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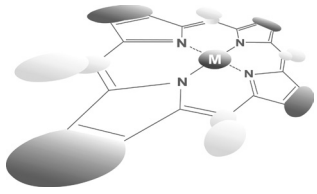

(Aminophenyl)porphyrins as precursors for the synthesis of porphyrin-modified siloxanes

José Almeida[a†], Maria E. Fortună[b†], Lucia Pricop[b], Andrei Lobiuc[c,d], Andreia Leite[a], André M. N. Silva[a], Rodrigo P. Monteiro[a], Maria Rangel[e], Valeria Harabagiu*[b] and Ana M. G. Silva*[a]

[a] *LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal*
[b] *Department of Inorganic Polymers "Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, 700487 Iasi, Romania*
[c] *CERNESIM, "Alexandru Ioan Cuza" University, Carol I Bd., 700505, Iasi, Romania*
[d] *"Stefan cel Mare" University, Universitatii St. 13, Suceava, Romania*
[e] *LAQV/REQUIMTE, Instituto de Ciências Biomédicas de Abel Salazar, Universidade do Porto, 4050-313 Porto, Portugal*

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ABSTRACT: The present research reports the efficient synthesis of mono- and di-(aminophenyl) porphyrins and their metalation with Zn(II) using microwave irradiation. The subsequent reaction of amino-functionalized porphyrins with siloxane moieties bearing epoxy or carboxyl functional groups provided four new porphyrin-modified siloxanes. The structure of the resulting derivatives was established by ^{1}H-NMR and MALDI-TOF-MS. The optical properties of the porphyrin chromophores were preserved, as proven by comparing the absorption and emission spectra of the initial porphyrins to those of the porphyrin-modified siloxanes.

KEYWORDS: porphyrins, siloxane, microwave irradiation, optical properties.

INTRODUCTION

Polysiloxanes are hybrid organic-inorganic polymers composed of a Si–O–Si backbone and organic radicals linked to silicon atoms. Their properties are strongly dependent on the nature of organic substituents (aliphatic, aromatic, organo- or silico-functional groups). The most representative polydimethylsiloxane is well known for its high flexibility (Tg ≈ -125 °C), thermal stability (380 °C) and other properties, such as unusually low characteristic pressure, bulk viscosity, temperature coefficient of viscosity and large gas permeability [1]. The modification of siloxane chains either by adding organic functional groups or linking siloxane moieties into copolymer structures [2] is extensively explored to obtain new materials with specific properties and a large spectrum of biomedical [3], personal care [4] and industrial applications (protective coatings [2b], surfactants [5] and anti-fouling agents [6] or gas separation membranes [7] and flame resistant materials [8]). One of the most important applications of siloxane materials is as a flexible spacer in the preparation of semi-conducting materials [9]. Due to their low dielectric constants, siloxane moieties have a small impact on the electronic properties of a semi-conductor but have an almost exclusive function of providing different physical attributes to the final material [9].

Porphyrins are also important compounds for incorporating into functional materials [10]. Typically, porphyrin macrocycles are endowed with remarkable photophysical properties, including high absorption coefficients in

*Correspondence to: Ana M. G. Silva, Tel: +351220402585, Fax: +351220402659, email: ana.silva@fc.up.pt; Valeria Harabagiu, email: hvaleria@icmpp.ro.

† These authors contributed equally to this work.

the visible region and tunable fluorescence emission, enabling potential applications in photodynamic therapy (PDT) and diagnosis [11], as artificial photosynthetic materials [12] or oxidation catalysts [13] as well as chromophores in molecular recognition and sensing [10a, 14]. Usually, porphyrins retain their photochemical and redox properties after their incorporation in devices. They are usually processed by electropolymerization onto electrodes or by mixing into polymers for use as antibacterial materials [15]. Polymerization could be performed directly on the porphyrin moiety by the reactions of different functional groups.

Only few examples are available in the literature on the functionalization of siloxanes with porphyrins. In one example, a tetramethyldisiloxane group was attached to a porphyrin in order to design a material with liquid crystalline properties by using hydrosilation reactions [16]. García-Sánchez *et al.* reported interesting synthetic routes to entrap porphyrins in silica networks, mainly by sol-gel methods [17]. Dai *et al*. prepared different generations of porphyrin-cored siloxane-poly(amido/amine) dendrimers by reacting azide-modified 5,10,-15,20-tetrakis(4-hydroxyphenyl)porphyrin with propargyl derived siloxanes; some properties of these materials would be very useful for applications in biomedical imaging and treatment [18]. In another example, Fagadar-Cosma *et al.* described the preparation of a porphyrin-grafted polysiloxane; this material showed increased thermal stability and optical properties suitable for formulations in sensor devices [19]. More recently, Borisov *et al*. used Pt(II) and Pd(II) benzoporphyrins as crosslinkers in a catalytic hydrosilation reaction to prepare a silicone rubber, which showed chemical and mechanical stability and high permeability to oxygen, enabling the measurement of low oxygen concentrations [20].

Among the functionalized porphyrins [21], (aminophenyl)porphyrins appear as key components to obtain a wide range of porphyrin-(bio)molecule conjugates, *via* amide linkage, giving them the favorable properties of amides, such as high polarity, stability and conformational diversity [22]. On the other hand, epoxy-functionalized siloxanes were proven to easily react with amino compounds or amino-functionalized polymers [23]. More recently, the synthesis of a linear poly(hydroxyurethane) was described by reacting carbon-dioxide, siloxane-containing bisepoxide and a diamine; this material exhibited strong fluorescence either in bulk or solution with high photostability, allowing its use in the fabrication of cool white LEDs [24].

In the present work we report the microwave (MW)-assisted reduction of (nitrophenyl)porphyrins to the corresponding amino derivatives and further metalation with Zn(II). Low molecular weight disiloxane and trisiloxane model compounds having epoxy or carboxyl functional groups were conveniently combined with (aminophenyl)porphyrins, either by conventional or MW heating, in order to obtain materials with desired features, such as photophysical properties provided by the porphyrin macrocycle and structural flexibility offered by the siloxane, for application in optoelectronics. The structure of the porphyrin-modified siloxanes was established by ^{1}H-NMR and MALDI-TOF-MS spectometry. Furthermore, the porphyrin-modified siloxanes were found to preserve the optical properties of the porphyrin chromophore as observed by comparing the absorption/emission spectra of the pristine porphyrins and porphyrin modified siloxane compounds.

EXPERIMENTAL

General methods

All reagents and solvents were purchased as reagent grade and used without further purification unless otherwise stated. 5,10,15,20-Tetraphenylporphyrin (**1**) was prepared according to a literature method [25]. The carboxypropyl-siloxane derivative (**9**) was acquired from Gelest.

NMR spectra were recorded on a Bruker Avance III 400 spectometer operating at 400.15 MHz for proton, with TMS as the internal reference (except for the siloxanes **4** and **5**, where no TMS was added) and $CDCl_3$ or DMSO-d_6 as solvents. The chemical shifts (δ) are quoted in ppm and the coupling constants (*J*) are in Hz. (see Figs S1 and S2 in Supporting information).

Flash chromatography was carried out using silica gel (Merck, 230–400 mesh). Preparative thin-layer chromatography (TLC) was carried out on 20 × 20 cm glass plates coated with Merck 60 silica gel (1 mm thick). Analytical TLC was carried out on precoated sheets with silica gel (Merck 60, 0.2 mm thickness).

Microwave irradiation experiments were carried out in a CEM Discovery Labmate circular single-mode cavity instrument (300 W max magnetron power output) from CEM Corporation. Reactions were performed under closed-vessel conditions.

Mass spectrometry analysis was performed on a Bruker UltrafleXtreme MALDI-TOF/TOF mass spectrometer equipped with a nitrogen laser. Samples were analyzed in the reflector positive ion mode for the *m/z* range between 600–3500. No signals were detected at *m/z* values above 2000. Good ionization was achieved at laser attenuation values between 35 and 50% and *ca*. 3000 laser shots were acquired. For matrix-assisted laser desorption ionization (MALDI), the samples were dissolved in acetone or dichloromethane and mixed in a 1:1 ratio with the matrix preparation before being applied to the MALDI target plate. The matrix preparation was 5 mg/ml α-cyano-4-hydroxycinnamic acid, 50% (v/v) methanol, 0.1% (v/v) trifluoroacetic acid (TFA) in water. For **2Zn** and **6a**, the high resolution MS analysis was carried out by electrospray ionization (ESI) in a LTQ-Orbitrap-XL instrument (Thermo Scientific) operated

in the positive ionization mode with the following ESI source parameters: electrospray needle voltage +3 kV, sheath gas nitrogen 5, capillary temperature 275 °C, capillary voltage 35 V and tube lens voltage 80 V (Figs S3 and S4, respectively, in Supporting information).

Electronic absorption spectra were recorded on a UV-Vis spectrophotometer (UV-3600 Shimadzu) connected with a TCC controller (TCC-240A). The compounds were studied in anhydrous chloroform solutions ranging in concentration from 10^{-6} to 10^{-7} moles per liter.

Fluorescence measurements were carried out on a Varian spectrofluorometer, model Cary Eclipse, equipped with a constant-temperature cell holder (Peltier single cell holder) on solutions obtained by dilution of a stock solution with chloroform. To minimize reabsorption effects, the values of the absorbances for each sample were kept below 0.1. The emission spectra were obtained between 550 and 800 nm by using λ_{exc} in the range 420–424 nm, with excitation and emission slit widths of 10 nm and 650 V.

Measurements of absolute photoluminescence quantum yields were carried out in an absolute photoluminescence quantum yield spectrometer (Quantaurus QY C11347–11 spectrometer (Hamamatsu)) equipped with an integrating sphere to measure all the luminous flux.

Synthesis of mono- and di-(aminophenyl)porphyrins

5-(4-Aminophenyl)-10,15,20-triphenylporphyrin (**2**) and 5,15-bis(4-aminophenyl)-10,20-diphenylporphyrin (**3**) were prepared in two steps: nitration of **1** followed by catalytic transfer hydrogenation of the resulting nitro derivative, using slight modifications of the previously described methods [26, 27].

Nitration. A solution of 5,10,15,20-tetraphenylporphyrin **1** (0.207 g, 0.338 mmol) in TFA (10 ml) was treated at room temperature with 1.8 equiv of $NaNO_2$ for a duration of 3 min for mono-nitration and 8.1 equiv of $NaNO_2$ for di-nitration, for a duration of 1.5 min, in an air-open round-bottom flask, under stirring. The reaction mixture was diluted with water (60 ml) and extracted several times with dichloromethane (6 × 25 ml). The organic layer was washed with saturated aqueous $NaHCO_3$, brine and then dried over anhydrous Na_2SO_4. After filtration, the organic solvent was evaporated under vacuum. The resulting residue (0.180 g) containing (nitrophenyl)porphyrins was directly used for the microwave-assisted reduction reaction.

Reduction using microwave-assisted catalytic transfer hydrogenation. A mixture containing the previously obtained residue (0.180 g), cyclohexene (320 µl, 3.16 µmol) and DMF (10 ml) was placed in a 35 ml vial, the air was displaced with N_2 and a catalytic amount of 10% Pd/C (w/w) (7.7 mg) was added, under N_2 air flux. The reaction vial was closed, and the suspension was subjected to MW heating using 1 min ramp to 130 °C and 20 min hold time at 130 °C (using 50 W maximum power), under medium stirring. The reaction was filtered, diluted with water (10 ml) and extracted several times with ethyl acetate. The organic phase was washed with brine. After drying over Na_2SO_4 and filtering, the organic phase was evaporated and purified by column chromatography, eluting first porphyrin **1** (11.6 mg, 6% recovery) with chloroform and then porphyrin **2** (68.5 mg, 32% yield from **1**) using a mixture of chloroform/acetone (9:1). This protocol was successfully extended to synthesize the di-(aminophenyl)porphyrins, which were purified by column chromatography with dichloromethane, allowing the isolation of the *opposite* isomer of the diamino derivative **3**. The spectroscopic data obtained for the title compounds are in agreement with those in the literature [26].

(**2**) ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ, ppm -2.70 (2H, s, pyrrole-N*H*), 4.04 (2H, s, -NH_2), 7.08 (2H, d, J = 8.4 Hz, 5-H$_{meta}$-Ar), 7.75–7.83 (9H, m, 10,15,20-H$_{meta+para}$-Ph), 8.03 (2H, d, J = 8.4 Hz, 5-H$_{ortho}$-Ar), 8.24–8.26 (6H, m, 10,15,20-H$_{ortho}$-Ph), 8.866–8.872 (6H, m, pyrrole-*H*), 8.97 (2H, d, J = 4.4 Hz, pyrrole-*H*). MS (ESI): *m/z* 630.264 [M+H]$^+$, calcd. for $C_{44}H_{32}N_5^+$ 630.265.

(**3**) ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ, ppm -2.70 (2H, s, pyrrole-N*H*), 4.05 (4H, s, 2 × -NH_2), 7.08 (4H, d, J = 8.2 Hz, 5,15-H$_{meta}$-Ar), 7.74–7.80 (6H, m, 10,20-H$_{meta+para}$-Ph), 8.01 (4H, d, J = 8.2 Hz, 5,15-H$_{ortho}$-Ar), 8.23–8.25 (4H, m, 10,20-H$_{ortho}$-Ph), 8.84 (4H, d, J = 4.8 Hz, pyrrole-*H*), 8.95 (4H, d, J = 4.8 Hz, pyrrole-*H*). MS (ESI): *m/z* 645.271 [M+H]$^+$, calcd. for $C_{44}H_{33}N_6^+$ 645.276.

Synthesis of zinc(II) complex of mono-(aminophenyl)porphyrin

A solution of 5-(4-aminophenyl)-10,15,20-triphenylporphyrin **2** (70.0 mg, 0.11 mmol) and zinc(II) acetate dihydrate (244 mg, 1.11 mmol) in acetonitrile (1 ml) was placed in a 10 ml vial [28]. The vessel was than sealed with a silicone septum and placed into the MW cavity. The reaction mixture was heated to 120 °C for 1 min using a maximum irradiation power of 150 W, which was automatically modulated until the total reaction time had elapsed. The resulting mixture was washed with deionized water, the organic phase was dried with anhydrous Na_2SO_4, filtered and then concentrated. The resulting solid was recrystallized (*n*-hexane/$CHCl_3$) to give **2Zn** in quantitative yield.

(2Zn) ^{1}H NMR (400 MHz; DMSO-d_6; Me_4Si): δ, ppm 5.48 (2H, s, -NH_2), 6.98 (2H, d, J = 8.4 Hz, 5-H$_{meta}$-Ar), 7.79–7.81 (9H, m, 10,15,20-H$_{meta+para}$-Ph), 7.83 (2H, d, J = 8.4 Hz, 5-H$_{ortho}$-Ar), 8.17–8.20 (6H, m, 10,15,20-H$_{ortho}$-Ph), 8.74–8.75 (6H, m, pyrrole-*H*), 8.92 (2H, d, J = 4.6 Hz, pyrrole-*H*). HRMS (ESI): *m/z* 691.173 [M$^{\bullet+}$], calcd for $C_{44}H_{29}N_5Zn^{\bullet+}$ 691.171. UV-vis

($CHCl_3$): λ_{max}, nm (log ε) 420 (5.2), 548 (4.0), 588 (3.4). Fluorescence ($CHCl_3$): λ_{max} 599, 645 nm; $\Phi_F = 0.022$.

Synthesis of glycidoxypropyl-modified siloxanes 4 and 5

1,3-Bisglycidoxypropyl-2,2,3,3-tetramethyldisiloxane (**4**) and 3-glycidoxypropyl-heptamethyltrisiloxane (**5**) were prepared by hydrosililation of allyglycidyl ether (AGE) with the corresponding hydrogen-functionalized siloxanes, according to a previously reported procedure [23]. In a typical experiment, **4** or **5** were reacted with AGE (Si–H/AGE = 1/1.01 molar ratio), in the presence of a Karsted catalyst (1 ml/mol Si–H). The reaction was conducted in toluene (50% w/w) for 6 h at 70–80 °C. The formation of AGE modified siloxanes was monitored by following the disappearance of the Si–H characteristic absorption band at 2160 cm^{-1} in FT-IR spectra of the reaction mixtures. After the complete hydrosilylation, the reaction products were separated by vacuum distillation of the solvents and AGE excess, and were purified by dissolution in *n*-hexane, filtration and vacuum evaporation of *n*-hexane.

(4) ^{1}H NMR (400 MHz; $CDCl_3$): δ, ppm 0.01–0.07 (Si–C*H*$_3$), 0.46–0.50 (Si–C*H*$_2$), 1.53–1.61 (-CH_2-C*H*$_2$-CH_2), 2.57–2.78 (C*H*$_2$ of epoxy cycle), 3.01–3.14 (C*H* of epoxy cycle), 3.35–3.695 (C*H*$_2$O). FTIR (KBr), (cm^{-1}): 2958 (CH_2, CH_3), 1257 (Si-CH_3), 1100–1000 (Si-O-Si), 910 (epoxy cycle), 842 (Si-CH_3).

(5) ^{1}H NMR (400 MHz; $CDCl_3$): δ, ppm 0.01 (Si–C*H*$_3$), 0.50–0.70 (Si–C*H*$_2$), 1.30–1.70 (-CH_2-C*H*$_2$-CH_2), 3.15 (C*H* of epoxy cycle), 2.60–2.80 (C*H*$_2$ of epoxy cycle), 3.40–3.70 (C*H*$_2$O). FTIR (KBr), (cm^{-1}): 2958 (CH_2, CH_3), 1257 (Si-CH_3), 1100–1000 (Si-O-Si), 910 (epoxy cycle), 842 (Si-CH_3).

Reaction of mono-(aminophenyl)porphyrin with siloxane 4

Using conventional heating. A mixture of siloxane **4** (20 mg; 0.054 mmol) and porphyrin **2** (68 mg, 0.108 mmol) in toluene (10 ml) in the presence of 2-propanol (0.078 ml) (OH/NH_2 = 1/1 molar) was heated at 90 °C, under stirring, for 72 h. After vacuum distillation of toluene and 2-propanol, the resulting residue was washed with petroleum ether to remove any possible non- reacted siloxane and then it was purified by preparative TLC using a mixture of toluene/ethyl acetate (75:25) as an eluent. Three fractions were obtained: porphyrin **2** (more than 80% recovered), compound **6a** (0.4 mg, 1% yield) and compound **6b** (1.8 mg, 2% yield).

Using microwave irradiation. In a 10 ml thick walled glass tube, siloxane **4** (289 µl, 0.80 mmol) was introduced in a solution of porphyrin **2** (50 mg, 0.08 mmol) in a 3 mL 2:1 mixture of 2-propanol and toluene. The resulting solution was purged with N_2 for 20 min, the vessel was then sealed with a septum and placed into the MW cavity. All experiments were performed under stirring using a Teflon-coated magnetic stir bar in the vessel. The initial MW power of 20 W was used to reach the targeted temperature (80 °C) which was then held by automatically modulating the MW power until the end of the reaction time (60 min). Then, the solvents, 2-propanol and toluene, were evaporated and a viscous residue was obtained. The unreacted siloxane was removed by washing the mixture with *n*-hexane and the porphyrin-modified siloxane was purified by preparative TLC, using a mixture of toluene/ethyl acetate (75:25) as an eluent. The first fraction consisted of porphyrin **2** (80% recovery) followed by compound **6a** (1.6 mg, 25% yield based on the recycled **2**).

(6a) ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ, ppm -2.76 (2H, s br, pyrrole-N*H*), 0.06–0.08 (12H, m, 4 × Si–C*H*$_3$), 0.49–0.55 (4H, m, 2 × Si–C*H*$_2$), 1.58–1.66 (4H, 2m, 2 × -CH_2-C*H*$_2$-CH_2), 2.57–2.63 and 2.80–2.83 (2H, 2m, C*H*$_2$O), 3.15–3.18, 3.38–3.74 and 3.98–3.99 (12H, 3m, C*H*-OH, C*H*$_2$-NH, 4 × C*H*$_2$O, C*H*-epoxy), 7.46–7.48, 7.74–7.93 and 7.91–7.93 (11H, 3m, Ar), 8.18–8.23 (8H, m, Ph), 8.83–8.88 (8H, m, pyrrole-*H*). MS (MALDI-TOF): *m/z* 992.510 $[M+H]^+$, calcd for $C_{60}H_{66}N_5O_5Si_2^+$ 992.460 (Δm = 50 ppm). HRMS (ESI): *m/z* 991.451 $[M^{\bullet+}]$, calcd for $C_{60}H_{65}N_5O_5Si_2^{\bullet+}$ 991.452. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 420 (5.8), 515 (4.1), 549 (4.1), 590 (3.8), 646 (3.5). Fluorescence ($CHCl_3$): λ_{max} 597, 651, 716 nm; $\Phi_F = 0.031$.

(6b) ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ, ppm -2.74 (4H, s br, pyrrole-N*H*), 0.12 (12H, s, 4 × Si–C*H*$_3$), 0.59–0.63 (4H, m, 2 × Si–C*H*$_2$), 1.69–1.73 (4H, m, 2 × -CH_2-C*H*$_2$-CH_2), 3.35–3.68 (12H, m, 6 × C*H*$_2$O), 4.10–4.31 (2H, m, 2 × C*H*-OH), 6.98 (4H, d, *J* = 8.6 Hz, 2 × 5-H$_{meta}$-Ar), 7.69–7.76 (18H, m, 10,15,20-H$_{meta+para}$-Ph), 7.99 (4H, d, *J* = 8.6 Hz, 2 × 5-H$_{ortho}$-Ar), 8.17–8.20 (12H, m, 10,15,20-H$_{ortho}$-Ph), 8.79–8.80 (12H, m, pyrrole-*H*), 8.93 (4H, d, *J* = 4.8 Hz, pyrrole-*H*). MS (MALDI-TOF): *m/z* 1621.664 $[M + H]^+$, calcd for $C_{104}H_{97}N_{10}O_5Si_2^+$ 1621.718 (Δm = 33 ppm). UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 420 (5.0), 517 (3.6), 555 (3.5), 591 (3.2), 649 (3.0). Fluorescence ($CHCl_3$): λ_{max} 606, 657, 720 nm.

Reaction of di-(aminophenyl)porphyrin with siloxane 5

A mixture of siloxane **5** (28 mg, 0.084 mmol) and the *opposite* isomer of the diamino derivative **3** (27 mg, 0.042 mmol) in toluene (total concentration, 20%) in the presence of 2-propanol (OH/NH_2 = 1/1 molar) was heated at 90 °C, under stirring, for 72 h. After vacuum distillation of toluene and 2-propanol, the resulting residue was washed with petroleum ether to remove the possible not reacted siloxane and then it was purified by preparative TLC using a mixture of ethyl acetate and *n*-hexane as an eluent. Two fractions were collected including porphyrin **3** (more than 80% recovered) and compound **8a** (0.8 mg, 2% yield).

(8a) ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ, ppm -2.75 and -2.72 (2H, 2s br, pyrrole-N*H*), 0.05 to 0.14 (21H,

m, 7 × Si-CH_3), 0.82–0.93 (2H, m, Si-CH_2), 1.59–1.72 (2H, m, Si-CH_2CH_2), 3.10–3.90 (6H, m, 2 × CH_2O and CH_2NH), 4.04 (2H, s br, NH_2), 4.25 (1H, s br, C*H*-OH), 7.07 (4H, d, J = 8.2 Hz, 2 × H_{meta}-5,15-Ar), 7.72–7.77 (10H, m, $H_{meta+para}$-Ph), 7.99 (4H, d, J = 8.2 Hz, 2 × H_{ortho}-5,15-Ar), 8.81–8.83 (4H, m, pyrrole-*H*), 8.92–8.94 (4H, m, pyrrole-*H*). MS (MALDI-TOF): *m/z* 981.438 $[M + H]^+$, calcd for $C_{57}H_{65}N_6O_4Si_3^+$ 981.437 (Δm = 1 ppm). UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 423 (5.6), 519 (4.3), 557 (4.1), 593 (3.9), 650 (3.8). Fluorescence ($CHCl_3$): λ_{max} 658, 721 nm.

Reaction of Zn(II) complex of the mono-(aminophenyl)porphyrin with siloxane 9

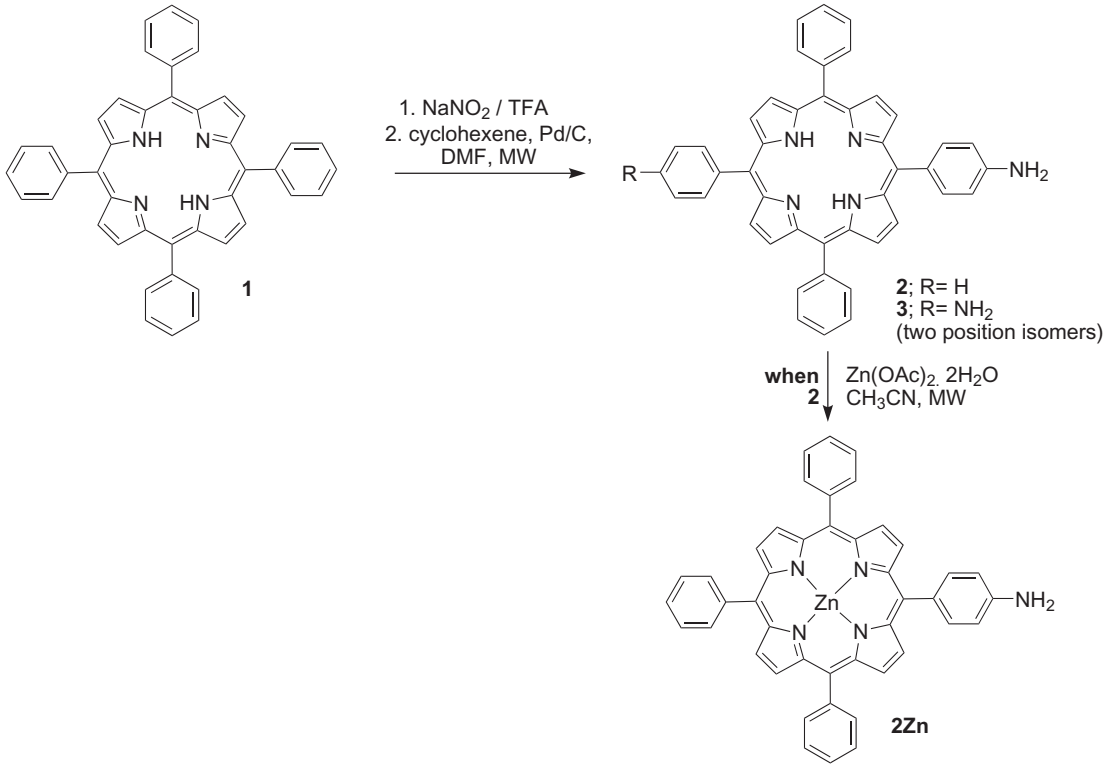
A mixture of 1,3-bis-(3-carboxypropyl)tetramethyl-disiloxane **9** (1 g, 3.3 mmol) and $SOCl_2$ (7.5 ml) was refluxed for 6 h, then 0.05 ml DMF was added and the reflux was continued for another 30 min. The product was purified by distilling the solvent and $SOCl_2$ excess. Over 9.8 mg (0.032 mmol) from the obtained product (1,3-bis-(acylchloride-3-propyl) tetramethyldisiloxane), 1 mL of toluene, 1 mL of trimethylamine as acceptor of HCl and 40 mg of **2Zn** porphyrin (0.058 mmol) were added and the mixture was stirred for 24 h. Then, the temperature was raised to 60 °C and the stirring was continued for another 5 h. The resulting mixture was purified by preparative TLC using a mixture of ethyl acetate and *n*-hexane as an eluent, affording compound **10a** (0.9 mg, 3% yield).

(10a) ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ, ppm 0.05 to 0.15 (12H, m, 4 × Si-CH_3), 0.57–0.68 and 0.86–0.88 (4H, 2m, 2 × CH_2), 1.42–1.43 (4H, m, 2 × CH_2), 1.94–2.05 and 2.28–2.45 (4H, 2m, 2 × CH_2), 7.73–7.76 (11H, m, Ar), 8.19–8.23 (8H, m, Ar), 8.91–8.97 (8H, m, pyrrole-*H*). MS (MALDI-TOF): *m/z* 979.313 $[M^{\bullet+}]$, calcd for $C_{56}H_{53}N_5O_4Si_2Zn^{\bullet+}$ 979.293 (Δm = 20 ppm). UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 424 (5.1), 554 (3.8), 595 (3.4). Fluorescence ($CHCl_3$): λ_{max} 604, 654, 718 nm.

RESULTS AND DISCUSSION

Synthesis of amino-functionalized porphyrins and Zn(II) complex

The synthesis of amino-functionalized porphyrins used in this study, namely 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (**2**) and 5,15-bis(4-aminophenyl)-10,20-diphenylporphyrin (**3**), was performed by using a two-step method (Scheme 1). The first step involved the regioselective *para*-phenyl nitration of 5,10,15,20-tetraphenylporphyrin (**1**), by using the well-known protocol based on nucleophilic substitution of the aromatic ring with sodium nitrite in the presence of trifluoroacetic acid (TFA) [26]. By changing the ratios between **1** and sodium nitrite reagents and the reaction time, one monosubstituted and two isomeric disubstituted nitro derivatives (bearing the nitro groups in adjacent or opposite positions of the macrocycle) were obtained.



Scheme 1. Microwave-assisted synthesis of amino-functionalized porphyrins and Zn(II) complex

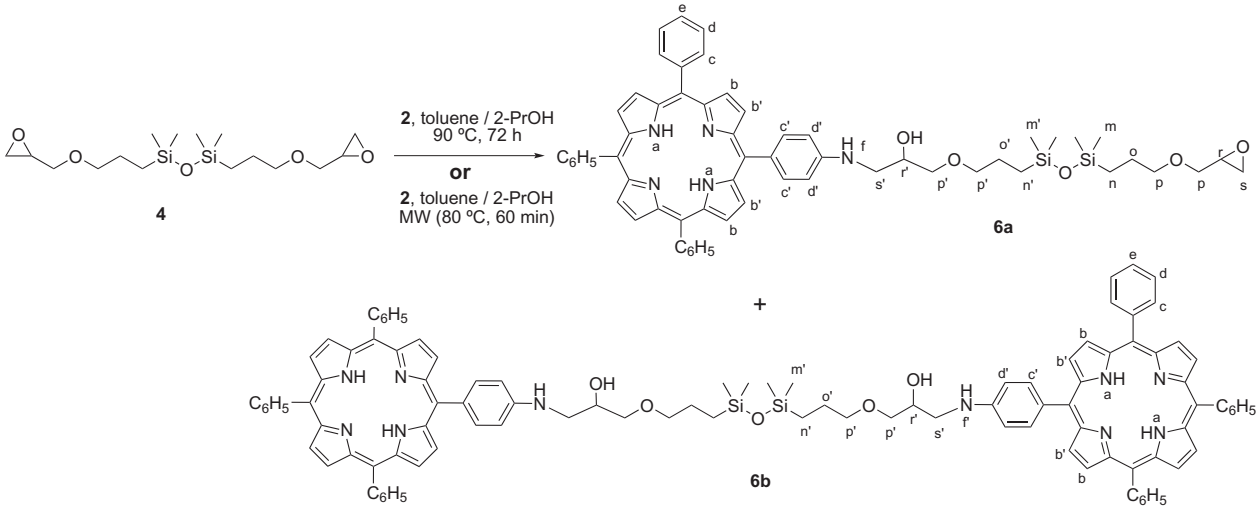
In a second step, the reduction of nitrophenyl groups to the corresponding aminophenyl derivatives was accomplished by microwave-assisted catalytic transfer hydrogenation method. Cyclohexene and 10% Pd/C were used as hydrogen donor and catalyst, respectively [29]. To optimize the process, different amounts of cyclohexene and 10% Pd/C, in *N*,*N*-dimethylformamide (DMF), were reacted with the nitroporphyrin under closed-vessel MW irradiation conditions (130 °C, 20 min). The best result was obtained for a reaction mixture containing 320 µl of cyclohexene per 180 mg of the nitration crude product in 10 ml of DMF (concentration of 36 g/l) and adding a catalytic amount (7.7 mg) of 10% Pd/C. When comparing with the standard reduction that uses an excess of tin(II) chloride in concentrated hydrochloric acid, and other less-explored protocols based on hydrogenation methods [21, 26], the MW-assisted technique presents some advantages in terms of simpler and milder reaction conditions and higher reaction rates.

The subsequent MW irradiation of a solution containing porphyrin **2** and $Zn(OAc)_2 \cdot 2H_2O$ in acetonitrile, efficiently afforded the corresponding **2Zn** complex within 1 min at 120 °C, in a quantitative yield.

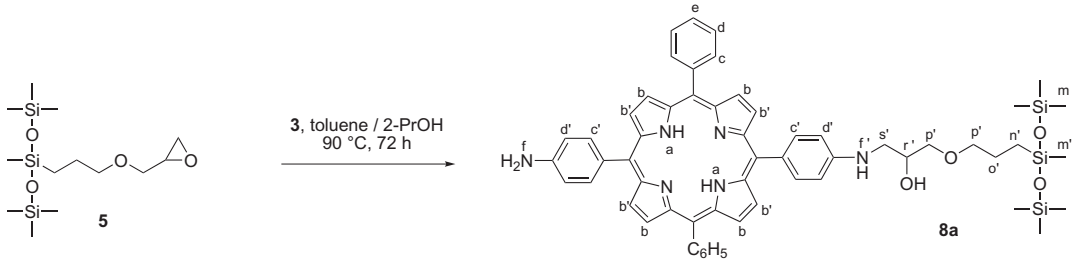
Synthesis of porphyrin-modified siloxanes

Having in hand the amino-functionalized porphyrins, their coupling to the siloxane moiety was approached in two convenient ways: (a) *via* nucleophilic ring opening of glycidoxy groups attached to the siloxane moiety or (b) *via* amidation of an acyl chloride substituted siloxane (Schemes 2 and 3).

To the best of our knowledge, there are no precedent reports on coupling (aminophenyl)porphyrins with epoxides, so we attempted this reaction using conventional heating (oil bath) and MW irradiation. An evaluation of these two methods will be performed in order to select the most suitable method for a future combination of porphyrins with higher molecular-weight polysiloxanes. A bis-epoxy-functionalized disiloxane and a mono-epoxy-functionalized trisiloxane were used as partners in this approach (Schemes 2a and 2b, respectively). The reaction under conventional heating was performed by mixing the mono-(aminophenyl)porphyrin (**2**) with the disiloxane containing two epoxy functional groups (**4**) (NH_2/epoxy = 2/1 molar) in a mixture of toluene and 2-propanol, at 90 °C. It is expected that 2-propanol acts as an activating agent and as a blocker of the possible

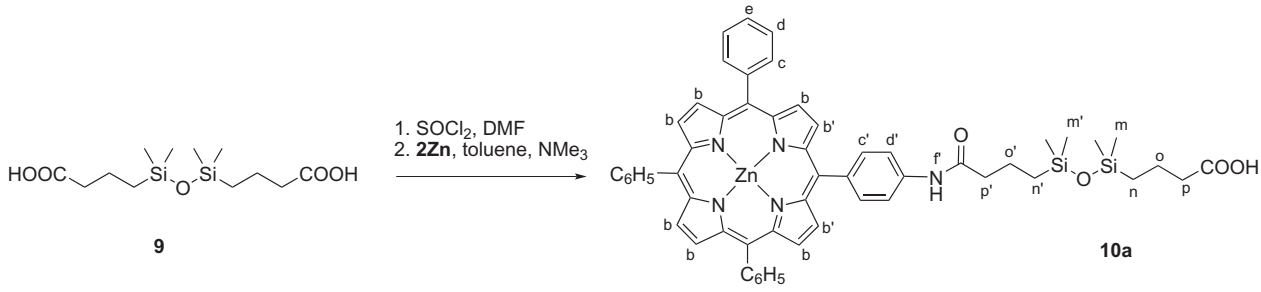


(a)



(b)

Scheme 2. Coupling reactions of (aminophenyl)porphyrins with epoxy-functionalized siloxanes **4** and **5**



Scheme 3. Amide coupling reaction of **2Zn** with the carboxylate-functionalized siloxane **9**

reactions between the resulting OH groups and the epoxy group [23a]. After 72 h, a mixture of products of higher polarity than the starting porphyrin were detected by TLC. Preparative TLC allowed the separation of three fractions. By ^{1}H NMR and MS spectra the assignment of these fractions were made to the following structures: starting porphyrin **2** as the least polar fraction; compound **6a** as the middle fraction and compound **6b** as the most polar fraction.

The use of MW irradiation was explored in order to accelerate the progress of the reaction. When using equimolar amounts of precursors **2** and **4** in a mixture of 2-propanol/toluene (MW, 30 min, 60 °C) no product formation was evidenced by TLC. It was only when an excess of 10 equiv of **4** was used that apparent consumption of the starting porphyrin was observed by TLC. When raising the reaction temperature from 80 °C to 100 °C, no further reaction evolution was observed. Therefore, the optimized conditions for the preparation of compound **6a** were obtained by MW irradiating a solution of **2** in a mixture of 2-propanol/toluene (2:1) and 10 equiv of **4** with 20 W of magnetron power until it reached 80 °C and holding it for 60 min. With these conditions it was possible to obtain **6a** as the sole derivatized siloxane compound in 2% yield, with approximately 80% of the starting porphyrin being recovered. Recycling the unreacted porphyrin **2** affords **6a** in 25% yield. A comparison of the two heating methods reveals that under conventional heating, the reaction affords the desirable compounds **6a** and **6b** within 72 h, while under MW irradiation compound **6a** was obtained as the sole product, with a substantial reduction in the reaction time (60 min).

The reaction of bis-amino-functionalized porphyrin **3** with the epoxy-functionalized trisiloxane **5** containing one epoxy functional group (NH_2/epoxy = 1/2 molar) was performed using a conventional heating protocol (90 °C, 72 h) (Scheme 2b). After separation by preparative TLC, compound **8a** was isolated as the sole product, while a significant amount of the porphyrin **3** was recovered.

The amide coupling was carried out *via* the reaction of **2Zn** and the carboxyl-functionalized siloxane by the *in situ* generation of the corresponding acyl chloride with thionyl chloride, according to Scheme 3. After the work-up and preparative TLC separation, compound **10a** was isolated as the sole reaction product, with a significant amount of **2Zn** being recovered.

Structural characterization of compounds

After purification, the porphyrin-modified siloxane compounds were characterized by ^{1}H NMR, MALDI-TOF-MS, UV-vis and fluorescence spectroscopies.

^{1}H NMR spectra of the starting porphyrins and final products are presented in Fig. 1, and also in Figs S1 and S2 (see Supporting information). Unfortunately, the spectra of all porphyrin-modified siloxanes show the presence of *n*-hexane solvent used for the purification/separation of compounds, some of the signals of the products of interest being partially covered by those of the solvent. The assigned peaks are made in correlation with the structures depicted in Schemes 2 and 3.

Figure 1 compares the spectra of **2** and the resulting mono- (**6a**) and disubstituted disiloxane (**6b**). In the spectra of both **6a** and **6b**, the aromatic signals of the porphyrin frame (a–e and b′–d′) remain almost unchanged. Compound **6a** shows Si-CH_3, Si-CH_2 and Si-CH$_2$-CH_2 resonance peaks at 0.06–0.08 (signals m, m′), 0.49–0.55 (signals n, n′) and 1.58–1.66 ppm (signals o, o′), respectively. Moreover, two signals at 2.57–2.63 and 2.80–2.83 corresponding to CH_2O protons (signals s) of the non-modified epoxy ring are also visible in the aliphatic region. The peaks corresponding to the open epoxy ring C*H*-OH (signal r′) and CH_2-NH protons (signal s′) are found together with those of CH_2O (signals p, p′) and C*H* of epoxy ring (signal r) in the region 3.15–3.99 ppm. From the ratio of the significant signal integrals (*e.g.* each one of the aromatic proton signal integrals and Si-CH_3 or Si-CH_2) one may conclude that only one porphyrin moiety was linked to the epoxy-siloxane molecule, leaving the second epoxy group intact.

By the contrary, the ^{1}H NMR spectrum of compound **6b** does not contain specific signals CH_2O protons of epoxy ring and the C*H*-OH peak (signal r′) is well individualized at 4.10–4.31 ppm. Moreover, the ratios of specific signal integrals indicate the presence of two porphyrin macrocycles per disiloxane unit, confirming the opening of both epoxy rings of the siloxane by their reaction with **2** (Fig. 1).

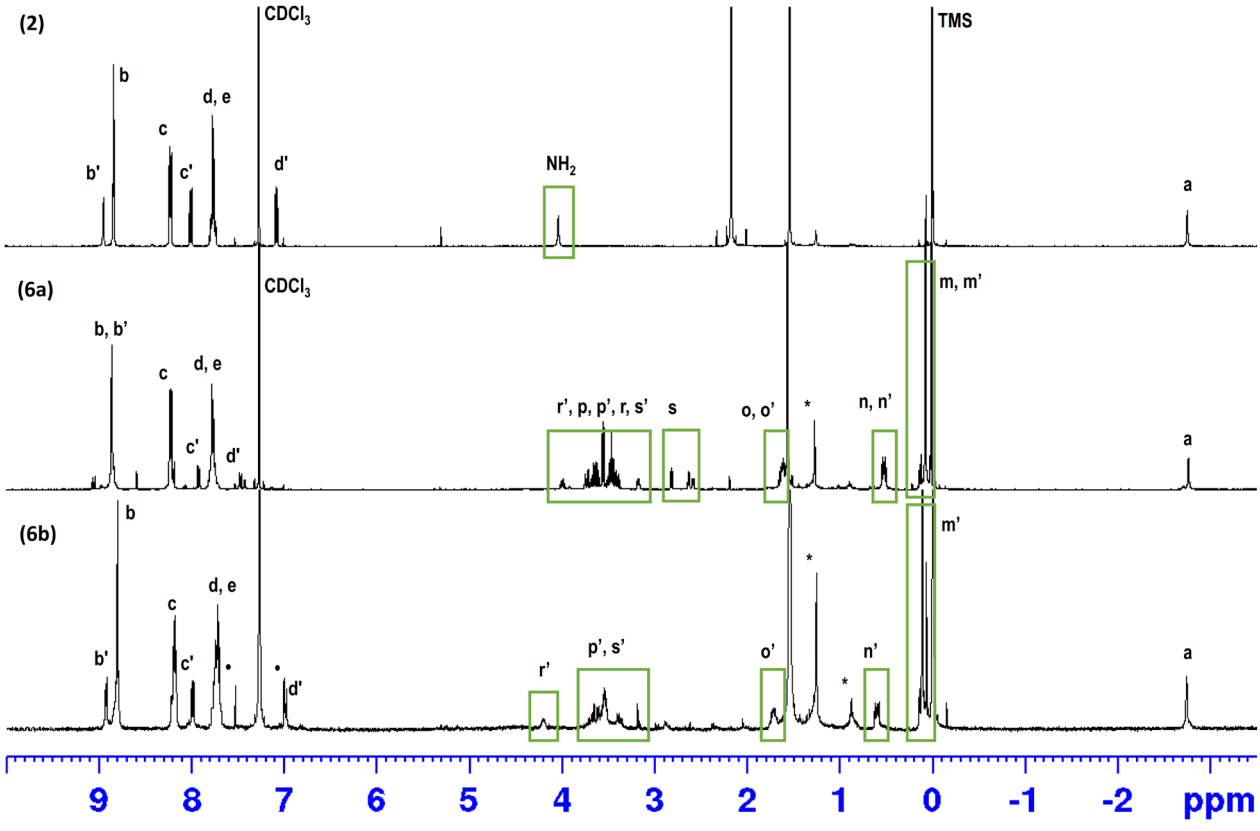


Fig. 1. ^{1}H NMR spectra in $CDCl_3$ of 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (**2**) and of porphyrin mono- (compound **6a**) and disubstituted (compound **6b**); * denote solvent peaks (hexane in the spectra of **6a** and **6b**); • are satellites

Although it was expected that the reaction of porphyrin **3** with siloxane **5** would result in the coupling of a porphyrin macrocycle per two siloxane frames, the ^{1}H NMR spectrum of the main isolated product shows that only one of the amino group of the porphyrin reacted with the epoxy ring of the trisiloxane (Fig. S1). By comparing with porphyrin **3**, the most important aspects of the proton NMR spectrum of compound **8a** are: (i) the inner N*H* protons, which appears as one broad singlet at -2.70 ppm in **3**, whereas two broad singlets at -2.75 and -2.72 ppm are detected in the compound **8a**, indicating the presence of an asymmetric molecule, resulting from the ring opening of the epoxy-siloxane by one NH_2 group of the porphyrin, leaving the second NH_2 group intact; (ii) the presence of broad signals at 4.04 (f) and 4.25 ppm (r′) corresponding to the resonance of the NH_2 and C*H*-OH protons in **8a** (iii) the resonance of Si-CH_3, Si-CH_2 and Si-CH_2-CH_2 protons are found at 0.05–0.14, 0.82–0.93 and 1.59–1.72 ppm, respectively; (iv) large signal containing superposed resonance peaks of CH_2-O and CH_2-NH protons (signals p′, s′) between 3.10 and 3.90 ppm. These results are in agreement with the structure of compound **8a**.

In the ^{1}H NMR spectrum of compound **10a** (Fig. S2), the presence of one porphyrin per one siloxane frame is confirmed by the 8 aromatic pyrrole-*H* and the 19 phenyl protons corresponding to the porphyrin unit and by the 24 aliphatic protons of the siloxane frame. The absence of the signal corresponding to NH_2 group of the porphyrin (5.48 ppm) confirms the success of the coupling reaction and the absence of the inner N*H* signal confirms the presence of the porphyrin's metal complex.

MALDI-TOF spectra of the synthesized compounds are represented in Fig. 2. The molecular ion (MH^+) of compounds **6a**, **6b** and **8a** could be observed, respectively at *m/z* values 992.510 (theoretical MH^+ = 992.460), 1621.664 (theoretical MH^+ = 1621.718) and 981.438 (theoretical MH^+ = 981.437). In the case of compound **8a**, dissociation to the starting porphyrin under ionization condition was extensively observed (MH^+ = 645.309). Compound **10a** was seen as a radical cation ($M^{\bullet+}$) at *m/z* = 979.313 (theoretical $M^{\bullet+}$ = 979.293). The isotopic pattern observed for compound **10a**, characteristic of zinc natural isotopes, confirms the presence of this element.

Photophysical properties: Absorption and fluorescence spectra

The photophysical properties of the amino-functionalized porphyrins and porphyrin-modified siloxane compounds were evaluated in solution, using chloroform as solvent. For all the compounds that derivate from the free-base amino-functionalized porphyrins, the UV-vis spectra display a typical porphyrin UV-vis

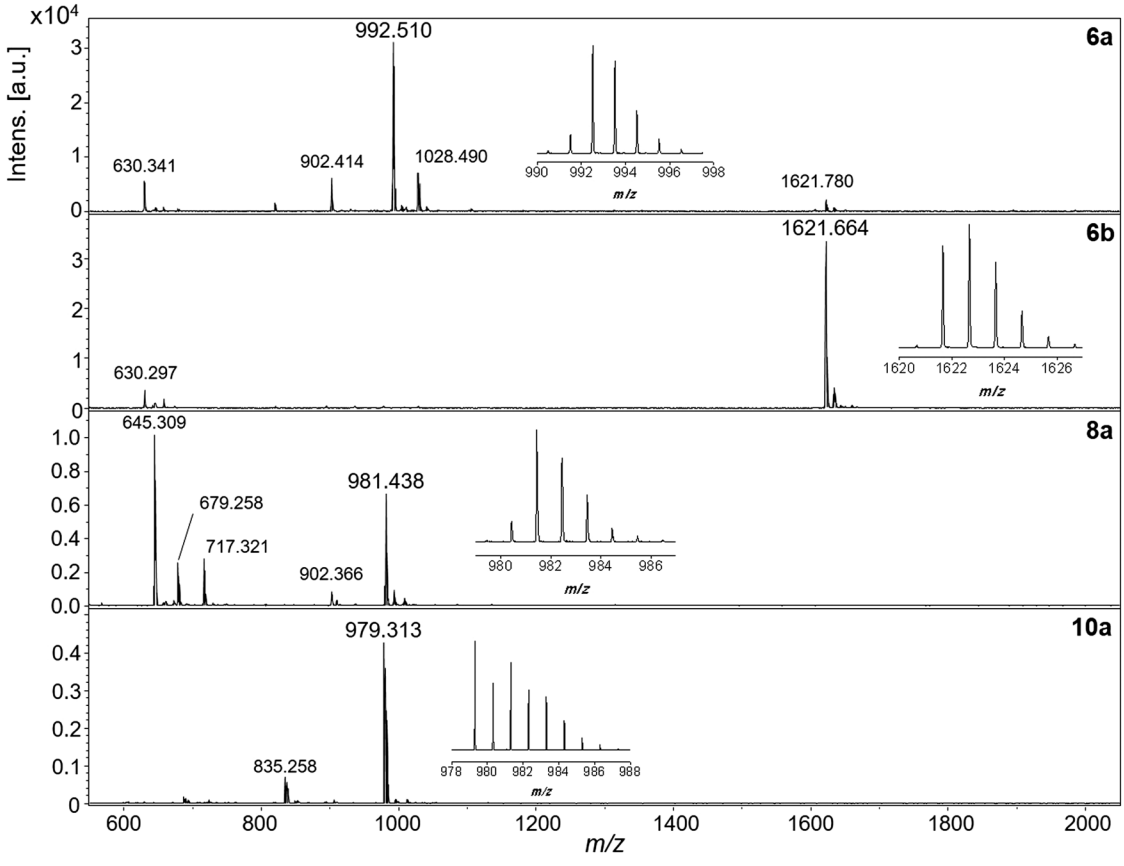


Fig. 2. Positive ion mode MALDI-TOF mass spectra of compounds **6a**, **6b**, **8a** and **10a**. Graphical inlets display the isotopic patterns observed for the MH^+ ions of compounds **6a**, **6b** and **8a**, and the $M^{\bullet+}$ ion of compound **10a**

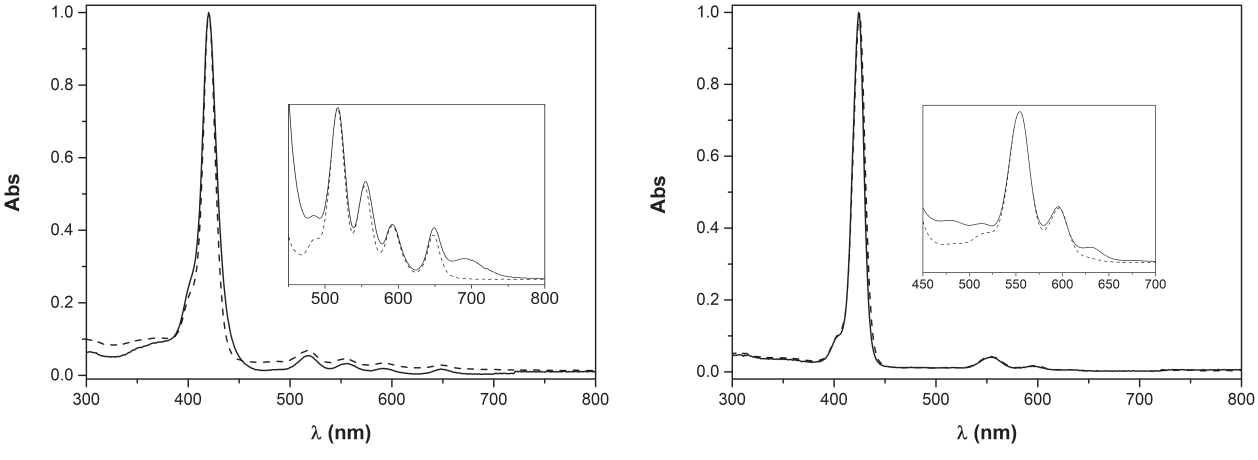


Fig. 3. Absorption spectra of: (a) compound **6b** (solid line) and **2** (dashed line) and (b) compound **10a** (solid line) and **2Zn** (dashed line) in chloroform. Zoom of the corresponding Q bands was inserted

profile with a strong $B_x(0,0)$ band at 420–424 nm and a shoulder at 400 nm corresponding to $B_y(0,0)$. The four Q bands appear around 517 ($Q_y(1,0)$), 555 ($Q_y(0,0)$), 590 ($Q_x(1,0)$) and 650 nm ($Q_x(0,0)$), presenting an etio-type absorption spectrum where the intensities decrease significantly from Q_{IV} to Q_I as presented in Fig. 3 [30]. For the zinc(II) metalloporphyrin and the corresponding porphyrin-modified siloxane compound **10a**, the introduction of the metal ion in the porphyrin core increases the symmetry and causes the spectral features in the visible region (500–650 nm) to collapse from four Q bands to two Q bands, corresponding to the Q(0,0)

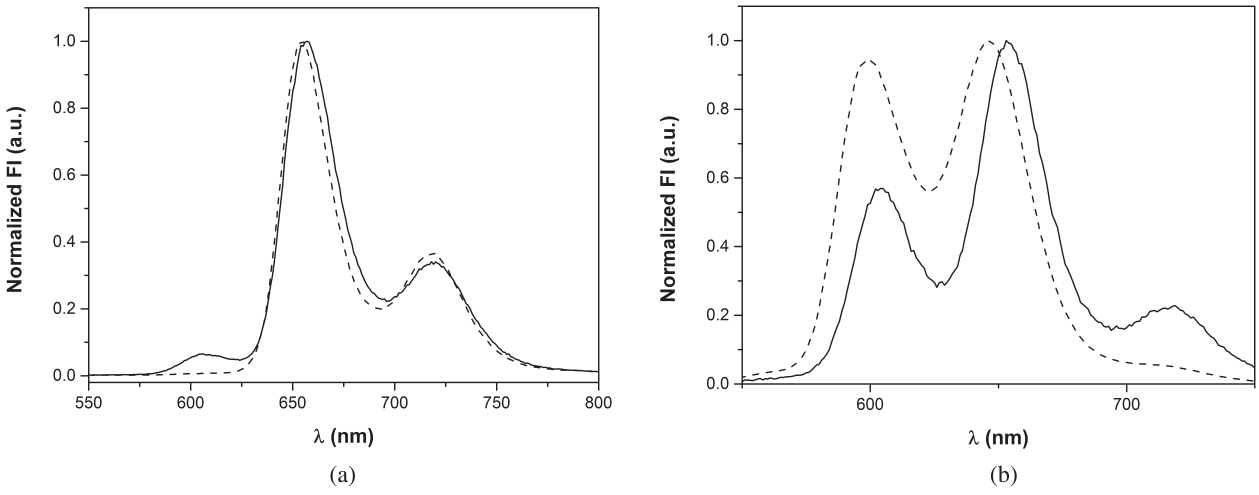


Fig. 4. Emission spectra of: (a) compound **6b** (solid line) and **2** (dashed line) and (b) compound **10a** (solid line) and **2Zn** (dashed line) in chloroform

and Q(1,0) transitions [30]. The absorption spectra of the zinc(II) metalloporphyrin occurs at shorter wavelength as compared to that of the free-base porphyrin. Comparing the absorption spectra of the amino-functionalized porphyrins and porphyrin-modified siloxane compounds no significant changes can be observed. However for compounds **6a**, **6b** and **10a**, a low-intensity band appears at 690 nm and 630 nm, respectively.

The emission spectra of the amino-functionalized porphyrins and porphyrin-modified siloxane compounds are depicted in Fig. 4. The spectra of the free-base porphyrins and corresponding porphyrin-modified siloxane compounds shows a $Q_x(0,0)$ band at around 655 nm and a $Q_x(0,1)$ band at around 720 nm, both corresponding to the S1→S0 transition [31]. For the zinc(II) porphyrin, both bands observed at 599 nm and 645 nm are probably belonging to the $Q_x(0,0)$ fluorescence band. Additionally, for compounds **6b** and **10a** a low-intensity band can be observed at 606 nm and 718 nm, respectively, probably belong to the $Q_x(0,0)$ and $Q_x(0,1)$ fluorescence band.

The quantum yield value obtained for compound **6a** (Φ_F = 0.031 in chloroform) was found to be similar to the reported value for the pristine mono-(aminophenylporphyrin) **2** (Φ_F = 0.05 in DMF [32]), which indicate that the presence of the siloxane unit does not affect the fluorescence properties which remained similar to those of aminoporphyrin derivatives. Also, the quantum yield value obtained for complex **2Zn** (Φ_F = 0.022 in chloroform) is in agreement with the reported value for the zinc(II) complex of **1** (Φ_F = 0.033 in toluene [33]).

CONCLUSIONS

In this work, the coupling capabilities of (aminophenyl) porphyrins to epoxide and carboxyl functionalized siloxanes were demonstrated.

After conventional *p*-nitration of 5,10,15,20-tetraphenylporphyrin, the resulting (nitrophenyl)porphyrins were efficiently reduced to their corresponding amines through the microwave-assisted catalytic transfer hydrogenation using cyclohexene as a hydrogen donor and 10% Pd/C as a catalyst, in DMF. This method is comparable with previous methods in yield, but avoids moisture sensitive reagents ($NaBH_4$) [27] and tin(II) salts [26] which are highly toxic and make the workup process more difficult. The zinc(II) complex of mono-(aminophenyl)porphyrin was also efficiently obtained using MW irradiation with $Zn(OAc)_2 \cdot 2H_2O$ in acetonitrile.

Having established the synthesis of the starting aminoporphyrins, their coupling to the siloxane moiety was approached, and the following conclusions were drawn: (i) the reaction of mono-(aminophenyl)porphyrin with bis-epoxide disiloxane **4** yields the desirable compounds **6a** and **6b**, while the same reaction under MW irradiation afforded compound **6a** as the sole product; (ii) the di-(aminophenyl)porphyrin reacted with the monoepoxide trisiloxane **5** to afford exclusively the compound **8a**; (iii) The low reaction yields involving both epoxides **4** and **5** reflect the low nucleophilicity of (aminophenyl)porphyrins, which is in contrast to the results obtained in the epoxide-functionalized siloxane aminolysis by aniline [23a]; (iv) In a similar way, a low extent of reaction was observed by the amidation of zinc(II) complex of mono-(aminophenyl)porphyrin with carboxyl-functionalized siloxane, yielding compound **10a** as the sole product.

Altogether, the results showed a series of porphyrin-modified siloxane structures, bearing in mind the future combination of porphyrins with higher molecular weight polysiloxanes. In addition, mono-derivatized porphyrins including compounds **6a**, **8a** and **10a** have a free amino functional group available for further future transformations.

Acknowledgments

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Supporting information

^{1}H NMR data for compounds **8a** and **10a** and HRMS (ESI) for compounds **2Zn** and **6a** are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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