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On the synthesis of functionalized porphyrins and porphyrin conjugates via β-aminoporphyrins

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The synthesis of functionalized porphyrins and conjugates from meso-tetraarylporphyrins through the acylation and the oxidation of β-aminoporphyrins was investigated. 2,3-Dioxochlorins were prepared by the oxidation of a variety of β-aminoporphyrins and subsequently used in a condensation reaction with functionalized aromatic aldehydes and ammonium acetate to form β-functionalized porphyrins bearing a fused imidazole ring. Under optimized experimental conditions both reactions tolerate various functional groups and afford the products in an appropriate overall yield. The mildness and usefulness of this methodology is illustrated by several examples including the synthesis of porphyrins bearing receptor groups and water-soluble conjugates.

Introduction

Porphyrin chemistry, inspired by natural processes, has evolved into a vast field of knowledge unlocking the applications of tetrapyrrolic compounds in solar energy transformation, cancer photodynamic therapy, catalysis, development of novel functional materials and so forth. 1-10 However, there is still a key difference between natural and synthetic porphyrins. Indeed, the majority of naturally occurring porphyrins do not contain meso-substituents and the utilization of meso-substituted porphyrins as “natural” mimics and the optimal structure of the tetrapyrrole molecules studied nowadays is questionable. This irrational modelling origins from the difficulties of the synthesis of β-substituted porphyrins due to the complexity of preparing 3,4-disubstituted pyrrole starting materials. Therefore, the development of synthetic routes leading to β-functionalized porphyrins has become a priority in porphyrin synthesis. 11-14 Futhermore, functionalization of the outer periphery of the porphyrin macrocycle was recognized in the last decades as a versatile synthetic approach to β-substituted derivatives. 15-18 Among synthetic porphyrins designed for applications, there is a broad series of modular systems comprising of a tetrapyrrolic macrocycle, a suitable linker and a functional moiety. These compounds are useful for the development of drugs, supported catalytic systems, chemosensors, biomarkers, hydrophilic porphyrins soluble under physiological conditions, as well as conjugates of porphyrins with other molecules exhibiting dual functions required in biomedicine and photovoltaic devices. We have studied the preparation of these modular systems from available meso-tetraarylporphyrins 2H-1 focusing our studies on the mild procedures tolerated by different functional groups (Scheme 1). In this regard, monob β-aminoporphyrins 2H-2 seem to be attractive intermediate compounds because of their ready availability from meso-tetraarylporphyrins 2H-1 by using nitration, 19-30 followed by the reduction of the nitro group, 21,31-36

Scheme 1 briefly summarizes different synthetc approaches to modular porphyrins from β-aminoporphyrins 2H-2. Commonly used acylation reaction (Scheme 1, Path A) does not tolerate many functional groups at the meso-aryl substituents because acyl halides are highly reactive towards nucleophilic substitution. 37-41 In addition, a flexible character of the alkylamide spacer could be somewhat inconvenient in part because of undesirable intramolecular interactions of the functional groups with the central metal ion of the porphyrin complex.

Recently, the Buchwald-Hartwig amination reaction was investigated as an alternative route to β-substituted porphyrin conjugates (Scheme 1, Path B). 42-44 The reported systems were prepared by using of the catalytic reactions of nickel (II) β-aminoporphyrinates with aromatic halides. It is noteworthy that highly acidic conditions (H2SO4) are needed for the demetallation of these conjugates that may result in their decomposition.

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According to the third approach (Scheme 1, Path C), the oxidation of β-aminoporphyrins 2H-2 to 2,3-dioxochlorins followed by their condensation with o-phenylenediamines yields a rigid quinoxaline linker between a porphyrin and a functional moiety.21,31-36 The structural features of the functional subunit defined by the substitution pattern of the starting o-phenylenediamines are a serious drawback for the design of modular systems. Furthermore, physico-chemical properties of these π-extended porphyrin systems significantly differ from those of their tetapyrrolic precursors, thereby limiting their utility for the preparation of functional molecular systems.

Another attractive approach was reported in late 90th by Crossley’s group and is still scarcely studied.45 According to this strategy, a fused imidazole moiety serves as a linker in modular molecules (Scheme 1, Path D). These conjugates are prepared by condensation of benzaldehydes, ammonium acetate (AMAC) and 2,3-dioxochlorins obtained by photo-oxidation of β-aminoporphyrins 2H-2 followed by hydrolysis of the resultant keto-imino chlorin. These reactions proceed under mild conditions and tolerate functional groups attached to the benzaldehyde. The rigid character of the imidazole spacer prevents the intramolecular interactions between the porphyrinic macrocycle and the functional moiety that is attractive for the preparation of supported catalytic systems, chemosensors or metal-organic framework materials.

Surprisingly, this strategy was only used for the elaboration of several hydrophobic porphyrin conjugates for photophysical studies.46-52 Accordingly, only behavior of 2,3-dioxo-5,10,15,20-tetraarylchlorins with mesityl and 3,5-di-tert-butylphenyl substituents in the condensation reaction were studied and the scope of this synthetic pathway remains unclear by now.
In the context of our ongoing projects in sensing, imaging and material chemistry, we are investigating viable synthetic pathways to functionalized porphyrins and porphyrin conjugates from meso-tetraarylporphyrins 2H-1 bearing different substituents at the meso-positions via β-functionalization strategy. Herein, the results on the synthesis of β-aminoporphyrins 2H-2 and their conjugation with functional moieties by using alkylamide and imidazole spacers (Scheme 1, Path A and D) are reported. In particular, we have explored the oxidation of a wide range of β-aminoporphyrins 2H-2 to 2,3-dioxochlorins and the condensation of these diones with aromatic aldehydes in the presence of AMAC. We also illustrate the usefulness of this methodology for the preparation of water-soluble porphyrin conjugates 2H-3.

Results and discussion

β-aminoporphyrins and their trnasformations.

The nitration reaction was chosen as an entry point for the functionalization of the periphery of meso-tetraarylporphyrins (Scheme 2). This reaction has been extensively studied and experimental procedures for selective mono-β-nitration were developed for a wide variety of porphyrins bearing meso-aryl substituents at the macrocycle periphery. Among different synthetic procedures developed for the nitration of meso-tetraarylporphyrins, the treatment of free base porphyrins with copper (II) nitrate in the presence of acetic anhydride seems to be the most convenient and general procedure. In fact, the reactivity of each porphyrin in 2H-1 series under these conditions was somewhat different but after optimization of the reagent amount, the temperature and the reaction time, all β-nitroporphyrins Cu-4a-f were obtained in good to high yields (Scheme 2, 68-84%) (see ESI, Table S1). Pentafluorophenyl substituted porphyrin 2H-1g was less reactive under the studied conditions and yields only copper (II) porphyrinate Cu-1g in quantitative yield. Therefore, nitration of this compound was carried out by using the reaction of nickel (II) derivative Ni-1g with copper (II) nitrate in the presence of succinic anhydride.

The demetallation of copper 2-nitroporphyrins under acidic conditions was also widely studied. Accordingly, demetallation of complexes Cu-4a,c,d,e by concentrated sulfuric acid smoothly proceeds in CH2Cl2 solution at room temperature whereas H2SO4/TFA mixture is needed for the decomplexation of porphyrinates Cu-4b,f and Ni-4g bearing ortho-substituted aryl groups at the macrocycle ring. All the obtained 2-nitroporphyrins 2H-4a-g were then reduced with a mixture of tin(II) chloride dihydrate and concentrated HCl in CH2Cl2 to give the crude 2-aminoporphyrins 2H-2a-g (Scheme 2). It should be also noted that the stability of the free-base β-aminoporphyrins 2H-2a-g is highly dependent on the meso-aryl substituents. Compounds 2H-2e,g bearing electron-withdrawing diethoxyphosphoryl or fluorine groups are more stable and can be isolated in a pure form by column chromatography over silica while other 2-aminoporphyrins 2H-2d,f should used in the next step without purification and directly after preparation due to their sensitivity to photo-oxidation and heating. This instability is a key factor limiting their utility for further elaboration of functionalized porphyrins and corresponding conjugates.

Going further, both acylation and alkylation of β-aminoporphyrins 2H-2 were explored. β-Aminoporphyrin 2H-2e bearing electron-withdrawing diethoxyphosphoryl substituents slowly reacted with succinic anhydride affording target product 2H-5e in 74% yield with 2,3-dioxochlorin 2H-6e (16%) formed through the competing oxidation reaction (Scheme 3). However, the aminolysis of
(2-pyridyl)methylbromide and ethyl bromoacetate by amine 2H-2e in the presence of different bases (K₂CO₃, K₂HPO₄, DIEA) led to inseparable mixtures of starting compound, alkyamines and oxidation products.

In this regard, the photo-oxidation of β-aminoporphyrins to 2,3-dioxochlorins followed by Debuss-Radziszewski condensation is of particular interest for the preparation of porphyrin conjugates (Scheme 1, Path D). Unfortunately, experimental conditions for both reactions were only briefly described in the first report and in later publications.

Our studies demonstrate that the outcome of the photo-oxidation of β-aminoporphyrins 2H-2 by air in the presence of hydrated silica in CH₂Cl₂ is strongly influenced by the nature of the substituents at the periphery of the porphyrin macrocycle (Scheme 4). After 2 h of irradiation by visible light, 2,3-dioxochlorins were isolated in good yields from β-aminoporphyrins bearing p-tolyl- (2H-2a), mesityl- (2H-2b), p-bromophenyl- (2H-2c), p-methylcarboxyphenyl- (2H-2d), and 2,6-dichlorophenyl (2H-2f) substituents. Surprisingly, the photo-oxidation of p-diethylphosphoryl substituted amine 2H-2e was more complicated and gave a mixture of inseparable products. We believe that a low yield of the porphyrin-α-dione 2H-6e, detected in the reaction mixture by MALDI-TOF mass analysis, is due to a competition between the oxidation of the 2-aminoporphyrin 2H-2e and the porphyrin-α-dione 2H-6e. Indeed, when stirring of the reaction mixture was prolonged for 8 h after stirring the light off, another product was detected in the reaction mixture using MALDI-TOF mass spectroscopy (m/z 1177). This compound was obtained in 35% yield by column chromatography on alumina and identified as the 2-oxa-3-oxochlorin 2H-7e by using NMR, IR spectroscopy and ESI mass spectrometry (see ESI). It is noteworthy that 2-oxa-3-oxochlorins were never obtained in the photo-oxidation of 2-aminoporphyrins by air but were already prepared reacting these amines with m-chloroperbenzoic acid or by the porphyrin-α-dione oxidation with benzeneselenic anhydride. These porpholactones have also been obtained by oxidation of mesotetraaryl-2,3-dihydroxy-chlorins with MnO₂. In agreement with these results, the photo-oxidation by air of electron deficient 2-aminoporphyrin 2H-2g bearing meso-penfauroporphyrin substituents resulted in a complicated mixture of products which were not identified.

Thus, our data show that strong electron-withdrawing groups attached to the porphyrin ring facilitate the oxidative degradation of porphyrin-α-diones. In contrast, photo-oxidation of sterically hindered amines 2H-2b,f having two o-alkyl or o-chloro substituents yielded the target porphyrin-α-diones 2H-6b,f in good yields indicating that steric factors are less important for the reaction course.

To overcome the limitations observed in the photo-oxidation of 2-aminoporphyrins 2H-2e,g, we explored different synthetic approaches to porphyrin-α-diones by using 2H-6e as a model compound. Firstly, we studied the oxidation of amine 2H-2e by air in the presence of acetic acid (AcOH, 10 equiv.) in CH₂Cl₂ at room temperature because as mentioned above porphyrin-α-dione 2H-6e was obtained as a side product when reacting amine 2H-2e with succinic anhydride (Scheme 3). According to MALDI-TOF mass analysis of the reaction mixture, amine 2H-2e was fully stable under these conditions even after 48 h of stirring. Its selective oxidation to porphyrin-α-dione 2H-6e was observed when anhydrous sodium acetate (10 equiv.) was added to the reaction mixture. However, the reaction was slow and did not go to completion even after 4 days of vigorous stirring. The better result was obtained when this compound was oxidized with the Dess–Martin periodinane (DMP) following the two-step procedure reported by Promarak and Burn. According to this protocol, the target product 2H-6e was obtained in 99% yield through stirring of arylamine 2H-2e with DMP (1.2 equiv.) in CH₂Cl₂ for 1 h in the dark followed by addition of diluted HCl to hydrolyse any imine intermediates that may have been formed during this oxidation. Porphyrin-α-dione 2H-6e was purified by column chromatography over alumina using degassed air-free eluents.

**Condensation of porphyrin-α-diones with substituted aromatic aldehydes.**

With porphyrin-α-diones in hands, we next investigated the Debuss-Radziszewski condensation. In the preliminary experiments the reaction of porphyrin-α-dione 2H-6a with aldehyde 8 was conducted according to literature procedures involving stoichiometric ratio of carbonyl compounds in the presence of an excess of AMAC (100 equiv) in CHCl₃/AcOH mixture (1:1, v/v) heated at reflux (Scheme 5). However, the product was obtained only in 25% yield (Table 1, entry 1). Therefore, the reaction was thoroughly investigated in order to obtain satisfying isolated product yields and reveal the influence of substituents on the reaction course. The results for the toly derivative 2H-6a are summarized in Table 1.
The increase of the aldehyde amount up to 2 equiv did not influence the product yield (entry 2). In contrast, the reaction outcome was dependent on the variation of CHCl₃/AcOH ratio. When 9:1 mixture of CHCl₃/AcOH was used, the product was obtained in 60% yield (entry 3). An over excess of aldehyde 8 appeared to be suited to maximize the formation of the imidazole under these conditions (entries 4 and 5). Moreover, it was possible to increase the reaction rate without deterioration of the product yield replacing AcOH by a stronger carboxylic acid, TFA (entry 6). However, a large over excess of aldehyde 8 was still needed for the successful condensation (entries 6-8).

On the basis of these outcomes, the reactions of 2,3-dioxo-5,10,15,20-tetraarylchlorins 2H-6a-f with an excess of aromatic aldehydes 8-13 (5 equiv) and AMAC (100 equiv) were performed in CHCl₃/TFA mixture (99:1, v/v) at reflux (Scheme 5). The product yield was found to be dependent on the substituent pattern of both carboxyl reagents. For instance, p-tolyl- and mesityl-substituted 2,3-dioxochlorins 2H-6a and 2H-6b reacted with aldehyde 8 and AMAC affording imidazoporphyrins 2H-14a and 2H-14b in 90% and 64% yields, respectively. This significant difference in the product yields demonstrates the strong influence of the porphyrin-α-dione structure on the reaction course. Nevertheless, under optimized conditions both porphyrin-α-diones 2H-6a and 2H-6b reacted smoothly with a series of aromatic aldehydes 8-13 always providing target products 2H-14-19 in good yields (48-90%). More interestingly, the condensation of 2,3-dioxochlorins 2H-6c-f bearing functional groups at the periphery of the macrocycle proceeded without negatively impacting on the product yield.

According to these reactions, we prepared valuable compounds with reactive functional groups suitable for further modifications (2H-14 and 2H-15) and with anchoring groups (2H-16 and 2H-17) for the further design of hybrid materials. Meanwhile, this methodology is also suitable for the preparation of porphyrins bearing a receptor unit at the periphery of the tetrapyrrolic macrocycle (2H-18 and 2H-19). All compounds were unambiguously characterized by NMR, ESI-MS, IR and UV-vis spectra and all data were in agreement with the assigned structures (see ESI).

**Synthesis of water-soluble conjugates of porphyrins.**

Finally, these outcomes were used for the preparation of water-soluble conjugates of porphyrin using peculiar amino acid α-sulfo-β-alanine (β-Ala(SO₃H)) as an effective hydrophilic substituent (Scheme 1, 2H-3). Recently, this sulfonated building block has proven its potential for water solubilizing of a wide range of organic-based fluorophores and organic supramolecular compounds through good to high-yield reactions namely Schotten-Baumann amidification, copper-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC, also named Huisgen-Sharpless-Meldal or "click" reaction) and palladium-catalyzed Sonogashira reaction. To apply this "post-synthetic" sulfonation methodology, an appropriate porphyrin carboxylic acid should be prepared and converted into the reactive N-hydroxysuccinimidyl (NHS) ester prior to amidinolysis by β-Ala(SO₃H) (20).

When carboxylic acid 2H-5e was reacted with peptide coupling reagent O-(N-succinimidyl)-1,1,3,3-tetramethyluronium tetrafluoroborate (TSTU) and DIEA in dry NMP, only imide 2H-21e was obtained according to the intramolecular acylation reaction (Scheme 6). In contrast, carboxylic acids 2H-16b, Zn-16b and Zn-16e bearing the porphyrin moiety covalently bonded through the imidazole linker were quantitatively converted into the corresponding NHS esters 2H-22b and Zn-22b,e (Scheme 6). Thereafter, these crude NHS esters were reacted with tetrabutylammonium (TBA) salt of α-sulfo-β-alanine (20) under anhydrous...
conditions to give water-soluble porphyrins 2H-3b, Zn-3b and Zn-3e (Scheme 6). This post-synthetic derivatization was performed in organic media both to minimize the premature hydrolysis and to suppress the precipitation of the involved active NHS ester of porphyrins, frequently encountered using standard Schotten–Baumann aqueous conditions. RP-HPLC purification using aqueous triethylammonium bicarbonate (TEAB) buffer and acetonitrile as eluents, followed by lyophilisation provided 2H-3b, Zn-3b and Zn-3e in a pure form (isolated yields were about 50%).

Free base conjugate 2H-3b and Zn complexes Zn-3b,e were soluble in water and related aqueous buffers in a concentration range (1.0 µM to 1.0 mM) suitable for biological labeling applications. The photophysical properties of fluorophore Zn-3b were evaluated in acetonitrile and under simulated physiological conditions (PBS, i.e., phosphate buffered saline, 100 mM phosphate + 150 mM NaCl, pH 7.5). Being excited at 427 nm, this fluorophore exhibits in acetonitrile a low red fluorescence emission (602 and 657 nm) with a 2.5% quantum yield. However, Zn-3b is non-emissive under physiological conditions that can be explained by the aggregation of porphyrin in aqueous media. Further optimization of the structural parameters of this long-wavelength fluorophore is needed for its use in physiological medium.

Conclusion

Synthetic approaches to functionalized porphyrins and porphyrin conjugates from meso-tetraarylporphyrins through the acylation and the oxidation of β-aminoporphyrrins were investigated. A series of meso-tetraarylporphyrin conjugates bearing water-soluble moieties, anchoring groups and receptor subunits was prepared by use of two steps methodology consisting of their oxidation to 2,3-dioxochlorins followed by Debus-Radziszewski condensation of these diones with aromatic aldehydes in the presence of AMAC. The experimental parameters influencing the outcome of these reactions were briefly investigated and valuable procedures tolerating the variation of the substitution pattern of β-aminoporphyrrins and aldehydes were developed. The reported results demonstrate mildness and usefulness of this methodology for the preparation of modular β-substituted meso-tetraarylporphyrins required in optics, sensing, biomedicine and material chemistry. In very successful ongoing work in our laboratory, the meso-tetraarylporphyrins equipped with anchoring groups, 2H-16 and 2H-17, are being used in the development of hybrid organic-inorganic catalysts for oxidation reactions. These studies will be reported soon.
Experimental

Materials and instruments

Unless otherwise noted, all chemicals and starting materials were obtained commercially from Acros® or Aldrich® and used without further purification. The starting free-base porphyrins, 5,10,15,20-tetratolylporphyrin (2H-1a), 5,10,15,20-tetramesitylporphyrin (2H-1b), 5,10,15,20-tetrakis(4-bromophenyl)porphyrin (2H-1c), 5,10,15,20-tetakis(4-methylcarboxyphenyl)porphyrin (2H-1d), 5,10,15,20-tetrakis(4-diethoxyphosphorylphenyl)porphyrin (2H-1e), and 5,10,15,20-tetrakis(4-formylphenyl)porphyrin (2H-1f) were prepared according to published procedures. [5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin]nickel (Ni-1g) was prepared according to the literature procedure. 4’-(Formylphenyl)-2,2′:5′,2″-terpyridine was prepared from 4’-(4-methylphenyl)-2,2′:5′,2″-terpyridine according to the literature procedure. 4’-Formylbenzo-15-crown-5 was prepared according to the literature procedure. Phosphate buffered saline (PBS, 100 mM phosphate + 150 mM NaCl, pH 7.5) and aqueous mobile-phases for HPLC were prepared using TEA and CO\(_3\) bicarbonate (TEAB, 1.0 M) buffer was prepared from distilled water purified with a PURELAB Ultra system from ELGA (purified to 18.2 MΩ cm). Peptide synthesis grade DIEA was used without further purification. The starting free-base porphyrins, were obtained commercially from Acros® or Aldrich® and used as such.

Materials and instruments

Fluorescence quantum yield of Zn-3b was measured at 25 °C by a relative method using Ru(bpy)\(_3\)Cl\(_2\) (Φ = 4.2% in water) as a standard. The following equation was used to determine the relative fluorescence quantum yield:

\[
\phi_F = \frac{\phi_F^0 \cdot A^2 \cdot n^2}{\phi_S \cdot A \cdot n_S^2}
\]

where A is the absorbance (in the range of 0.01-0.1 a.u.), F is the area under the emission curve, n is the refractive index of the solvent (at 25 °C) measured in ultraviolet, and the subscript s represents the standard. The following refractive index value is used: 1.333 for water and 1.341 for CH\(_2\)CN.

Several chromatographic systems were used for the purification steps: System A: semi-preparative RP-HPLC (SiliCycle SiliaChrom C\(_18\) column, 10 μm, 20 × 250 mm) with CH\(_2\)CN and aqueous TEAB (50 mM, pH 7.5) as eluents [0% CH\(_2\)CN (5 min), then 20% to 100% CH\(_2\)CN (80 min)] at a flow rate of 20.0 ml/min. Quadruple UV-vis detection was achieved at 220, 260, 430 and 450 nm. System B: system A with the following gradient [20% CH\(_2\)CN (5 min), followed by a gradient of 0% to 100% CH\(_2\)CN (40 min)]. Quadruple UV-vis detection was achieved at 220, 260, 423 and 450 nm. System C: system A with the following gradient [10% CH\(_2\)CN (5 min), followed by a gradient of 10% to 100% CH\(_2\)CN (45 min)]. Quadruple UV-vis detection was achieved at 220, 260, 427 and 450 nm.

Procedure for the synthesis of copper (II) and nickel (II) 2-nitrotetraarylporphyrinates (Cu-4a-f and Ni-4g).

Copper (II) and nickel (II) nitrotetraarylporphyrinates, Cu-4a, Cu-4b, Cu-4c, Cu-4d, Cu-4e, Cu-4f and Ni-4g, were prepared according to a modified literature protocol for similar compounds. Experimental conditions for the preparation of these compounds are summarized in Table S1 (see ESI). The detailed experimental procedures for the preparation of novel compounds are given below.

[2-Nitro-5,10,15,20-tetralolylporphyrinato]copper(II) (Cu-4a)

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5,10,15,20-Tetraplylporphyrin (2H-1a) (335 mg, 0.5 mmol) was dissolved in CHCl₃ (500 mL). Glacial acetic acid (5 mL), acetic anhydride (31 mL), copper nitrate trihydrate (334 mg, 1.38 mmol) were added to the solution. The reaction mixture was stirred at r.t. for 16 h. The progress of the reaction was monitored by TLC. On completion of the nitration reaction, the mixture was cooled and 200 mL of water were added. Acetic acid was neutralized with aqueous sodium carbonate. The organic phase was washed with water (200 mL x 2), dried over sodium sulfate anhydrous. The solvent was removed under reduced pressure. The resulting crude solid was purified by silica gel column chromatography using a hexane/CH₂Cl₂ (7:3) mixture to afford Cu-4a (263 mg, 68%) as a purple solid.

HRMS (ESI+): m/z calcd for [Cu₂H₂Br₂CuN₅O₄]: 1287.25102; found: 1287.25576 [M+Na⁺]. Amax(CHCl₃)/nm (log ε) 425 (5.14), 549 (4.00), 590 (3.81). IR: νmax/cm⁻¹ 3430 (w), 3296 (s), 2957 (m), 2926 (m), 2856 (m), 1720 (s), 1638 (s), 1522 (s, NO₂), 1482 (s), 1374 (m, NO₂), 1338 (s), 1267 (s), 1196 (m), 1162 (w), 1114 (m), 1007 (s), 997 (s), 922 (m), 849 (m), 825 (m), 795 (s), 752 (s), 726 (s), 698 (m).

[2-Nitro-5,10,15,20-tetramethylporphyrinato]copper(II) (Cu-4b)

The compound Cu-4b was obtained from 2H-1b in 90% (400 mg) yield as a purple solid. Spectral data are in agreement with those reported in the literature.²⁴

HRMS (ESI): m/z calcd for [Cu₅H₃₃Cu₅N₅O₅]: 776.20813; found: 776.20905 [M⁺]. Amax(CHCl₃)/nm (log ε) 422 (5.08), 551 (3.86), 593 (3.70). IR: νmax/cm⁻¹ 2956 (m), 2922 (m), 2853 (m), 1722 (s), 1527 (m, NO₂), 1505 (m), 1456 (m), 1377 (m, NO₂), 1339 (m), 1329 (m), 1305 (w), 1266 (s), 1247 (s), 1180 (m), 1114 (s), 1101 (s), 1074 (m), 1019 (m), 998 (s), 967 (s), 923 (m), 873 (w), 845 (m), 822 (m), 796 (s), 751 (m), 729 (s), 688 (m).

[2-Nitro-5,10,15,20-tetramethylporphyrinato]copper(II) (Cu-4c)

5,10,15,20-Tetrasubstituted porphyrins were obtained by refluxing the corresponding porphyrin with acetic anhydride (7 mL), succinic anhydride (5 g, 50.0 mmol) and copper (II) nitrate trihydrate (796 mg, 3.29 mmol) were added to the solution. The reaction mixture was refluxed for 30 min. The reaction progress was monitored by TLC. The reaction mixture was cooled and 200 mL of water were added. Acetic acid was neutralized with aqueous sodium carbonate. The organic phase was washed twice with water (50 mL × 2) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure.

HRMS (ESI+): m/z calcd for [Cu₃H₉Br₂CuN₅O₄]: 1287.25120; found: 1287.25576 [M+Na⁺]. Amax(CHCl₃)/nm (log ε) 425 (5.26), 549 (4.09), 592 (3.97). IR: νmax/cm⁻¹ 3430 (w), 2982 (w), 2906 (w), 1601 (m), 1520 (m, NO₂), 1442 (w), 1390 (m), 1337 (m, NO₂), 1239 (s, P=O), 1161 (m, P=O), 1129 (m), 1098 (w), 1047 (m), 1012 (s), 955 (s, P=O), 794 (s), 764 (s), 717 (s), 584 (s).

[2-Nitro-5,10,15,20-tetraakis(2,6-dichlorophenyl)porphyrinato]copper(II) (Cu-4f)

5,10,15,20-Tetrasubstituted porphyrins were obtained by refluxing the corresponding porphyrin with acetic anhydride (70 mL) and copper nitrate trihydrate (252 mg, 1.04 mmol) was added to the solution. The reaction mixture was heated up to 120 °C and kept at this temperature for 5-10 min. The progress of the reaction was monitored by TLC. The starting compound and the product have the same Rf which restricts TLC control. On the completion of the nitration reaction, the acetylated anhydride was distilled from the reaction mixture under reduced pressure. The residue was dissolved in CHCl₃ and the solution was washed twice with water (100 mL x 2). The organic phase was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The resulting crude solid was purified by silica gel column chromatography using a CH₃Cl₂/MeOH (97:3) mixture to afford Cu-4e (270 mg, 82%) as a purple solid.

HRMS (ESI+): m/z calcd for [Cu₇H₆Br₃CuN₅O₆]: 1287.25120; found: 1287.25576 [M+Na⁺]. Amax(CHCl₃)/nm (log ε) 425 (5.26), 549 (4.09), 592 (3.97). IR: νmax/cm⁻¹ 3430 (w), 2982 (w), 2906 (w), 1601 (m), 1520 (m, NO₂), 1442 (w), 1390 (m), 1337 (m, NO₂), 1239 (s, P=O), 1161 (m, P=O), 1129 (m), 1098 (w), 1047 (m), 1012 (s), 955 (s, P=O), 794 (s), 764 (s), 717 (s), 584 (s).

[2-Nitro-5,10,15,20-tetraakis(2,6-dichlorophenyl)porphyrinato]copper(II) (Cu-4f)

5,10,15,20-Tetrasubstituted porphyrins were obtained by refluxing the corresponding porphyrin with acetic anhydride (70 mL) and copper nitrate trihydrate (252 mg, 1.04 mmol) was added to the solution. The reaction mixture was heated up to 120 °C and kept at this temperature for 5-10 min. The progress of the reaction was monitored by TLC. The starting compound and the product have the same Rf which restricts TLC control. On the completion of the nitration reaction, the acetylated anhydride was distilled from the reaction mixture under reduced pressure. The residue was dissolved in CHCl₃ and the solution was washed twice with water (100 mL x 2). The organic phase was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The
resulting crude solid was purified by silica gel column chromatography using a hexane/CH₂Cl₂ (1:1) mixture to afford Cu-4f (748 mg, 75%) as a purple solid. Spectral data are in agreement with those reported in the literature.²⁷

[5,10,15,20-Tetakis(pentafluorophenyl)porphyrinato]copper(II) (Cu-1g)
5,10,15,20-Tetakis(pentafluorophenyl)porphyrin (2H-1g) (98 mg, 0.1 mmol) was dissolved in CH₂Cl₂ (65 mL). Glacial acetic acid (1.5 mL), succinic anhydride (500 mg, 5.0 mmol) and copper nitrate trihydrate (121 mg, 0.5 mmol) were added to the solution. The reaction mixture was refluxed for the night, washed with water (30 mL × 2) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The resulting crude solid was purified by short silica gel column using a hexane/CH₂Cl₂ (1:1) mixture to afford Cu-1g with quantitative yield (107 mg).

Spectral data are in agreement with those reported in the literature.²⁸

[2-Nitro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato]nickel(II) (Ni-4g)
The porphyrin Ni-1g (670 mg, 0.65 mmol) was dissolved in CH₂Cl₂ (115 mL). Glacial acetic acid (6 mL), succinic anhydride (3.25 g, 32.5 mmol) and copper nitrate trihydrate (787 mg, 3.25 mmol) were added to the solution. The reaction mixture was refluxed for 24 h. The progress of the reaction was monitored by TLC. On the completion of the nitration reaction, the mixture was cooled and 100 mL of water were added. Acetic acid was neutralized with aqueous solution of sodium carbonate. The organic phase was washed with water (100 mL × 2) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The resulting crude solid was purified by silica gel column chromatography using a hexane/CH₂Cl₂ (4:1) mixture to afford Ni-4g (615 mg, 88%) as a purple solid.

δₒ (600 MHz; CDCl₃); 25 °C) -7.27 (2 H, br s, internal NH), 7.84 (2 H, d, J = 8.3 Hz, Br-Ph), 7.74 (2 H, d, J = 8.3 Hz, Br-Ph), 8.02 (2 H, 2d, J = 8.3 Hz, Br-Phortho), 8.03 (2 H, 2d, J = 8.3 Hz, Br-Phortho), 8.05 (2 H, d, J = 8.3 Hz, Br-Phortho), 8.06 (2 H, d, J = 8.3 Hz, Br-Phortho), 8.58 and 8.70 (2 H, AB system, J₉₉ = 4.7 Hz, 12,13-H), 8.87 (1 H, d, J = 4.9 Hz, 17-H), 8.88 and 8.92 (2 H, AB system, J₉₉ = 4.9 Hz, 7,8-H), 8.95 (1 H, d, J = 4.9 Hz, 18-H), 9.01 (1 H, s, 3-H) ppm. HRMS (ESI+): m/z calcd for (Cₑ₉H₁₆Br₂N₉O₄): 971.88145; found: 971.88277

General procedure for the preparation of the free-base 2-nitro-5,10,15,20-tetraarylporphyrins 2H-4a, 2H-4c-e.²⁸

[2-Nitro-5,10,15,20-tetraarylporphyrinato]copper(II) Cu-4 (0.3 mmol) was dissolved in CH₂Cl₂ (110 mL). Concentrated H₂SO₄ (1.3 mL) was added dropwise to the vigorously stirred solution. The progress of reaction was monitored by TLC. On the completion of demetallation (10-30 min), the reaction mixture was washed twice with water (50 mL × 2), saturated solution of sodium carbonate (30 mL) and with water (50 mL) to neutralize sulfuric acid. The organic phase was separated and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure. The resulting crude solid was purified by silica gel column chromatography to afford the appropriate 2-nitro-5,10,15,20-tetraarylporphyrin 2H-4.

2-Nitro-5,10,15,20-tetratolylporphyrin (2H-4a) was obtained in 74% (159 mg) yield as a purple solid. It has already been described. Spectral data are in agreement with those reported in the literature.²⁷

2-Nitro-5,10,15,20-tetramesitylporphyrin (2H-4b) was prepared according to the literature protocol²⁷ and was obtained in 80% (198 mg) yield as a purple solid. Spectral data are in agreement with those reported in the literature.²⁸

2-Nitro-5,10,15,20-tetrakis(4-bromophenyl)porphyrin (2H-4c) was obtained in 88% (257 mg) yield as a purple solid. δₒ (600 MHz; CDCl₃; 25 °C) -7.27 (2 H, br s, internal NH), 7.84 (2 H, d, J = 8.3 Hz, Br-Ph), 7.74 (2 H, d, J = 8.3 Hz, Br-Ph), 8.02 (2 H, 2d, J = 8.3 Hz, Br-Phortho), 8.03 (2 H, 2d, J = 8.3 Hz, Br-Phortho), 8.05 (2 H, d, J = 8.3 Hz, Br-Phortho), 8.06 (2 H, d, J = 8.3 Hz, Br-Phortho), 8.58 and 8.70 (2 H, AB system, J₉₉ = 4.7 Hz, 12,13-H), 8.87 (1 H, d, J = 4.9 Hz, 17-H), 8.88 and 8.92 (2 H, AB system, J₉₉ = 4.9 Hz, 7,8-H), 8.95 (1 H, d, J = 4.9 Hz, 18-H), 9.01 (1 H, s, 3-H) ppm. HRMS (ESI+): m/z calcd for (C₇₆H₅₇Br₂N₉O₄): 1397.84743; found: 1397.84744

2-Nitro-5,10,15,20-tetrakis(4-methylcarboxyphenyl)porphyrin (2H-4d) was obtained in 95% (254 mg) yield as a purple solid. δₒ (600 MHz; CDCl₃; 25 °C) -2.67 (2 H, br s, internal NH), 4.06 (3 H, s, CH₃), 4.10 (6 H, s, CH₃), 4.11 (3 H, s, CH₃), 8.25 (2 H, d, J = 8.0 Hz, MeCO₂-Phortho), 8.26 (2 H, d, J = 8.0 Hz, MeCO₂-Phortho), 8.28 (2 H, d, J = 8.0 Hz, MeCO₂-Phortho), 8.30 (2 H, d, J = 8.0 Hz, MeCO₂-Phortho), 8.32 (8 H, d, J = 8.0 Hz, MeCO₂-Phortho), 8.44 (4 H, d, J = 8.0 Hz, MeCO₂-Phortho), 8.45 (4 H, d, J = 8.0 Hz, MeCO₂-Phortho), 8.47 (2 H, d, J = 8.0 Hz, MeCO₂-Phortho), 8.66 and 8.67 (2 H, AB system, J₉₉ = 4.8 Hz, 12,13-H), 8.85 (1 H, d, J = 5.0 Hz, 17-H), 8.87 and 8.90 (2 H, AB system, J₉₉ = 4.9 Hz, 7,8-H), 8.96 (1 H, d, J = 5.0 Hz, 18-H), 9.00 (1 H, s, 3-H) ppm. HRMS (ESI+): m/z calcd for (C₇₆H₅₇N₉O₁₆): 1342.324; found: 1342.3257 (M+Na⁺)

2-Nitro-5,10,15,20-tetrakis(4-diethoxycarbonylphenyl)porphyrin (2H-4e) was obtained in 88% (318 mg) yield as a purple solid.
δ(500 MHz; CDCl₃; 25 °C) -2.69 (2 H, br s, internal NH), 1.47 (6 H, t, J = 7.2 Hz, CH₃), 1.50 (12 H, t, J = 7.2 Hz, CH₃), 1.51 (6 H, t, J = 7.2 Hz, CH₃), 4.26–4.43 (16 H, m, CH₂), 8.14 (2 H, dd, J₀ = 13.2 Hz, J₁ = 8.1 Hz, (EtO)OP-Ph₅meta), 8.18–8.25 (6 H, m, (EtO)OP-Ph₅meta), 8.28 (2 H, dd, J = 8.1 Hz, J₀ = 4.0 Hz, (EtO)OP-Ph₅ortho), 8.29 (2 H, dd, J = 8.1 Hz, J₀ = 4.0 Hz, (EtO)OP-Ph₅meta), 8.30 (2 H, dd, J = 8.1 Hz, J₀ = 4.0 Hz, (EtO)OP-Ph₅ortho), 8.32 (2 H, dd, J = 8.1 Hz, J₀ = 4.0 Hz, (EtO)OP-Ph₅ortho). 8.66 and 8.67 (2 H, AB system, J = 5.0 Hz, 12.13-Hβ), 8.86 (1 H, d, J = 5.0 Hz, 17-Hδ), 8.87 and 8.89 (2 H, AB system, J = 5.0 Hz, 7.8-Hδ), 8.97 (1 H, s, 3-Hδ), 8.98 (1 H, d, J = 5.0 Hz, 18-Hδ) ppm. δᵦ(102 MHz; CDCl₃; 25 °C) 18.03 (1 P), 18.29 (1 P), 18.36 (2 P) ppm. HRMS (ESI+): m/z calc for [(C₅H₅N₂O₄)P₄]¹⁺: 1204.35512; found: 1204.35785 [M+H]¹⁺, m/z calc for [(C₅H₅N₂O₄)P₄]¹⁻: 1226.33707; found: 1226.33805 [M+Na]⁻. δ₁ₐₓ(27Al(2CHCl₃))/nm (log e) 426 (5.34), 526 (4.14), 599 (3.65), 664 (3.79). IR: νmax/cm⁻¹ 3430 (w), 2981 (m), 2915 (m), 2849 (m), 1735 (m), 1601 (m), 1569 (w), 1439 (w), 1233 (s), 1161 (m), 1129 (m), 1094 (w), 1046 (m), 1010 (s), 962 (s), 793 (s), 759 (s), 717 (s), 698 (s), 578 (s), 543 (s).

2-Nitro-5,10,15,20-tetakis(2,6-dichlorophenyl)porphyrin (2H-4f) was prepared according to the literature protocol.27 This compound was obtained from Cu-4f (200 mg, 0.2 mmol) in 75% (141 mg) yield as a purple solid. δ(600 MHz; CDCl₃; 25 °C) -2.48 (2 H, br s, internal NH), 7.67 (1 H, t, J = 8.5 Hz, Cl₈Ph₅para), 7.70 (2 H, t, J = 8.5 Hz, Cl₈Ph₅para), 7.705 (2 H, d, J = 8.5 Hz, Cl₈Ph₅meta), 7.71 (1 H, t, J = 8.5 Hz, Cl₈Ph₅para), 7.78 (6 H, d, J = 8.5 Hz, Cl₈Ph₅meta), 8.53 and 8.54 (2 H, AB system, J₀ = 4.6 Hz, 12.13-Hβ), 8.70 (1 H, AB system, J = 4.9 Hz, 17-Hδ), 8.72 (2 H, 2d, J = 4.9 Hz, 7.8-Hβ), 8.74 (1 H, AB system, J = 4.9 Hz, 18-Hβ), 8.90 (1 H, s, 3-Hδ) ppm. HRMS (ESI+): m/z calc for [(C₅H₅N₂O₄)P₄]¹⁻: 931.92762; found: 931.93118 [M+H]¹⁺, δ₁ₐₓ(27Al(2CHCl₃))/nm 424 (5.42), 523 (4.22), 558 (3.72), 601 (4.03), 656 (3.49). IR: νmax/cm⁻¹ 3337 (w, NH), 2922 (m), 2852 (m), 1723 (m), 1557 (m), 1520 (m, NO₂), 1427 (s), 1359 (m, NO₂), 1337 (m), 1268 (m), 1220 (w), 1191 (m), 1152 (m), 1102 (m), 1018 (w), 994 (m), 981 (m), 963 (m), 919 (w), 881 (m), 846 (m), 829 (m), 802 (s), 784 (s), 774 (s), 714 (s), 641 (m).

2-Nitro-5,10,15,20-tetakis(pentafluorophenyl)porphyrin (2H-4g) was prepared by using the literature protocol for corresponding copper(II) complexes.27 The free-base porphyrin 2H-4g was obtained from Ni-4g (75 mg, 0.07 mmol) in 56% (40 mg) yield as a purple solid. Spectral data are in agreement with those reported in the literature.27

General procedure for the preparation of free-base 2-amino-5,10,15,20-tetraarylporphyrins 2H-2a-g.27

Tin(II) chloride dihydrate SnCl₂·2H₂O (340 mg, 1.5 mmol) and concentrated hydrochloric acid (3.2 mL) were added to a solution of 2H-4 (0.15 mmol) in dichloromethane (26 mL) under N₂ atmosphere in a light shielded flask. The reaction mixture was stirred for 24 h. The reaction was monitored by MALDI spectrometry and stopped when the starting compound was consumed (24-48 h). The reaction mixture was diluted with 20 mL of dichloromethane and aqueous solution of sodium carbonate (5%) was added to neutralize the reaction mixture. The organic phase was separated, washed twice with water (50 mL x 2) and dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure. 2H-2e and 2H-2g were isolated by column chromatography using degassed eluents. Other compounds were oxidized without additional purification.

2-Amino-5,10,15,20-tetakis(4-diethoxyphosphorylphenyl)porphyrin (2H-2e) was obtained from 2H-4e (27 mg, 0.023 mmol) in 56% (15 mg) yield as a purple solid after purification by column chromatography on alumina using degassed CHCl₃. δ(300 MHz; CDCl₃; 25 °C) -2.85 (2 H, very br s, internal NH), 1.49 (24 H, t, J = 7.1 Hz, CH₃), 4.29–4.44 (16 H, m, CH₂), 7.68 (1 H, s, 3-Hδ), 8.12–8.31 (16 H, m, (EtO)OP-Ph), 8.41 (1 H, d, J = 4.9 Hz, 18-Hδ), 8.63 (1 H, d, J = 4.9 Hz, 7.8-Hδ), 8.66 (1 H, d, J = 4.9 Hz, 17-Hδ), 8.72 (1 H, d, J = 4.9 Hz, 8-Hδ), 8.74 (2 H, AB system, 12.13-Hβ) ppm. NH₂ protons are not observed. δ₁ₐₓ(121 MHz; CDCl₃; 25 °C) 17.88 (1 P), 18.87 (1 P), 18.98 (1 P) ppm. HRMS (ESI+): m/z calc for [(C₅H₅N₂O₄)P₄]⁻: 1174.38094; found: 1174.38164 [M+H]⁺, δ₁ₐₓ(27Al(2CHCl₃))/nm (log e) 403 (5.26), 524 (3.98), 593 (3.64), 652 (3.62) 672 (3.13). IR: νmax/cm⁻¹ 3460 (w, NH), 3312 (w, NH), 2979 (m), 2905 (m), 1632 (w), 1599 (m), 1538 (m), 1453 (m), 1390 (m), 1238 (s, P=O), 1162 (m), 1128 (s, P=O), 1095 (w), 1047 (m), 1013 (s, P-O), 965 (s), 788 (s), 765 (s), 717 (s), 579 (s).
mg, 74%) as a purple solid and **2H-6e** (7 mg, 16%) as a brown solid.

**2H-5e** \( \delta_{\beta}(300 \text{ MHz}; \text{CDCl}_3; 25 ^\circ \text{C}) -2.89 \) (2 H, br s, internal NH), 1.49 (24 H, t, \( J = 6.9 \text{ Hz} \), \( \text{CH}_2 \)), 2.27-2.34 (2 H, m, \( \text{CH}_2 \)), 2.65-2.73 (2 H, m, \( \text{CH}_2 \)), 4.27-4.45 (16 H, m, \( \text{O}-\text{CH}_2 \)), 7.62 (1 H, s, 
\( \text{NH} \)), 8.10-8.37 (16 H, m, \( \text{EtO}_2\text{OPh} \)), 8.57 (1 H, d, \( J = 4.9 \text{ Hz} \), 
\( \text{H}_{2a} \)), 8.70 (1 H, d, \( J = 4.9 \text{ Hz} \), 
\( \text{H}_{2b} \)), 8.73(2 H, s, \( \text{H}_{2f} \)), 8.75-8.82 (2 H, 
\( J = 5.0 \text{ Hz} \)), 9.21 (1 H, s, 3-H) ppm. \( \delta_{1211 \text{ MHz}; \text{CDCl}_3; 25 ^\circ \text{C}} \): 17.48 (1 P), 18.65 (2 P), 18.67 (1 P) ppm. HRMS (ESI+): \( m/z \) calc for \( \text{C}_{24}\text{H}_{27} \text{N}_2 \text{Os}_5 \text{P}_4 \): 1274.3699; found: 1274.36907 [M+H]^+; \( m/z \) calc for \( \text{C}_{24}\text{H}_{27} \text{N}_2 \text{Os}_5 \text{P}_4 \): 1296.37893; found: 1296.37956 [M+Na]^+. \( \lambda_{\max} \text{(CHCl}_3) / \text{nm (log e)} \) 423 (5.43), 519 (4.32), 550 (3.86), 593 (3.83), 648 (3.40). IR: \( \nu_{\text{max}} / \text{cm}^{-1} \): 3422 (w, NH), 3323 (w, NH), 2979 (m), 2929 (m), 2905 (m), 1723 (s, C=O), 1704 (s, amide I), 1599 (s, amide II), 1509 (s), 1475 (m), 1442 (m), 1389 (s), 1367 (m), 1235 (s, P=O), 1161 (s, P=O), 1127 (s), 1097 (m), 1047 (s), 1012 (s), 955 (s, P=O), 789 (s), 764 (s), 718 (s), 579 (s).

**General procedure for the preparation of 2,3-dioxy-5,10,15,20-tetraarylorchlorins 2H-6a-d,** \( n \)

To the crude 2-aminotetraarylporphyrin **2H-2** silica gel (525 mg) and \( \text{CH}_2\text{Cl}_2 \) (75 mL) were added. The reaction mixture was stirred under irradiation (lamp bulb or Luzchem Ring illuminator) in the open flask for 2 h. The progress of reaction was monitored by TLC. On the completion of oxidation an additional portion (1.5 g) of silica gel was added and the reaction mixture was evaporated under reduced pressure. The residue was loaded on a top of a silica gel column. The product was eluted with hexane/\( \text{CH}_2\text{Cl}_2 \) (3:2) (**2H-6a, 2H-6b, 2H-6c, 2H-6f**) or \( \text{CH}_2\text{Cl}_2 \)/methanol (99:0.2) mixtures (**2H-6d**). The yield of **2H-6** was calculated using to the amount of **2H-4** isolated in the reduction (total yield for two steps).

**2,3-Dioxy-5,10,15,20-tetratolylchlorin 2H-6a** was obtained as a brown solid in 60% (64 mg) yield from the crude **2H-2a** prepared from **2H-4a** (109 mg, 15 mmol).

**2,3-Dioxy-5,10,15,20-tetratolylchlorin 2H-6b** was obtained as a brown solid in 60% (64 mg) yield from the crude **2H-2b** prepared from **2H-4b** (380 mg, 0.46 mmol).

**2,3-Dioxy-5,10,15,20-tetramesitylchlorin 2H-6c** was obtained as a brown solid in 80% (300 mg) yield from the crude **2H-2f** prepared from **2H-4f** (139 mg, 0.15 mmol).

**2,3-Dioxy-5,10,15,20-tetrafluorohydrochlorin 2H-6f** was obtained as a brown solid in 66% (90 mg) yield from the crude **2H-2f** prepared from **2H-4f** (139 mg, 0.15 mmol).
The photooxidation of 2-aminoporphyrin 2H-2e according to this procedure yields a complex mixture of products in which target 2,3-dioxochlorin 2H-6e is presented in low ratio according to MALDI-TOF analysis. Our attempts of its isolation by column chromatography on silica or alumina were unsuccessful. An effective procedure is given below.

A solution of Dess-Martin periodinane (55 µL of 0.3 M solution in CH₂Cl₂, 0.0166 mmol) was added to a solution of porphyrin 2H-2e (15 mg, 0.0128 mmol) in degassed CH₂Cl₂ (3 mL) under N₂ atmosphere. The reaction mixture was stirred at r.t. when monitored by MALDI spectrometry. After 2 h the reaction mixture was diluted with CH₂Cl₂ (15 mL). The reaction mixture was treated with 10 mL of 1M HCl and stirred for 20 min. The organic layer was separated, washed with aqueous solution of sodium carbonate (10 mL x 2) and water (10 mL), and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on alumina using a CH₂Cl₂/MeOH (99:1) mixture as eluent. The product 2H-6e (15 mg, 99%) was obtained as a brown solid.

δ₁(300 MHz; CDCl₃; 25 °C) -2.12 (2 H, br s, internal NH), 1.47 (12 H, t, J = 7.1 Hz, CH₃), 1.49 (12 H, t, J = 7.1 Hz, CH₃), 4.25-4.43 (16 H, m, CH₂), 7.99 (4 H, dd, J = 8.3 Hz, JAB= 4.1 Hz, (EtO)₂OP-ortho), 8.09-8.23 (12 H, m, 4 H (EtO)₂OP-Phortho and 8 H (EtO)₂OP-Phmeta), 8.51 (2 H, s, 12,13-H₂β), 8.56-8.60 (2 H, br d, J = 5.0 Hz, 8,17-H₂β), 8.71-8.75 (2 H, br d, J = 5.0 Hz, 7,18-H₂β) ppm. δ₁(C121 MHz; CDCl₃; 25 °C) 18.26 (2 P), 18.75 (2 P) ppm. HRMS (ESI+): m/z calcd for (CₙH₂₆N₄O₈P₂)⁺: 1121.3267; found: 1121.3239 [M+Na]⁺. λₘₐₓ(CHCl₃)/nm (log ε) 404 (5.18), 524 (3.98), 562 (3.92), 600 (3.84), 652 (3.88). IR: νmax/cm⁻¹ 3348 (w, NH), 2923 (m), 2853 (m), 2849 (m), 1734 (m), 1657 (w), 1632 (w), 1602 (w), 1456 (w), 1258 (m), 1017 (s), 971 (s), 796 (s), 580 (s), 558 (s).

Procedure for the preparation of 2-oxa-3-oxo-5,10,15,20-tetrakis(4-dioxygenophosphoryl)chlorin (2H-7e).

Silica gel (57 mg) was added to a solution of 2-aminoporphyrin 2H-2e (15 mg, 0.0128 mmol) in CH₂Cl₂ (15 mL). The reaction mixture was stirred under irradiation (Luzchem Ring Illuminator) in the open flask and monitored by MALDI-TOF spectrometry. After 2 h of the irradiation no more starting material was observed and the lamp was switched off. The reaction mixture was stirred for 8 h before an additional portion (1.5 g) of silica gel was added and the reaction mixture was evaporated under reduced pressure to dryness. The residue was loaded on a top of an alumina column. The product was eluted with a CHCl₃/MeOH (50:1) mixture as a rose-violet solid. Yield 33% (5 mg).

δ₁(500 MHz; CDCl₃; 25 °C) 1.24 (6 H, t, J = 7.1 Hz, CH₃), 1.25 (6 H, t, J = 7.1 Hz, CH₃), 1.27 (12 H, t, J = 7.1 Hz, CH₃), 4.06-4.16 (16 H, m, CH₃), 7.85-7.98 (10 H, m, (EtO)₂OP-Ph), 8.00-8.06 (6 H, m, (EtO)₂OP-Ph), 8.25 (1 H, d, J = 4.7 Hz, H₃β), 8.31 (1 H, d, J = 4.7 Hz, H₈β), 8.34 (1 H, d, J = 4.7 Hz, H₂β), 8.47 (1 H, d, J = 4.7 Hz, H₄β), 8.55 and 8.59 (2 H, AB system, J = 4.4 Hz, H₉α) ppm. NH protons are not observed. δ₁(202 MHz; CDCl₃; 25 °C) 18.76 (1 P), 18.81 (1 P), 19.22 (1 P) ppm. HRMS (ESI+): m/z calcd for (C₉H₈N₄O₈P₂)⁺: 1177.34422; found: 1177.34304 [M+H]⁺; m/z calcd for (C₉H₈N₄O₈P₂)⁺: 1199.32617; found: 1199.32381 [M+Na⁺]. λₘₐₓ(CHCl₃)/nm (log ε) 281 (3.62), 419 (4.89), 520 (3.51), 558 (3.51), 590 (3.29), 644 (3.08). IR: νmax/cm⁻¹ 3337 (w, NH), 2980 (m), 2930 (m), 1772 (s, CH=O), 1726 (m, C=O), 1602 (m), 1564 (m), 1452 (m), 1391 (m), 1367 (w), 1240 (s, P=O), 1189 (w), 1162 (m, P=O), 1129 (s), 1097 (w), 1048 (m), 1016 (s, P=O), 955 (s), 793 (s), 765 (s), 716 (s), 578 (s).

General procedure for the preparation of imidazoporphyrins 2H-14-19.

2,3-Dioxy-5,10,15,20-taetaarylchlorin 2H-6 (0.1 mmol) was dissolved in chloroform (20 mL). Aldehyde 8-13 (0.5 mmol), ammonium acetate (770 mg, 10 mmol) and trifluoroacetic acid (200 µL) were added to this solution. The reaction mixture was stirred at reflux and monitored by TLC. On the completion of the condensation (3-7 h), the reaction mixture was washed with water (20 mL x 2). The organic phase was separated and dried over anhydrous sodium sulfate. The solution was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using a hexane/CH₂Cl₂ (1:1) or CH₂Cl₂/MeOH (99:1) mixture to afford imidazoporphyrins 2H-14-19.

2-(4-Bromophenyl)-1H-imidazo[4,5-b]5,10,15,20-tetraarylporphyrin (2H-14a) was obtained from 2,3-dioxo-5,10,15,20-tetraarylchlorin (2H-6a) and 4-bromobenzoic acid (8) in 90 % (78 mg) yield.

δ₁(300 MHz; CDCl₃; 25 °C) -2.92 (2 H, br s, internal NH), 2.70 (6 H, s, CH₃), 2.75 (3 H, s, CH₃), 2.81 (3 H, s, CH₃), 7.55 (4 H, br d, J = 7.8 Hz, Tol-meta), 7.59 (4 H, br d, Br-Ph), 7.61 (2 H, d, J = 7.8 Hz, Tol-meta), 7.73 (2 H, d, J = 7.8 Hz, Tol-meta), 8.10 (4 H, d, J = 7.8 Hz, Tol-meta), 8.14 (2 H, d, J = 7.8 Hz, Tol-meta), 8.15 (2 H, d, J = 7.8 Hz, Tol-meta), 8.54 (1 H, br s, imidazole NH), 8.79 (2 H, s, H₈β), 8.90 (1 H, d, J = 4.8 Hz, H₉α), 8.93 and 8.96 (2 H, AB system, JAB = 4.8 Hz, H₉β), 8.96 (1 H, d, J = 4.8 Hz, H₁₀β) ppm. HRMS (ESI+): m/z calcd for (C₉H₈BrN₄)⁺: 865.26488; found: 865.26391 [M+H]⁺. λₘₐₓ(CHCl₃)/nm (log ε) 421 (5.25), 518 (4.15), 552 (3.83), 588 (3.77), 647 (3.25). IR: νmax/cm⁻¹ 3437 (w, NH), 3330 (w, NH), 2923 (m), 2852 (m), 2603 (m), 2497 (m), 1722 (m), 1471 (m), 1456 (m), 1398 (m), 1381 (m), 1267 (s), 1247 (m), 1181 (m), 1172 (m), 1163 (m), 1102 (m), 1072 (m), 1037 (m), 1019 (m), 1010 (m), 995 (w), 979 (m), 965 (m), 905 (w), 852 (m), 831 (m), 800 (s), 753 (s), 730 (s).
2-(4-Bromophenyl)-1H-imidazo[4,5-b]-5,10,15,20-tetramethylporphyrin (2H-14b) was obtained from 2,3-dioxo-5,10,15,20-tetramethylchlorin (2H-6b) and 4-bromobenzaldehyde (8) in 64% (62 mg) yield. 

δ (300 MHz; CDCl3; 25 °C) -2.70 (2 H, br s, internal NH), 1.84 (6 H, s, CH3), 1.85 (6 H, s, CH3), 1.86 (6 H, s, CH3), 1.87 (6 H, s, CH3), 2.62 (6 H, s, CH3), 2.67 (3 H, s, CH3), 2.74 (3 H, s, CH3), 2.72 (4 H, br s, Mes), 7.32 (2 H, br s, Mes), 7.48 (2 H, br s, Mes), 7.59 and 7.61 (4 H, AB system, JAB = 8.4 Hz, Br-Ph), 8.29 (1 H, br s, imidazole NH), 8.58 (2 H, s, HBrN), 8.79 (1 H, t, J = 7.9 Hz, Tol), 8.77 to 8.87 (2 H, m, 7,18-Hβ) ppm. HRMS (ESI+): m/z calcd for [C55H32BrN4O8]⁺: 1014.2240; found: 1014.2240 [M+H]⁺. λmax(CHCl3)/nm (log ε) 281 (4.30), 419 (5.44), 516 (4.25), 548 (3.75), 587 (3.82), 645 (3.24). IR: ν(νmax)/cm⁻¹: 3437 (w, NH), 3330 (w, NH), 2923 (m), 2852 (m), 2603 (m), 2497 (m), 1724 (m), 1611 (m), 1566 (m), 1555 (m), 1471 (m), 1454 (m), 1408 (m), 1377 (m), 1346 (m), 1269 (m), 1242 (m), 1214 (m), 1169 (m), 1149 (m), 1103 (m), 1074 (m), 1032 (w), 1010 (m), 996 (m), 969 (m), 947 (m), 908 (w), 881 (w), 851 (m), 827 (m), 800 (s), 775 (w), 754 (s), 729 (s), 664 (m).

2-(4-Bromophenyl)-1H-imidazo[4,5-b]-5,10,15,20-tetrakis(4-methylcarboxyphenyl)porphyrin (2H-14d) was obtained from 2,3-dioxo-5,10,15,20-tetramethylchlorin (2H-6d) (50 mg, 0.057 mmol) and 4-bromobenzaldehyde (8) in 69% (41 mg) yield.

δ (600 MHz; CDCl3; 25 °C) -2.95 (2 H, br s, internal NH), 4.10 (6 H, s, CH3), 4.13 (3 H, s, CH3), 4.17 (3 H, s, CH3), 7.53 and 7.59 (4 H, AB system, JAB = 8.4 Hz, Br-Ph), 2.88 (4 H, AB system, JAB = 8.3 Hz, MeCO2-Ph), 8.33 (2 H, d, J = 7.9 Hz, MeCO2-Ph), 8.36 (2 H, d, J = 7.9 Hz, MeCO2-Ph), 8.43 (4 H, AB system, JAB = 8.3 Hz, MeCO2-Ph), 8.49 (2 H, d, J = 7.9 Hz, MeCO2-Ph), 8.60 (3 H, br d, J = 7.9 Hz, imidazole NH and MeCO2-Ph), 8.73 (2 H, s, 12,13-Hα), 8.81 (1 H, d, J = 4.8 Hz, 7-Hα), 8.88 (2 H, br s, Hα), 8.90 (1 H, d, J = 4.8 Hz, 7-Hα) ppm. HRMS (ESI+): m/z calcd for [C57H36BrN4O8]⁺: 1041.2240; found: 1041.2240 [M+H]⁺. λmax(CHCl3)/nm (log ε) 291 (4.48), 421 (5.51), 517 (4.33), 550 (3.90), 588 (3.90), 645 (3.39). IR: ν(νmax)/cm⁻¹: 3347 (w, NH), 2925 (m), 2852 (m), 2603 (m), 2497 (m), 1724 (m), 1611 (m), 1566 (m), 1555 (m), 1471 (m), 1454 (m), 1408 (m), 1377 (m), 1346 (m), 1269 (m), 1242 (m), 1214 (m), 1169 (m), 1149 (m), 1103 (m), 1074 (m), 1032 (w), 1010 (m), 996 (m), 969 (m), 947 (m), 908 (w), 881 (w), 851 (m), 827 (m), 800 (s), 775 (w), 754 (s), 729 (s), 664 (m).

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2-(4-Carboxyphenyl)-1H-imidazo[4,5-b]-5,10,15,20-tetrakis(4-diethoxyphosphoryl)porphyrin (2H-16e) was obtained from 2,3-dioxo-5,10,15,20-tetrakis(4-diethoxyphosphoryl)chlorin (2H-6e) (34 mg, 0.029 mmol) and 4-carboxybenzaldehyde (307 mg) in 19% (19 mg) yield. δH (300 MHz; CDCl3; 25 °C) -2.97 (2 H, br s, internal NH), 1.46–1.56 (24 H, m, CH2), 4.30–4.46 (16 H, m, CH2), 7.66 (2 H, d, J = 7.7 Hz, HO2C–Ph), 8.04 (2 H, d, J = 7.7 Hz, HO2C–Ph), 8.22 (6 H, dd, Jd = 12.9 Hz, J = 7.8 Hz, (EtO)2OP–Phmeta), 8.27–8.43 (10 H, m, 2H (EtO)2OP–Phmeta and 8H (EtO)2OP–Phortho), 8.73 (2 H, s, 12,13-Hβ), 8.92 (4 H, br s, 7,8,17,18-Hα) ppm. δ12(CDCl3; 25 °C) 17.95 (1 P), 18.73 (2 P), 19.62 (1 P) ppm. HRMS (ESI+): m/z calc for (C40H20N2O4P4)4+: 1319.3972; found: 1319.3972, [M+H]4+; m/z calc for (C40H20N2O4P4)2+: 1341.3972; found: 1341.39705 [M+Na]4+. λmax(CHCl3)/nm (log e) 421 (3.55), 517 (4.20), 549 (3.82), 645 (3.41). IR: 4νmax/cm−1 3418 (w, NH), 3323 (w, NH), 2956 (m), 2924 (m), 2852 (m), 1716 (m), 1699 (m, CO2), 1601 (m), 1456 (m), 1393 (m), 1246 (m, P=O), 1165 (m, P=O), 1129 (m), 1100 (m), 1049 (s), 1018 (s), 991 (s, P=O), 794 (m), 759 (m), 730 (m), 667 (w).

2-(4-Diethoxyphosphoryl)porphyrin 2H-17b was obtained from 2,3-dioxo-5,10,15,20-tetramethylsulfonylporphyrin (2H-17a) (292 mg, 0.36 mmol) and 4-carboxybenzaldehyde (307 mg) in 71% (246 mg) yield. δH (300 MHz; CDCl3; 25 °C) -2.69 (2 H, br s, internal NH), 1.83 (6 H, s, CH2ortho), 1.85 (12 H, s, CH2ortho), 1.86 (6 H, s, CH2ortho), 2.61 (6 H, s, CH2para), 2.67 (3 H, s, CH2para), 2.75 (3 H, s, CH2para), 4.04–4.25 (4 H, m, CH2), 7.26 (4 H, br s, Mes), 7.32 (2 H, s, Mes), 7.48 (2 H, s, Mes), 7.78 (2 H, dd, Jd = 8.3 Hz, J = 3.8 Hz, (EtO)2OP–Phortho), 7.90 (2 H, dd, Jd = 12.7 Hz, J = 8.3 Hz, (EtO)2OP–Phmeta), 8.36 (1 H, br s, imidazole NH), 8.57 (2 H, s, 12,13-Hα), 8.72 and 8.78 (2 H, AB system, Jd = 4.8 Hz), 17.18–18.93, 8.84 and 8.87 (2 H, AB system, Jd = 4.8 Hz, 8.72–9.93 ppm. δ12(CDCl3; 25 °C) 18.31 (1 P, s) ppm. HRMS (ESI+): m/z calc for (C40H20N2O4P4)2+: 1035.50850; found: 1035.50934 [M+H]+. λmax(CHCl3)/nm (log e) 421 (3.55), 517 (4.22), 548 (3.75), 587 (3.77), 647 (3.24). IR: νmax/cm−1 3418 (w, NH), 3323 (w, NH), 2957 (m), 2925 (m), 2859 (m), 1720 (s), 1606 (w), 1506 (w), 1458 (m), 1408 (m), 1379 (m), 1265 (s), 1247 (s, P=O), 1171 (m, P=O), 1115 (s), 1101 (s), 1019 (m), 969 (m, P=O), 874 (m), 801 (m), 729 (m).

Imidazo[4,5-b]porphyrin 2H-19a was obtained from 2,3-dioxo-5,10,15,20-tetramethoxycarbonylporphyrin (2H-6a) (70 mg, 0.01 mmol) and 4'-formylbenzo-15-crown-5 (13) in 50% (49 mg) yield. δH (300 MHz; CDCl3; 25 °C) -2.90 (2 H, br s, internal NH), 2.70 (6 H, s, CH3), 2.73 (3 H, s, CH3), 2.80 (3 H, s, CH3), 3.77-3.88 (8 H, m, CH3), 3.91–3.97 (2 H, m, CH2), 4.01–4.07 (2 H, m, CH2), 4.16–4.22 (2 H, m, CH2), 4.26–4.32 (2 H, m, CH2), 6.92 (1 H, d, J = 8.2 Hz, Ph), 7.09 (1 H, d, Jd = 8.2, J = 2.0 Hz, Ph), 7.54 (1 H, d, Jd = 2.0 Hz, Ph), 7.55 (4 H, d, J = 7.9 Hz, Tolmeta), 7.62 (2 H, d, J = 8.0 Hz, Tolmeta), 7.72 (2 H, d, J = 8.0 Hz, Tolmeta), 8.11 (4 H, d, J = 7.9 Hz, Tolortho), 8.15 (2 H, d, J = 7.9 Hz, Tolmeta), 8.18 (2 H, d, J = 8.0 Hz, Tolmeta), 8.19 (2 H, d, J = 8.0 Hz, Tolmeta), 8.53 (1 H, br s, imidazole NH), 8.81 (2 H, s, 12,13-Hα), 8.91 and 8.96 (2 H, AB system, Jd = 4.9 Hz, Tolmeta), 8.94 and 9.00 (2 H, AB system, Tolmeta = 4.9 Hz, Tolmeta) ppm. HRMS (ESI+): m/z calc for (C46H36N4O4)2+: 977.43850; found: 977.43951 [M+H]+; m/z calc for (C46H36N4O4)3+: 999.42044; found: 999.41570 [M+Na]+. λmax(CHCl3)/nm (log e) 420 (5.44), 518
Porphyrin carboxylic acids were linked with sulfonation of carboxylic acid 2H-5 and M-16. IR: ν\text{max}/cm\textsuperscript{-1} = 3354 (br, OH), 2977 (s, CH\textsubscript{3}), 1783 (w, C=O), 1650 (s, C=O), 1599 (s, C=O), 1478 (s, C=O), 1415 (w, C=O), 1334 (m, C=O), 1213 (m, C=O), 1173 (m, C=O), 1164 (m, C=O), 1076 (w, CH\textsubscript{3}), 1052 (w, CH\textsubscript{3}), 860 (w, CH\textsubscript{3}), 827 (w, CH\textsubscript{3}), 798 (w, CH\textsubscript{3}), 772 (w, CH\textsubscript{3}), 751 (w, CH\textsubscript{3}), 707 (w, CH\textsubscript{3}), 684 (w, CH\textsubscript{3}).

2-(4-(Carboxyphenyl)-1H-imidazo[4,5-b]-5,10,15,20-tetramethylporphyrinato)zinc (Zn-16b) was prepared by metallation of 2H-16b (86 mg, 0.09 mmol) by Zn(OAc)\textsubscript{2} (5 equiv) in CHCl\textsubscript{3}/MeOH (9:1) in 85% (78 mg) yield. δ\textsubscript{H} (300 MHz; CDCl\textsubscript{3}, 25 °C) 1.84 (12 H, 2, CH\textsubscript{2}tortol), 1.85 (12 H, 2, CH\textsubscript{2}tortol), 2.62 (6 H, s, CH\textsubscript{2}tortol). 2.65–2.80 (6 H, 2 br s, CH\textsubscript{2}tortol). 7.26 (4 H, s, Mes). 7.29–7.38 (2 H, br s, Mes). 7.43-7.53 (2 H, br s, Mes). 7.84 (2 H, d, J = 8.4 Hz, Ph), 8.18 (2 H, d, J = 8.4 Hz, Ph), 8.52 (1 H, br s, imidazole NH), 8.69 (2 H, s, 12,13-H\textsubscript{N}), 9.50 (3.89, 2 H, s, 12,13-H\textsubscript{N}), 9.64 (2 H, s, 12,13-H\textsubscript{N}), 9.72 (2 H, s, 12,13-H\textsubscript{N}).

HRMS (ESI+): m/z calcd for (C\textsubscript{54}H\textsubscript{49}N\textsubscript{10}O\textsubscript{3}Zn\textsuperscript{2+})\textsuperscript{2+}: 1242.31; found: 1242.30 [M+H\textsuperscript{+}]\textsuperscript{2+}.

Zn-22a: MS (ESI+): m/z calcd for (C\textsubscript{53}H\textsubscript{49}N\textsubscript{10}O\textsubscript{3}Zn\textsuperscript{2+}): 1195.28; found: 1195.32 [M+H\textsuperscript{+}]\textsuperscript{2+}.

2H-21e: Porphyrin carboxylic acid 2H-5e (22 mg, 17 μmol) were also reacted with TSTU under these conditions. However, the target product was not detected because imide Zn-21e was formed in the intramolecular acylation reaction. The reaction mixture was subjected to column chromatography on silica gel using gradual CHCl\textsubscript{3}/MeOH (0-5%) system as an eluent. Yield 42% (9 mg).

δ\textsubscript{H} (300 MHz; CDCl\textsubscript{3}, 25 °C) -2.83 (2 H, br s, internal NH), 1.46–1.54 (24 H, m, CH\textsubscript{2}), 2.86 (4 H, s, CH\textsubscript{2}, CH=CH), 4.27–4.44 (16 H, m, CH\textsubscript{2}), 8.11 (2 H, dd, J\textsubscript{H} = 13.1 Hz, J = 8.1 Hz, (EtO)\textsubscript{2}OP-Ph\textsubscript{meta}), 8.17 (2 H, dd, J\textsubscript{H} = 13.1 Hz, J = 8.1 Hz, (EtO)\textsubscript{2}OP-Ph\textsubscript{meta}), 8.19 (2 H, dd, J\textsubscript{H} = 13.1 Hz, J = 8.1 Hz, (EtO)\textsubscript{2}OP-Ph\textsubscript{meta}), 8.22 (2 H, dd, J\textsubscript{H} = 3.9 Hz, (EtO)\textsubscript{2}OP-Ph\textsubscript{meta}), 8.28 (2 H, dd, J\textsubscript{H} = 3.9 Hz, (EtO)\textsubscript{2}OP-Ph\textsubscript{meta}), 8.31 (4 H, 2dd, J = 8.2 Hz, J\textsubscript{H} = 3.9 Hz, (EtO)\textsubscript{2}OP-Ph\textsubscript{meta}), 8.61 (1 H, s, 3-H), 8.62 (1 H, d, J = 5.0 Hz, 8-H\textsuperscript{a}), 8.71 and 8.72 (2 H, AB system, J\textsubscript{AB} = 4.9 Hz, 17-18-H\textsuperscript{a}), 8.78 (1 H, d, J = 5.0 Hz, 8-H\textsuperscript{a}), 8.85 (2 H, br s, 12,13-H\textsubscript{N}) ppm. δ\textsubscript{C} (121 MHz; CDCl\textsubscript{3}, 25 °C) 17.83 (1 P), 18.52 (1 P), 18.60 (2 P) ppm. HRMS (ESI+): m/z calcd for (C\textsubscript{53}H\textsubscript{49}N\textsubscript{10}O\textsubscript{3}Zn\textsuperscript{2+}): 1195.28; found: 1195.28 [M+H\textsuperscript{+}]\textsuperscript{2+}.

To the solution of TBA salt of β-Ala(SO\textsubscript{3}H) (20) in NMP (600 μL of 0.25 M solution) was added with stirring a solution of DIEA in NMP (40 μL of 2.0 M solution). The resulting solution was cooled up to 4 °C. Then a solution of ester M-22 obtained in the step I was added by portions. The resulting reaction mixture was stirred at 4 °C for 15 min before to be warmed up to r.t. The stirring was continued for 2 h. Then the product M-3 was isolated by preparative RP-HPLC.
Ph$_{ortho}$, 8.29 (1 H, br s, imidazole NH), 8.56 (2 H, s, 12,13-H$_2$), 8.73 and 8.78 (4 H, 2 AB systems, $J = 4.8$ Hz, 7,8,17,18-H$_2$) ppm. HRMS (ESI$^+$): $m/z$ calc'd for (C$_{12}$H$_3$N$_2$O$_5$): 1094.46333; found: 1094.46406 [M$^+$H$^+$$]$; $m/z$ calc'd for (C$_{12}$H$_3$N$_2$NaO$_5$): 1116.44527; found: 1116.44535 [M+Na$^+$$]$.

References


max 20 words
A two steps methodology to prepare a series of meso-tetraarylporphyrin conjugates bearing water-soluble moieties, anchoring groups and receptor subunits.

colour graphic (8 x 4)