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β -Pyrazino-fused tetrarylporphyrins

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Abstract

A novel method for the preparation of β -fused porphyrin dyads was developed that exploits a one-pot reaction of 2,3-diaminoporphyrins with diethyl oxalate. This approach provides good yields of the zinc β -fused dyad and the corresponding free-base, opening the way for preparation of several metal derivatives to permit modulation of optoelectronic characteristics for commercial applications.

Keywords

β -fused-porphyrin; Diethyl oxalate; α -dione porphyrin; 2,3-Diaminoporphyrin; DSSC; Porphyrin dyad electrochemistry

1. Introduction

In the last decade great attention has been focused on the preparation of porphyrin derivatives characterized by an expanded aromatic system, because these molecules show novel optical and electronic properties, making them particularly interesting for potential applications in fields [1] ranging from PDT to chemical sensors, and especially in dye-sensitized solar cells (DSSC) [2]. In fact, the extension of the porphyrin core aromaticity causes a decrease in the HOMO-LUMO gap that leads to improved harvesting of solar energy in a broad spectral region. Recently, Yella et al. reported the highest power conversion efficiency of 12.3% in DSSCs by the combination of a new cobalt electrolyte with a porphyrin sensitizer [3]. However, the absorption wavelength values of the porphyrin dye did not reach the near IR region and the existence of a gap between the Soret and Q bands in monomeric porphyrins limits their cell performance. The more successful way to overcome this limit is to connect more porphyrin dyes through their *meso* and *beta* peripheral positions [4]. Different approaches have been followed to reach this goal, such as for example the preparation of expanded porphyrinoids [5], where the aromatic system spans over a macrocycle larger than that of porphyrins. Another approach is to synthesize polymeric species, where the porphyrin units are linked by bridges, such as for example ethynes that allow macrocyclic conjugation [6].

Recently, a route based on the fusion of other aromatic segments, including additional porphyrin units at the peripheral position of the macrocycle, has been described [7]. Within this scenario, we have been interested in the preparation of dyads and triads of porphyrins directly fused at their peripheral positions, which show novel optical features, particularly promising for optoelectronic applications [6,8]. For these β -fused systems, most of the synthetic procedures generally involve several reaction steps or laborious preparation of the starting materials, such as sulfolenosubstrates or pyrrole-porphyrin derivatives [9]. Taking into account these considerations, our work has been focused on the exploration of novel and straightforward synthetic approaches for the fusion of porphyrinoid macrocycles through their beta peripheral positions, with the aim to open simple routes to hybrid arrays, where two different macrocycles are fused at the peripheral positions, since such heterodyads could be of interest for optoelectronic applications.

2. Experimental section

2.1. General information

Reagents and solvents (Aldrich, Fluka) were of the highest grade available and were used without further purification. Silica gel 60 (70–230 mesh, Sigma Aldrich) was used for column chromatography. Tetrabutylammonium perchlorate (TBAClO₄, Fluka) supporting electrolytes and decamethylferrocene (Me₁₀Fc, Aldrich) were used as electrochemical probes in cyclic voltammetry (CV) measurements. ¹H NMR spectra were recorded on a Bruker AV300 (300 MHz) spectrometer and chemical shifts were reported as the delta scale in ppm relative to CHCl₃ (7.25 ppm). UV–vis spectra were recorded on a Cary 50 spectrophotometer. Mass spectra (FAB mode) were recorded on a VGQuattro spectrometer in the positive-ion mode using *m*-nitrobenzyl alcohol (Aldrich) as a matrix. Electronic spectra were measured in chloroform using a Perkin Elmer lambda 40 spectrophotometer. Corrected emission and excitation spectra (450 W Xe lamp) and excited state lifetimes were obtained with a modular UV–VIS–NIR spectrofluorimeter Edinbourg, equipped with a single photon-counting apparatus. Corrections for instrumental response, inner filter effects and phototube sensitivity were performed [10]. Ru(bpy)₃²⁺ in aerated H₂O (Φ = 0.028) was used as a standard for fluorescence quantum yields. Emission spectra in a rigid, transparent 2-methylcyclohexane matrix at 77 K were recorded using quartz tubes immersed in a quartz Dewar filled with liquid N₂. A correction for a difference in the refraction index was introduced when necessary. The CV measurements were carried out at 298 K using PalmSens PS-Trace handheld potentiostat (Palm Instruments, Netherlands) in the standard three-electrode cell with platinum button (2 mm diameter) working electrode, Pt wire (0.5 mm diameter, 3 cm length) counter electrode and Saturated Calomel reference electrode (SCE, AMEL, Italy). The 1 mM solutions of **4a** and ZnTPP in CH₂Cl₂ containing 0.1 M of TBAClO₄ supporting electrolyte were analyzed in the potential ranges from 0 to –2 V (reduction processes) and from 0 to 1.6 V (oxidation processes) with a scan rate of 0.1 V/s. Before the measurements, system was calibrated with 1 mM Me₁₀Fc probe ($E_{1/2}$ = –0.063 V).

2.2. Synthetic details and characterization

Porphyrin **1** has been prepared following the reaction pathway reported in Scheme 1, according to literature methods [11,12].

2.2.1. Synthesis of 4a by condensation with 3—A solution of the porphyrin **1** (100 mg, 0.142 mmol) and palladium on activated carbon 10% wt (150 mg) in a mixture of dichloromethane and methanol (50 mL and 5 mL) was degassed with N₂ for 10 min. Sodium borohydride (133 mg, 3.5 mmol) was added and the solution was stirred under nitrogen, at room temperature. The progress of the reaction was followed by TLC analysis and UV–vis

spectroscopy and after 2 h the mixture was filtered through a plug of Celite. The solvent was evaporated and the crude residue was dissolved in a mixture of dichloromethane, ethanol and acetic acid (10 mL, 10 mL and 2 mL); 1 equiv. of **3** (100 mg, 0.142 mmol) was added and the solution was heated to reflux for 3 h. After evaporation of the solvent, the crude product was purified on a short column of silica gel eluting with dichloromethane. The first fraction was collected and crystallized from dichloromethane/methanol affording the bis-porphyrin **4a** as a dark red powder (38 mg, 0.028 mmol; 20%).

2.2.2. Synthesis of 4a by condensation with diethyl oxalate—A solution of the porphyrin **1** (100 mg, 0.142 mmol) and palladium on activated carbon 10% wt (150 mg) in a mixture of dichloromethane and methanol (50 mL and 5 mL) was degassed with N₂ for 10 min. Sodium borohydride (133 mg, 3.5 mmol) was added and the solution was stirred under nitrogen, at room temperature. The progress of the reaction was followed by TLC analysis and UV–vis spectroscopy and after 2 h the mixture was filtered through a plug of Celite using dichloromethane (50 mL). Diethyl oxalate (474 μ L, 3.5 mmol) diluted in methanol (5 mL) was added to the filtered solution and the mixture was heated at reflux for 6 h and then left stirring to room temperature overnight. After evaporation of the solvent, the crude product was purified on a short column of silica gel eluting with dichloromethane. The first red fraction was collected and crystallized from dichloromethane/methanol affording the bis-porphyrin **4a** as a dark red powder (41 mg, 0.030 mmol; 42%).

UV–vis (CH₂Cl₂): λ_{max} , (log ϵ) 402 (4.92), 492 (5.06), 592 (4.61) nm. ¹H NMR (300 MHz, CDCl₃): δ 8.88 (d, 2H, J = 4.74 Hz, β -pyrrole), 8.87 (s, 2H, β -pyrrole), 8.64 (d, 2H, J = 4.83 Hz, β -pyrrole), 8.23 (m, 4H, phenyls), 7.79 (m, 10H, phenyls), 7.54 (m, 6H, phenyls) ppm. Anal. Calcd for C₈₈H₅₂N₁₀Zn₂: C, 76.6; H, 3.8; N, 10.1. Found: C, 76.5; H, 3.6; N, 10.9%. MS (FAB): m/z 1380 (M⁺).

Crystallographic data were collected using MoK α radiation (λ = 0.71073 Å) at T = 90 K on a Nonius KappaCCD diffractometer. Crystal data: C₉₀H₆₀O₂Zn₂ · 2(CH₃OH) · 4(CH₂Cl₂), M_r = 1848.01, triclinic space group P-1, a = 8.858(3), b = 13.756(4), c = 18.320(7) Å, α = 74.461(14), β = 80.523(15), γ = 78.378(18)°, V = 2092.1(12) Å³, Z = 1, D_x = 1.467 g cm⁻³, θ_{max} = 26.1°, R = 0.054 for 7548 data (4979 with $I > 2\sigma(I)$) and 548 refined parameters, CCDC 908512.

2.2.3. Synthesis of 4b by demetalation—To a chloroform solution (70 mL) of **4a** (50 mg, 0.036 mmol) was added trifluoroacetic acid (TFA) (ca. 200 μ L). The mixture was stirred at room temperature for 30 min, following the progress of the demetalation by TLC analysis and UV–vis spectroscopy. The resulting mixture was neutralized with saturated aqueous NaHCO₃ and extracted with chloroform; the organic phase was washed with water and dried over anhydrous Na₂SO₄. The product was directly crystallized from dichloromethane/methanol affording **4b** (43 mg, 0.034 mmol) in 94% yield.

UV–vis (CH₂Cl₂): λ_{max} , (log ϵ) 412 (4.27), 489 (4.56), 538 (sh), 614 (sh) nm. ¹H NMR (300 MHz, CDCl₃): δ 8.80 (d, 2H, J = 4.41 Hz, β -pyrrole), 8.76 (d, 2H, J = 4.74 Hz, β -pyrrole), 8.67 (s, 2H, β -pyrrole), 8.28 (m, 4H, phenyls), 7.95 (m, 3H, phenyls), 7.81 (m, 7H, phenyls), 7.62 (m, 6H, phenyls), -2.17 (brs, NH) ppm. Anal. Calcd for C₈₈H₅₆N₁₀: C, 84.3; H, 4.5; N, 11.2. Found: C, 84.5; H, 4.4; N, 11.1%. MS (FAB): m/z 1254 (M⁺).

2.2.4. Synthesis of 4c—Bis-porphyrin **4b** (40 mg, 0.032 mmol) was dissolved in chloroform (50 mL) and an excess of a saturated solution of Cu(OAc)₂ · H₂O in methanol was added. The resulting solution was heated under reflux for 2 h. The completion of metalation was verified by TLC analysis and UV–vis spectroscopy. After cooling, the

solvent was evaporated and the product was directly crystallized from dichloromethane/methanol affording **4c** as a green powder (35 mg, 0.026 mmol), in 81% yield.

UV-vis (CHCl_3): λ_{max} , nm (log ϵ) 402 (4.36), 492 (4.53), 594 (4.09) nm. Anal. Calcd for $\text{C}_{88}\text{H}_{52}\text{N}_{10}\text{Cu}_2$: C, 76.8; H, 3.8; N, 10.2. Found: C, 77.1; H, 3.4; N, 10.4%. MS (FAB): m/z 1375 (M^+).

3. Result and discussion

During our search of simple synthetic routes for the preparation of hetero- β -fused systems, we decided to investigate the preparation of a novel β -fused bis-porphyrin, characterized by having a pyrazine unit in the linker. Following the common acid catalyzed route to condense aromatic *o*-diamines with vicinal diketones [13], the zinc α -dione porphyrin derivative **3** [14] was reacted with the 2,3-diaminoporphyrin zinc complex **2**. Porphyrin **1** (Scheme 1) was synthesized and isolated according to literature procedures [11,12] and subsequently reduced with NaBH_4 , in the presence of Pd/C 10% wt, under nitrogen in a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (10:1) solution. Complete reduction was verified by UV-Vis spectroscopy and TLC and, after 2 h, the resulting solution of **2** was passed through a pad of Celite to remove the catalyst and hydride excess. After evaporation of the solvent, **2** was dissolved in CH_2Cl_2 and directly added to a solution of **3** in $\text{CH}_2\text{Cl}_2/\text{EtOH}/\text{HOAc}$ (5:5:1) and the mixture was heated at reflux for 3 h; purification of the resulting crude product on a silica gel column, eluting with CH_2Cl_2 , afforded the bis-porphyrin **4a** as a single product, in 20% yield.

Considering the overall yield of the reaction, we did not further investigate the scope of this approach until recently, when Akita et al. reported a novel route for preparation of similar fused diporphyrins by oxidative annulation of β -amino substituted porphyrins [15]. While this simple approach was satisfying in the case of porphyrin derivatives having an unsubstituted *meso*-position, in the case of tetraphenylporphyrin the reaction succeeded only for the Ni complex, and yields similar to those previously obtained by us were reported.

With this novel route in mind, we decided to investigate the possible preparation of **4a** by using **2**, as the starting substrate, to undergo the subsequent oxidative annulation with DDQ. In order to minimize the possible decomposition of **2**, the oxidation reaction was carried out in situ, adding DDQ (1 equivalent) directly to the solution of the *o*-diamino derivative, simply passed through Celite without evaporation of the solvent. The mixture was heated at reflux and reaction progress was followed by UV-Vis spectroscopy and TLC, which indicated a complete reaction after 1 h. However, chromatographic purification afforded only traces of the bisporphyrin **4a** together with other fractions, among which the dione **3** was identified.

Considering these results it was decided to explore milder reaction conditions and to carry out the oxidation at room temperature as described for the mono-amino procedure [15]. Reaction products were the same as those obtained at high temperature, with only slightly different yields. This led us to consider steric hindrance among the two fused macrocycles as the reason for the failure to obtain **4**, and this prompted us to investigate a modification of the synthetic pathway leading to the formation of a bridging group larger than the pyrazine unit.

For the foregoing reason it was decided to use diethyl oxalate, a well-known coupling reagent [16], with the idea of preparing a dioxo-pyrazine derivative to react in situ with *o*-diamino porphyrin to provide **6**, according to the pathway outlined in Scheme 2.

An excess of diethyl oxalate was added directly to the filtered solution of **2** and then the mixture was heated at reflux for 3 h; the work-up of the crude product afforded one major fraction, along with traces of a more polar compound. Surprisingly, the spectroscopic characterization led us to identify the compounds as **4a** and **3**, respectively.

Following this approach, the bisporphyrin **4a** was obtained in a satisfying 42% yield, a value more than double that previously obtained [15]. Furthermore, treatment of **4a** with a small amount of TFA afforded the corresponding free-base **4b**, in 90% yield, opening the possibility to obtain other metal derivatives, such as the biscopper complex **4c**, which indeed was obtained by addition of a saturated solution of Cu(OAc)₂.

Considering that the reaction also afforded also traces of zinc α -dione derivative **3** as a side product, we decided to further investigate the influence of the reagent stoichiometry and to closely follow the progress of the oxidative reaction. In fact, the most common and successful route for the preparation of dioxo porphyrinoids requires the use of Dess-Martin periodinane (DMP) as the oxidant [14a]. Such a compound is, however, quite photosensitive and rather expensive.

In Table 1 we report the results obtained by changing reaction conditions, such as reagent molar ratio, reaction time and solvent mixtures.

These results give some indication as to the role of diethyl oxalate in the unexpected formation of **4a**, and a plausible reaction pathway is reported in Scheme 3. The first step is the formation of the intermediate **5**, obtained by condensation of the zinc diamino derivative **2** with diethyl oxalate, in accord with the well known reactivity of this compound as a coupling reagent with diamines [16]. This hypothesis is supported by the formation of a broad absorption band around 550–600 nm and of a red-shifted shoulder on the Soret band in the UV–visible spectrum, observed during the monitoring of the reaction progress, which suggests the formation of the annulated dioxopyrazino ring. When a **2**/diethyl oxalate ratio of 1:25 was used, the formation of **5** was not complete and **2** was still present in the reaction mixture, which can lead to the formation of **4a** by nucleophilic attack upon **5**. When the **2**/diethyl oxalate reagent ratio was increased to 1:40, the formation of **5** was more complete and the reduced amount of unreacted **2** explains the significant decrease in the yield of **4a**. In this case the most abundant product is the α -dione porphyrin, produced by the hydrolysis of the labile intermediate **5**.

With these improvements in the synthetic route, sufficient material was available to grow single crystals, which allowed the X-ray crystallographic characterization of **4a** (Fig. 1).

The molecule lies on an inversion center in the crystal, and the central pyrazino ring is planar, with maximum deviation 0.002(3) Å. The four N atoms of each porphyrin are coplanar to within 0.064(3) Å, and these N₄ planes form dihedral angles of 30.2(1)° with the central pyrazino plane, as shown in Fig. 1. The Zn atoms have square-pyramidal coordination and lie 0.2719(5) Å out of the N₄ planes, with Zn–N distances 2.040(3) – 2.087(3) Å. The axial position is occupied by a coordinated MeOH molecule, with Zn–O distance 2.134(3) Å. The porphyrins have saddle conformations, with opposite pairs of β C atoms lying an average of 0.73 Å out of the 24-atom porphyrin plane, on the same side. The mean deviation of the 24 atoms from their best plane is 0.357 Å.

It is of interest to compare the structure of **4a** with that of the recently-reported Ni(II) complex of a similar dimeric ligand with 3,5-di-*tert*-butylphenyl groups at the 5, 10, and 15-positions [15]. Like **4a**, that molecule lies on a crystallographic inversion center, so its central pyrazino ring is also essentially planar. The bond distances in its central pyrazino

ring and two fused pyrroles agree well with those in **4a**. However, unlike the stepped overall shape of **4a**, the ring system of the Ni complex has an approximate C₂ axis connecting the two Ni atoms, and its porphyrins are twisted about this axis, with ruffled conformations.

4. Photophysical characterization

The absorption spectrum of **4a** in dichloromethane features a splitting of the Soret band, resulting in an intense absorptivity in a broad region of the visible spectrum ($\epsilon > 50,000 \text{ M}^{-1} \text{ cm}^{-1}$ between 390 and 510 nm) with two peaks at 402 and 492 nm ($\epsilon = 84,000$ and $114,000 \text{ M}^{-1} \text{ cm}^{-1}$ respectively) and indicating strong ground state electronic interactions between the two porphyrins. A Q-like set of broader, rather intense bands is also observed, with maximum at 592 nm ($\epsilon = 41,000 \text{ M}^{-1} \text{ cm}^{-1}$; Fig. 2). Treatment of **4a** with trifluoroacetic acid causes the protonation of the dyad, with the subsequent demetalation, forming the corresponding cationic freebase derivative; treatment of the protonated species with base affords the neutral free base, which can be metalated with $\text{Cu}(\text{OAc})_2$ to give **4c**. The corresponding absorption features changes are shown in Fig. 2. Similarly to previous observations in β -fused oligoporphyrins [17], the absorption bands are red-shifted compared with the parent TPP complex (ZnTPP, in this case), indicating a high degree of π -electron delocalization in the dimer.

The fluorescence spectrum at room temperature shows a low-intensity (Fig. 3), structured band with its maximum at 612 nm ($\Phi = 1.4 \times 10^{-3}$, to be compared with 4.0×10^{-2} for ZnTPP), presenting an excited state lifetime of 1.0 ns, much shorter than that observed for ZnTPP (2.7 ns) [18].

The excitation spectrum of **4a** is proportional to the absorption spectrum, indicating that the S₁ state is formed with almost unitary efficiency also when S₂ and other excited states are initially populated. Similar results were observed at 77 K, where an excited state lifetime of 1.3 ns was measured, that is very close to the one observed at RT. This indicates that the contribution of thermally activated processes is not predominant for the deactivation of the excited state of **4a** even at room temperature.

5. Electrochemical characterization of **4a**

To further characterize the degree of electronic interactions among the two porphyrin subunits in these β -fused dyads, we investigate the electrochemical properties of **4a** by CV technique, comparing them with those of 5,10,15,20-tetraphenylporphyrinato zinc (ZnTPP). In Fig. 4 we report the CV obtained, summarizing the redox data in Table 2.

The electrochemistry of ZnTPP is well documented, and the data we obtained are in good accord with those reported in the literature [19]. In the cathodic region, ZnTPP undergoes two well defined one-electron processes, corresponding to the first and second porphyrin ring reductions to give consecutively the π -anion-radical, ZnTPP^- , and the dianion ZnTPP^{2-} species, at $E_{1/2, \text{red1}} = -1.48 \text{ V}$ and $E_{1/2, \text{red2}} = -1.80 \text{ V}$ respectively, with a potential separation $\Delta E_{1/2, \text{red}} = 320 \text{ mV}$.

The CV of **4a** is more complex than that of ZnTPP, as showed in Fig. 4. When the potential sweep was initially moved to the cathodic region, **4a** undergoes two reduction processes, which are slightly shifted (60 mV) to more positive potentials than that of ZnTPP ($E_{1/2, \text{red1}} = -1.42 \text{ V}$, $E_{1/2, \text{red2}} = -1.74 \text{ V}$). The peak currents of these two processes are approximately double than that observed for the ZnTPP, indicating the overlapping of two independent one-electron reductions for each porphyrin unit of **4a**. In these reduction processes the two macrocycles behave as equivalent, but not interacting reaction centers.

The dyad **4a** shows a completely different behavior in the anodic region; while ZnTPP undergoes two one-electron porphyrin-ring centered oxidations at $E_{1/2,ox1} = 0.76$ V and $E_{1/2,ox2} = 1.06$ V with a potential separation of $\Delta E_{1/2,ox} = 300$ mV, in **4a** these ring-centered oxidations are split into two one-electron transfer processes, Fig. 4 (bottom), with the overall process resulting in four reversible oxidation waves.

The first two oxidations of **4a** lead to the formation of a bis- π -cation radical upon the stepwise oxidation of each Zn-porphyrin units of the dyad [Equations (1) and (2)], while the next two separated oxidations of **4a** finally give the corresponding bis-porphyrin dication [Equations (3) and (4)].

The splitting of these oxidation processes indicates that the porphyrin subunits in the dyad behave as two equivalent and interacting redox centers. The difference in $E_{1/2}$ between the first two oxidations is 170 mV ($E_{1/2,ox1} = 0.74$ and $E_{1/2,ox2} = 0.91$ V), while the splitting is more significant for the second oxidation processes, separated by 310 mV gap ($E_{1/2,ox3} = 1.00$ V and $E_{1/2,ox4} = 1.31$ V).

It should be noted that two non-coupled irreversible processes, located at $E_{pa} = 0.56$ V and $E_{pc} = -0.88$ V respectively, were also detected for dyad **4a**. Both these processes are indicated with an asterisk (*) in Fig. 4. Considering that the Zn ion is not redox active in these conditions, the suspect arose that these processes could be assigned to the redox behavior of pyrazine spacer of **4a**; this unit undergoes a rapid reduction process at $E_{pc} = -0.88$ V, which is in accord with data reported in literature [20]. This reduction could induce the formation of a dihydropyrazine-like species, which interrupts the conjugation among the two porphyrin moieties, explaining the absence of electronic coupling in the cathodic region. At the return sweep the cathodic wave corresponding to the oxidation of formed species was registered at $E_{pa} = 0.56$ V, which restores the pyrazine spacer and consequently the conjugation among the two porphyrin units in the dyad. This electronic coupling determines the observed splitting of the oxidation processes.

To further confirm this hypothesis, we started the potential sweep in the opposite order, beginning toward the anodic region of positive potentials. In this case we did not observe the wave at 0.56 V (Fig. 5) and only the four processes belonging to the porphyrin moieties were observed. A cathodic wave at -0.88 V corresponding to pyrazine oxidation was still observed, although with a lower intensity than the previous case, confirming our hypothesis on pyrazine-spacer related red-ox processes.

6. Conclusion

We have established a simple and efficient route for the preparation of a β -pyrazino-fused porphyrin dyad. The X-ray crystallographic and the photophysical characterization of the β -

fused porphyrin dyad highlight interesting features of this derivative. It is worth mentioning that the reported synthetic route allows the preparation of the free-base dyad, after mild treatment with acid. This easy demetalation process opens up the possibility to obtain different metal derivatives of the dyad and consequently to modulate the related photophysical characteristics, potentially making these species suitable for optoelectronic applications.

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Fig. 1.
Molecular structure of **4a** with 50% ellipsoids: a) front view; b) side view.

Fig. 2.
Absorption spectra of dyads in CH_2Cl_2 .

Fig. 3.
Absorption (solid line) and fluorescence (dotted line) spectra of **4a** in CH_2Cl_2 .

Fig. 4.
Cyclic voltammograms of **4a** and ZnTPP.

Fig. 5.
Cyclic voltammogram of dyad **4a**; first scan toward oxidation.

Scheme 1.

Synthesis of **4a** by condensation of 2,3-diaminophthalocyanine zinc complex **2** with zinc α -dione porphyrin derivative **3**.

Scheme 2.

Synthesis of **4a** by condensation of 2,3-diaminoporphyrin zinc complex **2** with diethyl oxalate. i) CHCl_3/TFA , r.t. ii) $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, $\text{CHCl}_3/\text{MeOH}$, Δ , 2 h.

Scheme 3.

Proposed reaction mechanism for the formation of **4a** and **3**. i) **2**/diethyl oxalate ratio of 1:25, $CH_2Cl_2/MeOH$, Δ , 6 h; ii) **2**/diethyl oxalate ratio of 1:40, $CH_2Cl_2/MeOH$, Δ , 6 h.

Table 1Products obtained from the preparation of **4a**.

2/Et ₂ oxalate ratio	Reaction conditions	Solvent mixture	Yield % (4a)	Yield % (3)
1:10	3 h, Δ	CH ₂ Cl ₂ /EtOH	Traces	Traces
1:25	3 h, Δ	CH ₂ Cl ₂ /EtOH	25	Traces
1:25	6 h, Δ	CH ₂ Cl ₂ /MeOH	42	6
1:40	6 h, Δ	CHCl ₃ /MeOH	5	48

Table 2Summary on cyclic voltammetry of **4a** and ZnTPP^a.

Compound	Oxidation	Reduction	HOMO-LUMO gap
	(E _{1/2} , V)	(E _{1/2} , V)	ν^b
ZnTPP	1.06; 0.76	−1.48; −1.80	2.24
4a	1.31; 1.00; 0.91; 0.74; 0.56*	−0.88*; −1.42; −1.74	2.16

^aData obtained in 3 electrode cell with button Pt WE, wire Pt CE, SCE reference; 1 mM solutions of **4a** and ZnTPP were prepared in CH₂Cl₂ solvent containing 0.1 M TBAClO₄ scan rate 0.1 V/s.

^bEvaluated as the potential difference between the first oxidation and first reduction.