SL800 Nd/YAG laser (532 nm, pulse width 8 ns) according to reference 21. Tetra-*t*-butylphthalocyaninatozinc(II) in toluene was used as a reference ($\Phi_T = 0.69$) [19].

*Singlet molecular oxygen quantum yields.* Time resolved singlet oxygen phosphorescence detection was employed to calculate singlet oxygen photoproduction quantum yields of **5** in THF and **6** in D$_2$O, according to reference 21. Methylene Blue in D$_2$O and 2,3,9,10,16,17,23,24-octakis(decyloxy)-
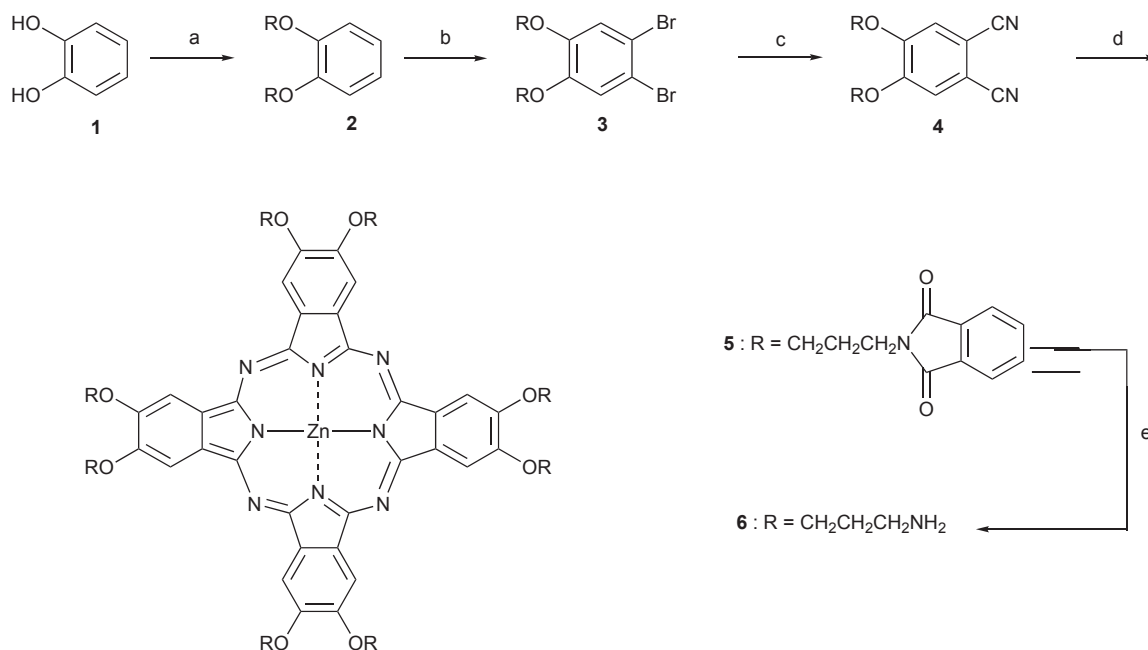
**Scheme 1.** Reagents and conditions: **a.** N-(3-bromopropyl)phthalimide, $K_2CO_3$, DMF, 60 °C; **b.** $Br_2$, $CH_2Cl_2$; **c.** CuCN, DMF, 136 °C; **d.** Zn, 238 °C; **e.** $H_2NNH_2$, THF

phthalocyaninatozinc(II) in THF were used as references [21]. The concentration of the samples was $1 \times 10^{-6}$ M.

***Determination of octanol:water partition coefficients.*** The octanol:water partition coefficient of **6** was determined by using a modified method of Minnock *et al*. [24]. In order to evaluate the influence of pH and ionic strenght on the logP of **6**, the partition coefficient between octanol:water was measured and this value compared with those of the octanol: sodium hydroxide solution (0.01M) and octanol: saline solution (0.01M) partition coefficients. Since **5** is not soluble in water, its octanol:water partition coefficient could not be measured.

## RESULTS AND DISCUSSION

### Synthesis

The synthesis of phthalocyanines **5** and **6** is depicted in Scheme 1. As shown, the sequence begins with the reaction of pyrocatechol (**1**) with N-(3-bromopropyl)phthalimide to give 1,2-di(3-phthalimidopropyloxy)bencene (**2**). The reaction of compound **2** with bromine in dichloromethane at room temperature afforded the dibromo derivative **3**, which was subsequently reacted with copper(I) cyanide in N,N-dimethylformamide to yield the required phthalonitrile **4**. Compound 1-bromo-2-cyano-4,5-di(3-phthalimidopropyloxy)bencene was obtained as a side product. Phthalocyanine **5** was readily prepared

by the cyclotetramization of phthalonitrile **4** with powdered zinc at 238 °C in a sealed tube. Attempts to obtain **5** by employing 1,8-diazabicyclo[5,4,0]undec-7-ene in butanol and zinc acetate failed.

Phthalocyanine **5** was purified by chromatography, followed by recrystallization to attain 34% of the desired 2,3,9,10,16,17,23,24-octakis(3-phthalimidopropyloxy)phthalocyaninatozinc(II). Treatment of **5** with hydrazine in tetrahydrofuran at room temperature gave phthalocyanine **6** in quantitative yield.

With regard to the solubility of the new phthalocyanines, both dyes have markedly different solubility properties; while **5** is soluble in almost all organic solvents, **6** is fully soluble in water. However, **6** is indeed amphiphilic as shown by the octanol:water partition coefficient value (log P = 0.6), which does not depend on pH and ionic strength of the aqueous phase. This dye has a hydrophobic macrocycle and alkyl chains as well as hydrophilic peripheral amino groups capable of forming hydrogen bonds and salt bridges when protonated.

### Spectroscopic and photophysical characterization

The absorption spectra of **5** in the 400-800 nm range in THF show a Q-band with a maximum at $\lambda_{max}$ = 674 nm, and no aggregation was observed in the concentration range between $1 \times 10^{-7}$ and $1 \times 10^{-5}$ M (Fig. 1).

Phthalocyanine **6** is highly soluble in water and aggregation is evidenced by dependence on concentration of the absorption spectrum shape (Fig. 2). As the concentration was raised, the absorption
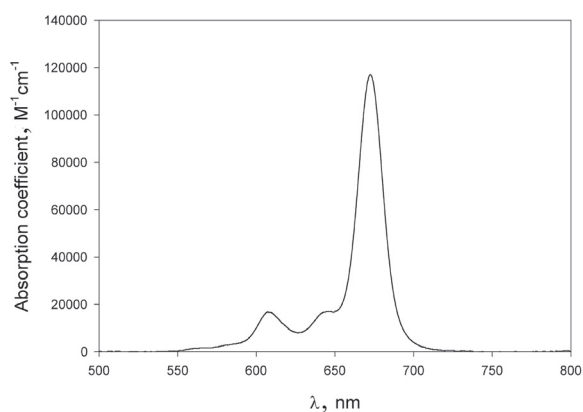
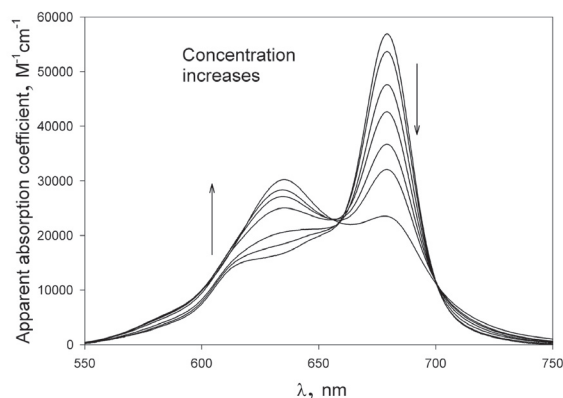**Fig. 1.** Normalized absorption spectrum for **5** in THF at 1 × $10^{-7}$ M



**Fig. 2.** Normalized absorption spectra for **6** in water at various concentrations: $2.2 \times 10^{-6}$, $1.11 \times 10^{-6}$, $8.35 \times 10^{-7}$, $5.58 \times 10^{-7}$, $3.55 \times 10^{-7}$, $2.53 \times 10^{-7}$, and $1.88 \times 10^{-9}$ M

band at 680 nm decreased and the band at 630 nm became higher, while the isosbestic point around 660 nm was shifted to shorter wavelengths.

Aggregation studies were performed in order to evaluate the monomer photophysical properties. Since the monomer spectrum of **6** was not attainable, even at 1 × $10^{-9}$ M, the absorption spectrum of **5** was used as an input for the deconvolution algorithm in the aggregation analysis. According to this, the absorption spectrum of **5** (Fig. 1) was assumed to be similar in shape to the monomer spectrum of **6** with a red shift of 6 nm. The monomer spectrum and the average spectrum of the oligomers were calculated upon deconvolution of the experimental absorption spectra (Fig. 3).

Different apparent dimerization constant values resulted at higher concentrations. The increasing value of the apparent dimerization constant shows that higher aggregation equilibria become important at higher dye concentrations. The existence of multiple equilibria between monomer and oligomers of similar spectra also explains the blue shift of the isosbestic point around 660 nm with increasing concentrations (Fig. 2). The following empirical equation indicates
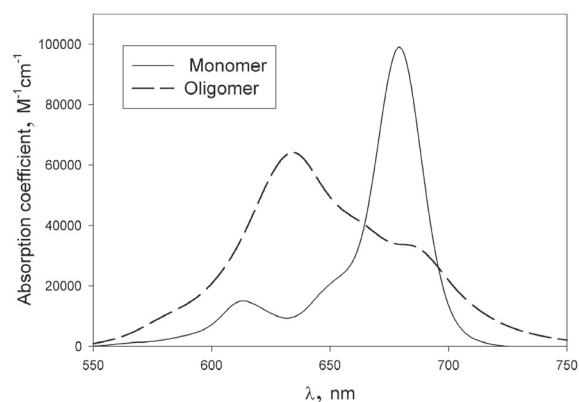


**Fig. 3.** Calculated monomer and average oligomer spectra for **6** in water

the dependence of $K_{dapp}$ on dye concentration:

$$K_{dapp} = 4.81 \times 10^{18} \times [6]^2 + 1.83 \times 10^{12} \times [6] + 3.51 \times 10^6 \quad (1)$$

According to this dependence, the experimental absorption spectra at different concentrations were exactly reproduced by means of the calculated monomer and average aggregate spectra.

Fluorescence excitation and emission spectra of **5** in THF and of **6** in water are similar to those previously reported for other monomer zinc(II) phthalocyanines (Fig. 4a,b) [19, 23].

The monomer absorption spectrum of **6**, calculated upon deconvolution, is in good agreement with its experimental fluorescence excitation spectrum (Fig. 4b).

The excitation and absorption spectra of the monomeric phthalocyanines are coincident for both compounds **5** and **6**. Therefore, fluorescence must be attributed only to the monomeric species.

Photophysical parameters of compounds **5** and **6** are summarized in Table 1.

The fluorescence quantum yield of **5** in THF is $\Phi_F = 0.30$ as expected for a zinc(II) phthalocyanine monomer [19, 23].

Fluorescence intensities of **6** were corrected taking into account the fraction of light absorbed by the monomer at different concentrations, in order to evaluate the fluorescence quantum yield of the monomer. Due to aggregation, the experimental quantum yields strongly depend on concentration, ranging between 0.07 and 0.09. After correction by means of the calculated aggregation parameters, expected values for a phthalocyanine monomer were obtained at each concentration.

Triplet quantum yields were obtained at the maximum of the triplet-triplet absorption spectra, where the ground state does not absorb (analysis wavelength, λ = 480 nm). The triplet quantum yield was $\Phi_{\Pi}$ (**5**) = 0.7. The intensities of the transient signals for **6** were too low to allow measurements at

**Table 1.** Spectral and photophysical parameters of compounds **5** and **6**

| Compound[a] | $\lambda_{max}$, nm | $\varepsilon_{mon}$, $M^{-1}.cm^{-1}$ | $\Phi_F$ | $\Phi_T$ | $\tau_T$, $\mu s$ | $\Phi_\Delta$ |
|---|---|---|---|---|---|---|
| 5 | 674 | $1.2 \times 10^5$ | $0.30 \pm 0.05$ | $0.7 \pm 0.1$ | $310 \pm 10$ | $0.7 \pm 0.1$ |
| 6 | 680 | $1.0 \times 10^5$ | $0.3 \pm 0.1b$ | $<10-2c$ | $\sim100$ | $<10-2c$ |

[a] Experiments were carried out in concentrations ranging between 0.20 and 2.2 μM, in THF (**5**) and water (**6**). [b] Corrected value (in the concentration range studied, $\Phi_F$ were approximately 0.07-0.09). [c] Although observable, the signal was non-quantifiable. Solvent: $D_2O$.
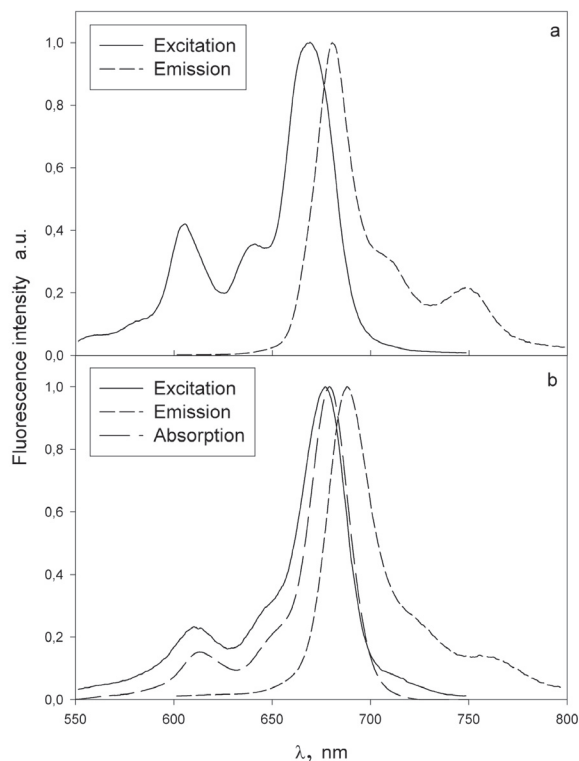


**Fig. 4.** a) Normalized excitation ($\lambda_{obs} = 770$ nm) and emission spectra ($\lambda_{exc} = 580$ nm) of **5** in THF; b) Normalized excitation ($\lambda_{obs} = 770$ nm) and emission spectra ($\lambda_{exc} = 580$ nm) of **6** in water. The normalized calculated absorption spectrum of the monomer is overlaid

different laser energies.

Singlet oxygen quantum yield of **5** is similar to those previously published (Table 1) [23]. Due to the low intensity of the obtained signals, $\Phi_\Delta$ of **6** could not be quantified.

Phthalocyanines **5** and **6** are photostable in a homogeneous solution and no changes in their absorption spectra were observed, even after lengthy irradiation times (30 min) with polychromatic light.

### Acknowledgements

### REFERENCES

1. a) Phthalocyanines, Properties and Applications, Leznoff CC and Lever R. (Eds) VCH: New York, 1989, 1992, 1993, 1996; Vols. 1-4. b) Gregory P. *J. Porhyrins Phthalocyanines* 2000; **4:** 423-437.
2. Pandey RK. *J. Porhyrins Phthalocyanines* 2000; **4:** 368-373.
3. MacDonald IJ and Dougherty TJ. *J. Porhyrins Phthalocyanines* 2001; **5:** 105-129.
4. Clarkson GJ, McKeown NB and Treacher KE. *J. Chem. Soc. Perkin Trans 1* 1995; 1817-1923.
5. Kasuga K, Mihara T, Nakao T and Takahashi K. *Inorg. Chim. Acta* 1991; **189:** 11-12.
6. Hauschel B, Jung R and Hanack M. *Eur. J. Inorg. Chem.* 1999; 693-703.
7. Kandaz M, Yarasir MNU, Koca A and Bekaroglu O. *Polyhedron* 2002; **21:** 255-263.
8. Kudrevich S, Brasseur N, La Madeleine C, Gilbert S and van Lier JE. *J. Med. Chem.* 1997; **40:** 3897-3904.
9. Oldham TC and Phillips D. *J. Photochem. Photobiol. B: Biol.* 2000; **55:** 16-19.
10. Urizzi P, Allen CM, Langlois R, Ouellet R, La Madeleine C and van Lier JE. *J. Porphyrins Phthalocyanines* 2001; **5:** 154-160.
11. Boyle RW, Leznoff CC and van Lier JE. *Br. J. Cancer* 1993; **62:**1177-1181.
12. Hu M, Brasseur N, Zeki Yildiz S, van Lier JE and Leznoff CC. *J. Med. Chem.* 1998; **41:** 1789-1802.
13. Leznoff CC, Vigh S, Svirskaya PI, Greenberg S, Drew DM, Ben-Hur E and Rosenthal I. *Photochem. Photobiol.* 1989; **49:** 279-284.
14. Fernández DA, Dicelio LE and Awruch J. *J. Heterocyclic Chem.* 1995; **32:** 519-522.
15. Rodriguez ME, Strassert CA, Dicelio LE and Awruch J. *J. Heterocyclic Chem.* 2001; **38:** 387-

389.

16. Fernández DA, Awruch J and Dicelio LE. *J. Photochem. Photobiol. B: Biol.* 1997; **41:** 227-232.

17. a) De Filippis MP, Dei D, Fantetti L and Roncucci G. *Tetrahedron Lett.* 2000; **41:** 9143-9147. b) Segalla A, Borsarelli CD, Braslavsky SE, Spikes JD, Roncucci G, Dei D, Chiti G, Jori G and Reddi E. *Photochem. Photobiol. Sci.* 2002; **1:** 641-648.

18. Burfield DR and Smithers RH. *J. Org. Chem.* 1978; **43:** 3966-3968.

19. Fernández DA, Awruch J and Dicelio LE. *Photochem. Photobiol.* 1996; **63:** 784-792.

20. Lagorio MG, Dicelio LE and San Roman E. *J. Photochem. Photobiol. A: Chem.* 1993; **72:** 153-161.

21. Rodriguez ME, Morán F, Bonansea A, Monetti M, Fernández DA, Strassert CA, Rivarola V, Awruch J and Dicelio LE. *Photochem. Photobiol. Sci.* 2003; **2:** 988-994.

22. Iriel A, Lagorio MG, Dicelio LE and San Roman E. *Phys. Chem. Chem. Phys.* 2002; **4:** 224-231, and references therein.

23. Rodriguez ME, Awruch J and Dicelio LE. *J. Porphyrins Phthalocyanines* 2002; **6:** 122-129.

24. Minnock A, Vernon D I, Schofield J, Griffiths J, Howard Parish J and Brown SB. *Antimicrob. Agents Chemother.* 2000; **44:** 522-527.