NJC

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

New Journal of Chemistry

ARTICLE

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Inna A. Abdulaeva,[a,b] Kirill P. Birin,[b,*] Julien Michalak,[a] Anthony Romieu,[a,c] Christine Stern,[a] Alla Bessmertnykh-Lemeune,[a] Roger Guilard,[a,*] Yulia G. Gorbunova[b,d] and Aslan Yu. Tsivadze[b,d]

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 photodymanic 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 does not contain *meso*-substituents and the utilization of *meso*-substituted porphyrins as "natural" mimics and the optimal structure of the tetrapyrrolic 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, mono-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]

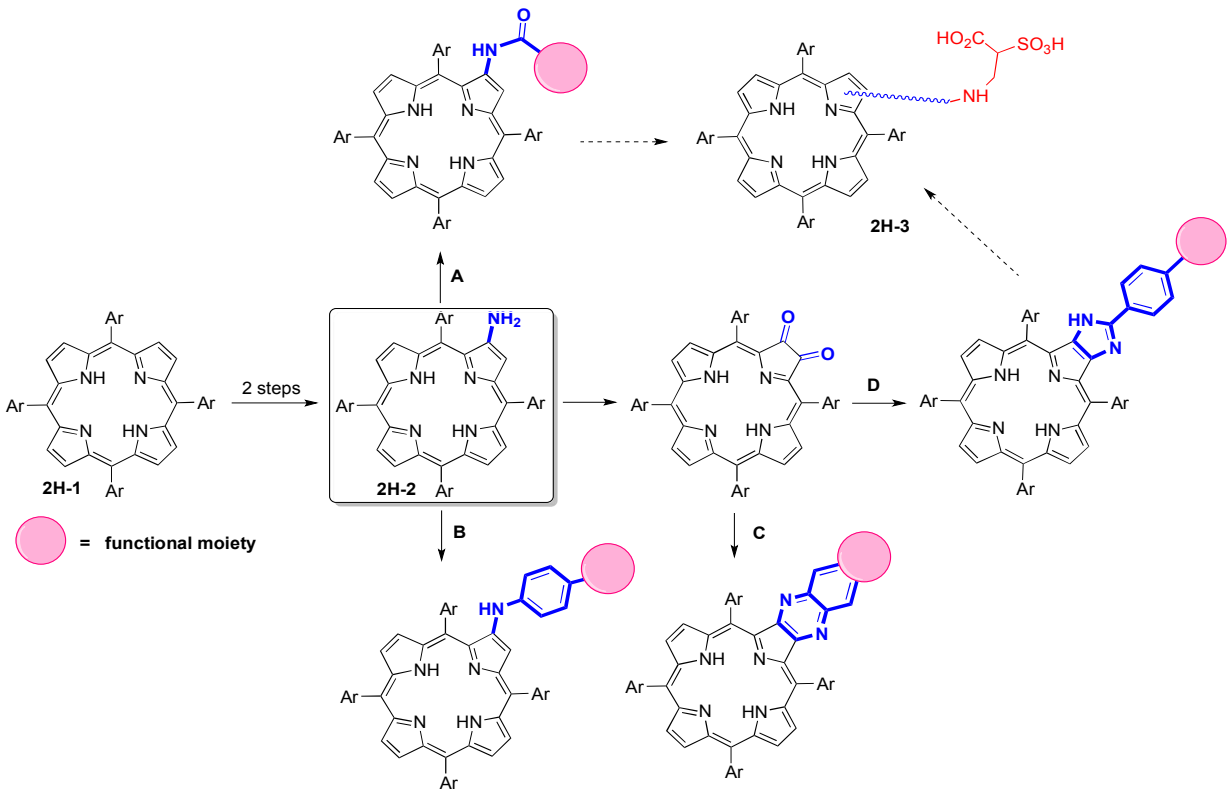
Scheme 1 briefly summarizes different synthetic approaches to modular porphyrins from β-aminoporphyrins **2H-2**. Commonly used acylation reaction (Scheme 1, Path A) does not tolerate many functional groups at the *meso*-aryl substituents because acyl halides are highly reactive towards nucleophilic 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 (H_2SO_4) are needed for the demetallation of these conjugates that may result in their decomposition.

[a] Institut de Chimie Moléculaire de l'Université de Bourgogne, UMR CNRS 6302, Univ. Bourgogne Franche-Comté, 9 Avenue Alain Savary, 21078 Dijon, France.
[b] Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky Pr. 31, Moscow, 119071, Russia.
[c] Institut Universitaire de France, 103, boulevard Saint-Michel, 75005 Paris, France.
[d] Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky Pr. 31-4, Moscow, 119991, Russia.
Electronic Supplementary Information (ESI) available. See
DOI: 10.1039/x0xx00000x

New Journal of Chemistry

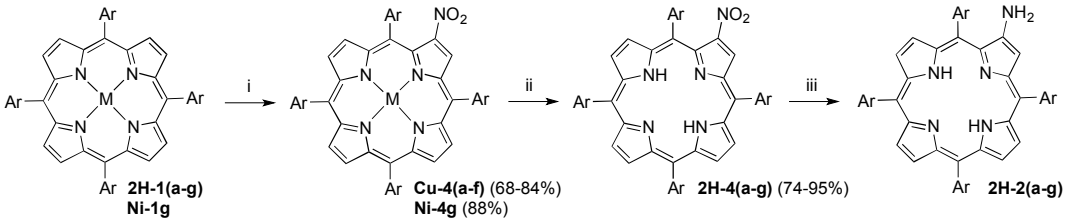
ARTICLE



Scheme 1. Conventional strategies for the β-functionalization of *meso*-tetraarylporphyrins **2H-1** through β-aminoporphyrins **2H-2** (solid arrays) and synthetic approaches to water-soluble porphyrin conjugates **2H-3** (dotted arrays).

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 tetrapyrrolic 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.



Ar = Tol (a), Mes (b), 4-Br-C_6H_4 (c), 4-$MeCO_2$-C_6H_4 (d), 4-$(EtO)_2P(O)$-C_6H_4 (e), 2,6-Cl_2-C_6H_3 (f), C_6F_5 (g)

Scheme 2. Synthesis of β-aminoporphyrins **2H-2a-g**. General conditions and reagents: i. $Cu(NO_3)_2$, acetic or succinic anhydride (see ESI, Table 1); ii. **Cu-4a,c,d,e**: H_2SO_4, CH_2Cl_2, r.t.; **Cu-4b,f** and **Ni-4g**: H_2SO_4/TFA, r.t. or reflux; iii. $SnCl_2{\cdot}2H_2O$, HCl, CH_2Cl_2, r.t.

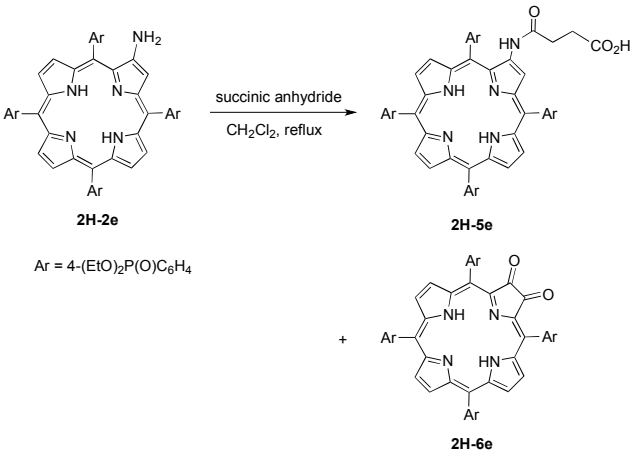
In the context of our ongoing projects in sensing, imaging and material chemistry, we are investigating viable synthetic pathways to functionalized porphyrins and porphyrin conjugates from *meso*-tetraarylporphyrins **2H-1** bearing different substituents at the *meso*-positions *via* β-functionalization 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 tranformations.

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.[19-29] 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.[19] 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-nitroporphyrinates under acidic conditions was also widely studied.[21] Accordingly, demetallation of complexes **Cu-4a,c,d,e** by concentrated sulfuric acid smoothly proceeds in CH_2Cl_2 solution at room temperature whereas H_2SO_4/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 CH_2Cl_2 to give the crude 2-aminoporphyrins **2H-2a-g** (Scheme 2).[32] 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-2a-d,f** should used in the next step without purification and directly after preparation due to their sensitivity to photo-oxidation[53,54] and heating[55,56]. This instability is a key factor limiting their utility for further elaboration of functionalized porphyrins and corresponding conjugates.

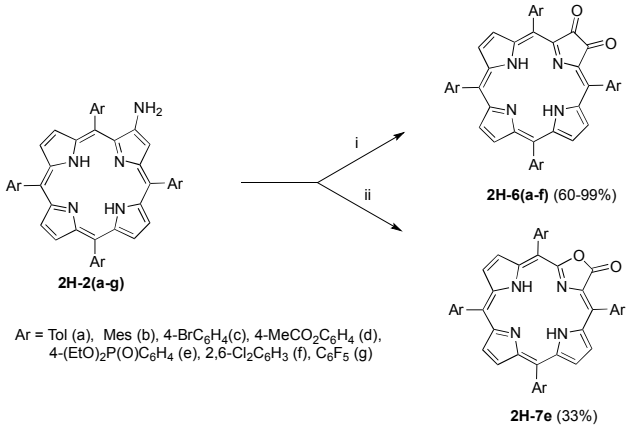


Scheme 3. Acylation of 2-aminoporphyrin **2H-2e**.

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 (K_2CO_3, K_2HPO_4, DIEA) led to inseparable mixtures of starting compound, alkylamines and oxidation products.

In this regard, the photo-oxidation of β-aminoporphyrins to 2,3-dioxochlorins followed by Debus-Radziszewski condensation[45] 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[45] and in later publications.[49,51]



Scheme 4. Photooxidation of β-aminoporphyrins **2H-2a-g**. Reagents and conditions: i. **2H-6a-d,f**: O_2, hv, H_2O, SiO_2, CH_2Cl_2, r.t., 2 h; **2H-2e**: i. a) DMP, CH_2Cl_2, r.t., 1 h; b) aq. HCl, r.t. ii. **2H-2e**: a) O_2, hv, H_2O, SiO_2, CH_2Cl_2, r.t., 2 h; b) stirring, r.t., 12 h.

Our studies demonstrate that the outcome of the photo-oxidation of β-aminoporphyrins **2H-2** by air in the presence of hydrated silica in CH_2Cl_2 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 obtained 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*-diethoxyphosphoryl 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**.[45,57] Indeed, when stirring of the reaction mixture was prolonged for 8 h after switching 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[45] or by the porphyrin-α-dione oxidation with benzeneselenic anhydride.[58] These porpholactones have also been obtained by oxidation of *meso*-tetraaryl-2,3-dihydroxy-chlorins with MnO_4^-.[59]

In agreement with these results, the photo-oxidation by air of electron deficient 2-aminoporphyrin **2H-2g** bearing *meso*-pentafluorophenyl 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 CH_2Cl_2 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)[58] following the two-step procedure reported by Promarak and Burn.[57] 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 CH_2Cl_2 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.

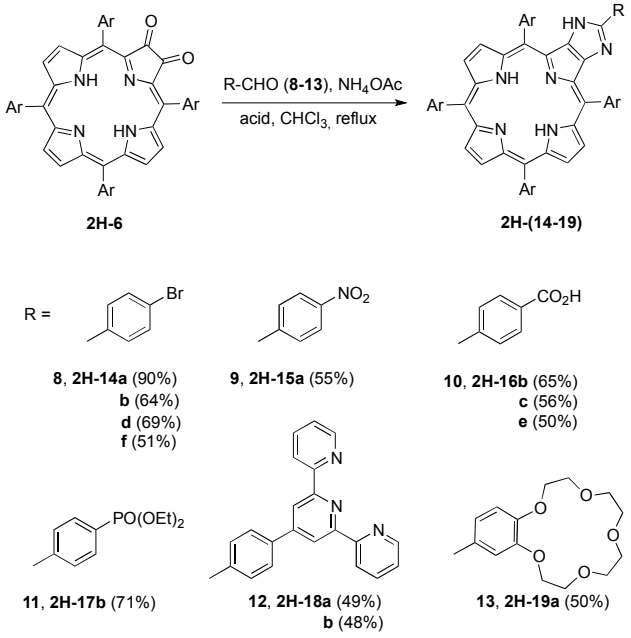
Condensation of porphyrin-α-diones with substituted aromatic aldehydes.

With porphyrin-α-diones in hands, we next investigated the Debus-Radziszewski condensation. In the preliminary experiments the reaction of porphyrin-α-dione **2H-6a** with aldehyde **8** was conducted according to literature procedures[45,49,51] involving stoichiometric ratio of carbonyl compounds in the presence of an excess of AMAC (100 equiv) in $CHCl_3$/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 tolyl derivative **2H-6a** are summarized in Table 1.

Table 1. Synthesis of imidazoporphyrin **2H-14a** by the condensation of 2,3-dioxo-5,10,15,20-tetra(4-tolyl)chlorin (**2H-6a**) and 4-bromobenzaldehyde **8**.

Entry	**8** (equiv)	**Acid** ($CHCl_3$/Acid ratio)	Time (h)	Yield (%)
1	1	AcOH (1:1)	6	25
2	2	AcOH (1:1)	6	25
3	2	AcOH (9:1)	6	60
4	5	AcOH (9:1)	6	86
5	20	AcOH (9:1)	6	90
6	5	TFA (99:1)	3.5	90
7	1	TFA (99:1)	3.5	0
8	2	TFA (99:1)	3.5	0

Reaction conditions: **2H-6a** (0.05 mmol), benzaldehyde **8** and AMAC (100 equiv) were refluxed in 10 mL of $CHCl_3$/acid mixture. TFA = trifluoroacetic acid.



Ar = Tol (a), Mes (b), 4-BrC_6H_4(c), $4MeCO_2C_6H_4$ (d), 4-$(EtO)_2P(O)C_6H_4$ (e), 2,6-$Cl_2C_6H_3$ (f)

Scheme 5. Synthesis of fused porphyrin imidazole systems through Debus-Radziszewski condensation.

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 $CHCl_3$/AcOH ratio. When 9:1 mixture of $CHCl_3$/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 $CHCl_3$/TFA mixture (99:1, v/v) at reflux (Scheme 5). The product yield was found to be dependent on the substituent pattern of both carbonyl 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).

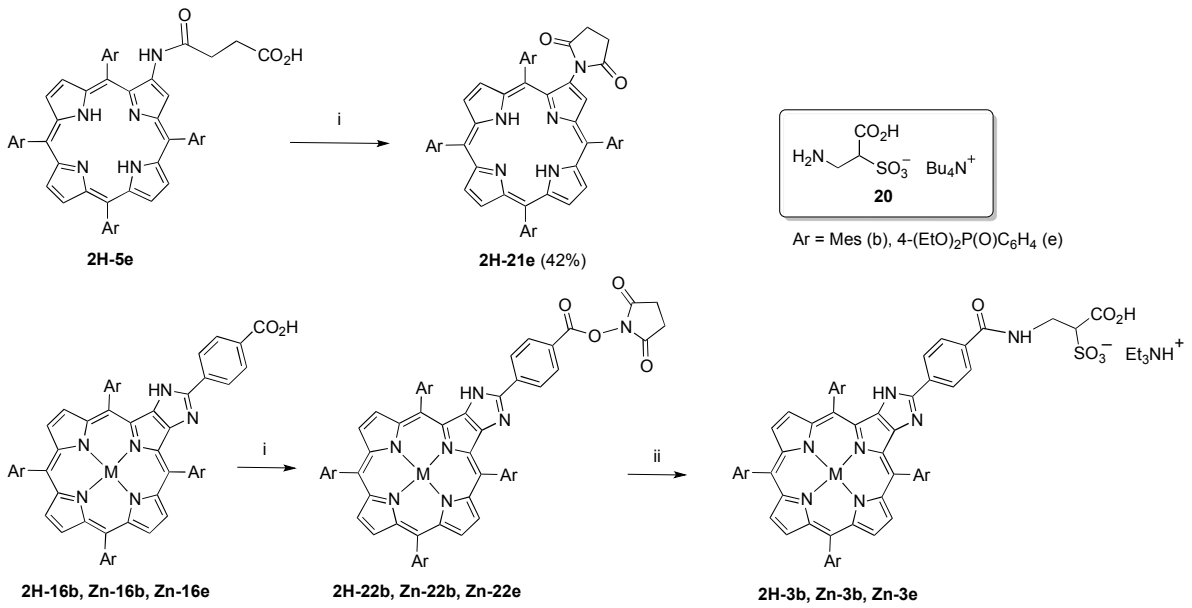
Synthesis of water-soluble conjugates of porphyrins.

Finally, these outcomes were used for the preparation of water-soluble conjugates of porphyrin using peculiar amino acid α-sulfo-β-alanine (β-Ala(SO_3H))[60,61] 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.[61-67] 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 aminolysis by β-Ala(SO_3H) (**20**).

When carboxylic acid **2H-5e** was reacted with peptide coupling uronium reagent *O*-(*N*-succinimidyl)-1,1,3,3-tetramethyluronium tetrafluoroborate (TSTU)[68] 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

New Journal of Chemistry

ARTICLE



Scheme 6. Synthesis of water-soluble porphyrins **2H-3 and Zn-3**. Reagents and conditions: i. TSTU, DIEA, NMP, r.t.; ii. **20**, DIEA, NMP, 4 °C to r.t.

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.[69-71] 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 bio-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-aminoporphyrins 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-aminoporphyrins 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 on-going 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**),[72] 5,10,15,20-tetramesitylporphyrin (**2H-1b**),[73] 5,10,15,20-tetrakis(4-bromophenyl)porphyrin (**2H-1c**),[74] 5,10,15,20-tetrakis(4-methylcarboxyphenyl)porphyrin (**2H-1d**),[75] 5,10,15,20-tetrakis(4-diethoxyphosphorylphenyl) porphyrin (**2H-1e**),[76] 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**2H-1f**),[77] and 5,10,15,20-tetrakis (pentafluorophenyl)porphyrin (**2H-1g**)[78] were prepared according to published procedures. [5,10,15,20-Tetrakis(pentafluorophenyl)porphyrinato]nickel (**Ni-1g**) was prepared according to the literature procedure.[79] 4'-(4-Formylphenyl)-2,2':6',2''-terpyridine was prepared from 4'-(4-methylphenyl)-2,2':6',2''-terpyridine[80] according to the literature procedure.[81] 4'-Formylbenzo-15-crown-5 was prepared according to the literature procedure.[82] Phosphate buffered saline (PBS, 100 mM phosphate + 150 mM NaCl, pH 7.5) and aqueous mobile-phases for HPLC were prepared using water purified with a PURELAB Ultra system from ELGA (purified to 18.2 MΩ cm). Peptide synthesis grade DIEA was provided by Iris Biotech GmbH. Triethylammonium bicarbonate (TEAB, 1.0 M) buffer was prepared from distilled TEA and CO_2 gas. β-Ala(SO_3H) was prepared according to reported procedures.[60,61]

All reactions were performed in air unless otherwise stated. The photooxidation was carried out using a Luzchem Ring Illuminator (Model RING-01, visible light ring, 22 W) or bulb lamb (200 W). Analytical thin-layer chromatography (TLC) was carried out using Merck silica gel 60 plates (precoated sheets, 0.2 mm thick, with fluorescence indicator F254). Column chromatography purification was carried out on silica gel (Silica 60, 63-200 µm, Aldrich) and neutral alumina (Aluminium oxide 90, 63-200 µm, Merck).

NMR spectra were acquired on Bruker Avance III 600 MHz, Bruker Avance III 500 MHz and Bruker Avance III Nanobay 300 MHz spectrometers and referenced to solvent residual protons. UV-visible spectra were obtained on a Varian Cary 50 spectrophotometer and THERMO Scientific Evolution 201 by using a rectangular quartz cell (Hellma, 100-QS, 45 × 12.5 × 12.5 mm, pathlength 10 mm, chamber volume: 3.5 mL). MALDI-TOF mass-spectra were obtained on a Bruker Ultraflex II LRF 2000 mass-spectrometer in positive ion mode unless otherwise stated with dithranol matrix. Low-resolution MS analyses were performed on a Bruker Amazon LS (ion trap) in positive mode unless otherwise stated. Accurate mass measurements (HRMS) were made on a THERMO LTQ Orbitrap XL. Solutions in $CHCl_3$/methanol (1:1) were used for the analysis. IR spectra were registered on FT-IR Nexus (Nicolet) and Bruker Vector 22 spectrophotometers. Micro-ATR accessory (Pike) was used in order to obtain IR spectra of polycrystalline solid complexes. All the spectrometers except THERMO Scientific Evolution 201, Nexus (Nicolet) and Bruker Avance III 600 MHz were available at the "Pôle Chimie Moléculaire", the technological platform for chemical analysis and molecular synthesis (http://www.wpcm.fr) which relies on the Institute of the Molecular Chemistry of University of Burgundy and Welience™, a Burgundy University private subsidiary.

RP-HPLC purifications were performed on a Thermo-Dionex Ultimate 3000 instrument equipped with a RS Variable Detector (four distinct wavelengths). Fluorescence spectroscopic studies (emission/excitation spectra) were performed with an HORIBA Jobin Yvon Fluorolog spectrophotometer (software FluorEssence) with a standard fluorometer cell (Labbox, LB Q, 10 mm). Emission spectra were recorded after excitation at the corresponding wavelength (shutter: Auto Open, excitation slit = 4 nm and emission slit = 4 nm). All fluorescence spectra were corrected.

Fluorescence quantum yield of **Zn-3b** was measured at 25 °C by a relative method using $Ru(bpy)_3Cl_2$ (Φ_F = 4.2% in water) as a standard.[83] The following equation was used to determine the relative fluorescence quantum yield:

$$\phi_F = \phi_F^S \frac{F * A^S * n^2}{F^S * A * n_S^2}$$

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 solvents (at 25 °C) used in measurements, and the subscript s represents the standard. The following refractive index value is used: 1.333 for water and 1.341 for CH_3CN.

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_3CN and aqueous TEAB (50 mM, pH 7.5) as eluents [0% CH_3CN (5 min), followed by a gradient of 0% to 20% CH_3CN (10 min), then 20% to 100% CH_3CN (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_3CN (5 min), followed by a gradient of 20% to 60% CH_3CN (20 min), then 60% to 100% CH_3CN (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_3CN (5 min), followed by a gradient of 10% to 100% CH_3CN (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.[19] 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-tetratolylporphyrinato]copper(II) (Cu-4a)

5,10,15,20-Tetratolylporphyrin (**2H-1a**) (335 mg, 0.5 mmol) was dissolved in $CHCl_3$ (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 twice (200 mL × 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/CH_2Cl_2 (7:3) mixture to afford **Cu-4a** (263 mg, 68%) as a purple solid.

HRMS (ESI): *m/z* calcd for $(C_{48}H_{35}CuN_5O_2)^+$: 776.20813; found: 776.20905 $[M]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 422 (5.08), 551 (3.86), 593 (3.70). IR: ν_{max}/cm^{-1} 2956 (m), 2922 (m), 2853 (m), 1722 (s), 1527 (m, NO_2), 1505 (m), 1456 (m), 1377 (m, NO_2), 1339 (m), 1329 (m), 1305 (w), 1266 (s), 1247 (s), 1180 (m), 1114 (s), 1101 (s), 1074 (m), 1019 (m), 998 (s), 967 (m), 923 (m), 873 (w), 845 (m), 822 (m), 796 (s), 751 (m), 729 (s), 688 (m).

[2-Nitro-5,10,15,20-tetramesitylporphyrinato]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.[84]

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

5,10,15,20-Tetrakis(4-bromophenyl)porphyrin (**2H-1c**) (437 mg, 0.47 mmol) was dissolved in $CHCl_3$ (305 mL). Glacial acetic acid (7 mL), acetic anhydride (42 mL), copper (II) nitrate trihydrate (796 mg, 3.29 mmol) were added to the solution. The reaction mixture was refluxed for 2 h. The progress of reaction was monitored by TLC. On the completion of nitration, the reaction mixture was cooled and 200 mL of water were added. Acetic acid was neutralized with aqueous solution of sodium carbonate. The organic phase was washed twice with water (200 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/CH_2Cl_2 (3:2) mixture to afford **Cu-4c** (341 mg, 70%) as a purple solid.

HRMS (ESI+): *m/z* calcd for $(C_{44}H_{23}Br_4CuN_5NaO_2)^+$: 1054.77735; found: 1054.77896 $[M+Na]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 425 (5.14), 549 (4.00), 590 (3.81). IR: ν_{max}/cm^{-1} 2956 (m), 2923 (m), 2855 (m), 1720 (s), 1586 (m), 1522 (s, NO_2), 1482 (s), 1374 (m, NO_2), 1338 (s), 1267 (s), 1196 (w), 1162 (w), 1114 (m), 1100 (m), 1070 (s), 997 (s), 922 (m), 849 (m), 825 (m), 795 (s), 752 (s), 726 (s), 698 (m).

[2-Nitro-5,10,15,20-tetrakis(4-methylcarboxyphenyl)porphyrinato]copper(II) (Cu-4d)

5,10,15,20-Tetrakis(4-methylcarboxyphenyl)porphyrin (**2H-1d**) (169 mg, 0.2 mmol) was dissolved in $CHCl_3$ (130 mL). Glacial acetic acid (3 mL), succinic anhydride (1 g, 10 mmol), copper nitrate trihydrate (242 mg, 1.0 mmol) were added to the solution. The reaction mixture was stirred at r.t. for 10 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 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. The resulting crude solid was purified by silica gel column chromatography using a CH_2Cl_2/MeOH (99.9:0.1) mixture to afford **Cu-4d** (151 mg, 79%) as a purple solid.

HRMS (ESI+): *m/z* calcd for $(C_{52}H_{35}CuN_5NaO_{10})^+$: 975.15721; found: 975.15468 $[M+Na]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 428 (4.93), 550 (3.80), 592 (3.64). IR: ν_{max}/cm^{-1} 2957 (m), 2925 (m), 2856 (m), 1718 (s, C=O), 1607 (m), 1523 (m, NO_2), 1462 (m), 1434 (m), 1406 (m), 1378 (m, NO_2), 1266 (s), 1248 (s), 1193 (w), 1174 (w), 1113 (s), 1100 (s), 1018 (m), 998 (m), 960 (w), 924 (w), 874 (m), 846 (w), 821 (m), 804 (m), 794 (m), 764 (m), 729 (s), 707 (m).

[2-Nitro-5,10,15,20-tetrakis(4-diethoxyphosphorylphenyl)porphyrinato]copper(II) (Cu-4e)

5,10,15,20-Tetrakis(4-diethoxyphosphorylphenyl)porphyrin (**2H-1e**) (301 mg, 0.26 mmol) was dissolved in 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 controlled by MALDI spectrometry because the starting compound and the product have the same R_f which restricts TLC control. On the completion of the nitration reaction, the acetic anhydride was distilled from the reaction mixture under reduced pressure. The residue was dissolved in CH_2Cl_2 and the solution was washed twice with water (100 mL × 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 CH_2Cl_2/MeOH (97:3) mixture to afford **Cu-4e** (270 mg, 82%) as a purple solid.

HRMS (ESI+): *m/z* calcd for $(C_{60}H_{63}Br_4CuN_5NaO_{14})^+$: 1287.25102; found: 1287.25576 $[M+Na]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 426 (5.26), 549 (4.09), 592 (3.97). IR: ν_{max}/cm^{-1} 3430 (w), 2982 (w), 2906 (w), 1601 (m), 1520 (m, NO_2), 1442 (w), 1390 (m), 1337 (m, NO_2), 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-tetrakis(2,6-dichlorophenyl)porphyrinato]-copper (II) (Cu-4f)

5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphyrin (**2H-1f)** (890 mg, 1.0 mmol) was dissolved in $CHCl_3$ (695 mL). Glacial acetic acid (15 mL), succinic anhydride (5 g, 50.0 mmol) and copper nitrate trihydrate (1.21 g, 5.0 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 after completion of nitration and 200 mL of water were added. Acetic acid was neutralized with aqueous solution of sodium carbonate. The organic phase was washed twice with water (200 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/CH_2Cl_2 (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-Tetrakis(pentafluorophenyl)porphyrinato]copper (II) (Cu-1g)

5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin (**2H-1g**) (98 mg, 0.1 mmol) was dissolved in $CHCl_3$ (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/CH_2Cl_2 (1:1) mixture to afford **Cu-1g** with quantitative yield (107 mg).

Spectral data are in agreement with those reported in the literature.[85]

[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 $CHCl_3$ (115 mL). Glacial acetic 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/CH_2Cl_2 (4:1) mixture to afford **Ni-4g** (615 mg, 88%) as a purple solid.

δ_H(600 MHz; $CDCl_3$; 25 °C) 8.66 (1 H_A, AB system, J = 5.1 Hz, 17-H_β), 8.67–8.73 (4 H, m, 7,8,12,13-H_β), 8.74 (1 H_B, AB system, J = 5.1 Hz, 18-H_β), 9.05 (1 H, 3-H_β) ppm. δ_F(282 MHz; $CDCl_3$; 25 °C) -161.32 – -161.08 (2 F, m), -160.73 – -160.49 (4 F, m), -160.30 – -160.08 (2 F, m), -150.39 (2 F, t, J = 21.3 Hz), -149.96 (1 F, t, J = 21.3 Hz), -149.76 (1 F, t, J = 21.3 Hz), -137.55 – -137.38 (2 F, m), -136.66 – -136.49 (4 F, m), -136.45 – -136.29 (2 F, m) ppm. HRMS (ESI+): *m/z* calcd for $(C_{44}H_7F_{20}N_5NaNiO_2)^+$: 1097.95261; found: 1097.95551 $[M+Na]^+$. λ_{max}($CHCl_3$)/nm (log ε) 419 (4.92), 536 (3.77), 584 (3.83). IR: ν_{max}/cm^{-1} 2930 (w), 2859 (w), 1557 (m), 1519 (s), 1516 (s, NO_2), 1489 (s), 1428 (s), 1337 (s, NO_2), 1300 (m), 1213 (m), 1192 (m), 1154 (m), 1083 (m), 1060 (s), 1012 (m), 983 (s), 964 (m), 954 (s), 943 (s), 925 (s), 878 (m), 817 (s), 802 (s), 773 (s), 760 (s), 714 (s), 706 (s), 667 (m).

General procedure for the preparation of the free-base 2-nitro-5,10,15,20-tetraarylporphyrins 2H-4a, 2H-4c-e.[86]

[2-Nitro-5,10,15,20-tetraarylporphyrinato]copper(II) **Cu-4** (0.3 mmol) was dissolved in CH_2Cl_2 (110 mL). Concentrated H_2SO_4 (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.[87]

2-Nitro-5,10,15,20-tetramesitylporphyrin (2H-4b) was prepared according to the literature protocol[84] and was obtained in 80% (198 mg) yield as a purple solid. Spectral data are in agreement with those reported in the literature.[84]

2-Nitro-5,10,15,20-tetrakis(4-bromophenyl)porphyrin (2H-4c) was obtained in 88% (257 mg) yield as a purple solid. δ_H(600 MHz; $CDCl_3$; 25 °C) -2.72 (2 H, br s, internal NH), 7.84 (2 H, d, J = 8.3 Hz, Br-Ph_{meta}), 7.91 (4 H, d, J = 8.3 Hz, Br-Ph_{meta}), 7.92 (2 H, d, J = 8.3 Hz, Br-Ph_{meta}), 8.02 (2 H, 2d, J = 8.3 Hz, Br-Ph_{ortho}), 8.03 (2 H, 2d, J = 8.3 Hz, Br-Ph_{ortho}), 8.05 (2 H, d, J = 8.3 Hz, Br-Ph_{ortho}), 8.06 (2 H, d, J = 8.3 Hz, Br-Ph_{ortho}), 8.68 and 8.70 (2 H, AB system, J_{AB} = 4.7 Hz, 12,13-H_β), 8.87 (1 H, d, J = 4.9 Hz, 17-H_β), 8.88 and 8.92 (2 H, AB system, J_{AB} = 4.9 Hz, 7,8-H_β), 8.95 (1 H, d, J = 4.9 Hz, 18-H_β), 9.01 (1 H, s, 3-H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{44}H_{26}Br_4N_5O_2)^+$: 971.88145; found: 971.88277 $[M+H]^+$. λ_{max}($CHCl_3$)/nm (log ε) 430 (5.22), 528 (4.08), 562, (3.56), 604 (3.50), 666 (3.84). IR: ν_{max}/cm^{-1} 3325 (w, NH), 2956 (m), 2923 (m), 2854 (m), 1721 (s), 1526 (m, NO_2), 1471 (m), 1344 (m, NO_2), 1266 (s), 1246 (s), 1177 (w), 1158 (m), 1116 (s), 1100 (s), 1070 (s), 1011 (s), 994 (m), 981 (m), 963 (m), 914 (m), 874 (m), 845 (m), 822 (m), 796 (s), 750 (m), 729 (s), 695 (m).

2-Nitro-5,10,15,20-tetrakis(4-methylcarboxyphenyl)porphyrin (2H-4d) was obtained in 95% (254 mg) yield as a purple solid. δ_H(600 MHz; $CDCl_3$; 25 °C) -2.67 (2 H, br s, internal NH), 4.06 (3 H, s, CH_3), 4.10 (6 H, s, CH_3), 4.11 (3 H, s, CH_3), 8.25 (2 H, d, J = 8.0 Hz, $MeCO_2$-Ph_{ortho}), 8.26 (2 H, d, J = 8.0 Hz, $MeCO_2$-Ph_{ortho}), 8.28 (2 H, d, J = 8.0 Hz, $MeCO_2$-Ph_{ortho}), 8.30 (2 H, d, J = 8.0 Hz, $MeCO_2$-Ph_{ortho}), 8.38 (2 H, d, J = 8.0 Hz, $MeCO_2$-Ph_{meta}), 8.44 (4 H, d, J = 8.0 Hz, $MeCO_2$-Ph_{meta}), 8.45 (2 H, d, J = 8.0 Hz, $MeCO_2$-Ph_{meta}), 8.66 and 8.67 (2 H, AB system, J_{AB} = 4.8 Hz, 12,13-H_β), 8.85 (1 H, d, J = 5.0 Hz, 17-H_β), 8.87 and 8.90 (2 H, AB system, J_{AB} = 4.9 Hz, 7,8-H_β), 8.96 (1 H, d, J = 5.0 Hz, 18-H_β), 9.00 (1 H, s, 3-H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{52}H_{37}N_5NaO_{10})^+$: 914.24326; found: 914.23963 $[M+Na]^+$. λ_{max}($CHCl_3$)/nm (log ε) 429 (4.94), 527 (3.75), 603 (3.20), 666 (3.52). IR: ν_{max}/cm^{-1} 2957 (m), 2927 (m), 2858 (m), 1719 (s, C=O), 1606 (m), 1463 (m, NO_2), 1433 (m), 1406 (m), 1380 (m, NO_2), 1266 (s), 1248 (s), 1189 (m), 1174 (w), 1113 (s), 1100 (s), 1019 (m), 961 (m), 873 (m), 819 (w), 797 (m), 762 (m), 729 (s), 707 (m).

2-Nitro-5,10,15,20-tetrakis(4-diethoxyphosphorylphenyl)porphyrin (2H-4e) was obtained in 88% (318 mg) yield as a purple

solid. δ_H(500 MHz; $CDCl_3$; 25 °C) -2.69 (2 H, br s, internal NH), 1.47 (6 H, t, *J* = 7.2 Hz, CH_3), 1.50 (12 H, t, *J* = 7.2 Hz, CH_3), 1.51 (6 H, t, *J* = 7.2 Hz, CH_3), 4.26–4.43 (16 H, m, CH_2), 8.14 (2 H, dd, J_{PH} = 13.2 Hz, *J* = 8.1 Hz, $(EtO)_2OP\text{-}Ph_{meta}$), 8.19–8.25 (6 H, m, $(EtO)_2OP\text{-}Ph_{meta}$), 8.28 (2 H, dd, *J* = 8.1 Hz, J_{PH} = 4.0 Hz, $(EtO)_2OP\text{-}Ph_{ortho}$), 8.29 (2 H, dd, *J* = 8.1 Hz, J_{PH} = 4.0 Hz, $(EtO)_2OP\text{-}Ph_{ortho}$), 8.30 (2 H, dd, *J* = 8.1 Hz, J_{PH} = 4.0 Hz, $(EtO)_2OP\text{-}Ph_{ortho}$), 8.32 (2 H, dd, *J* = 8.1 Hz, J_{PH} = 4.0 Hz, $(EtO)_2OP\text{-}Ph_{ortho}$), 8.66 and 8.67 (2 H, AB system, *J* = 5.0 Hz, 12,13-H_β), 8.86 (1 H, d, *J* = 5.0 Hz, 17-H_β), 8.87 and 8.89 (2 H, AB system, *J* = 5.0 Hz, 7,8-H_β), 8.97 (1 H, s, 3-H_β), 8.98 (1 H, d, *J* = 5.0 Hz, 18-H_β) ppm. δ_P(202 MHz; $CDCl_3$; 25 °C) 18.03 (1 P), 18.29 (1 P), 18.36 (2 P) ppm. HRMS (ESI+): *m/z* calcd for $(C_{60}H_{66}N_5O_{14}P_4)^+$: 1204.35512; found: 1204.35785 $[M+H]^+$, *m/z* calcd for $(C_{60}H_{65}N_5NaO_{14}P_4)^+$: 1226.33707; found: 1226.33805 $[M+Na]^+$. λ_{max}($CHCl_3$)/nm (log ε) 426 (5.34), 526 (4.14), 599 (3.65), 664 (3.79). IR: ν_{max}/cm^{-1} 3430 (w), 2981 (m), 2915 (m), 2849 (m), 1735 (m), 1601 (m), 1561 (w), 1439 (w), 1390 (m), 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-tetrakis(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_H(600 MHz; $CDCl_3$; 25 °C) -2.48 (2 H, br s, internal NH), 7.67 (1 H, t, *J* = 8.5 Hz, Cl_2Ph_{para}), 7.70 (2 H, t, *J* = 8.5 Hz, Cl_2Ph_{para}), 7.705 (2 H, d, *J* = 8.5 Hz, Cl_2Ph_{meta}), 7.71 (1 H, t, *J* = 8.5 Hz, Cl_2Ph_{para}), 7.78 (6 H, d, *J* = 8.5 Hz, Cl_2Ph_{meta}), 8.53 and 8.54 (2 H, AB system, J_{AB} = 4.6 Hz, 12,13-H_β), 8.70 (1 H_A, AB system, *J* = 4.9 Hz, 17-H_β), 8.72 (2 H, 2d, *J* = 4.9 Hz, 7,8-H), 8.74 (1 H_B, AB system, *J* = 4.9 Hz, 18-H_β), 8.90 (1 H, s, 3-H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{44}H_{22}Cl_8N_5O_2)^+$: 931.92762; found: 931.93118 $[M+H]^+$. λ_{max}($CHCl_3$)/nm 424 (5.42), 523 (4.22), 558 (3.72), 601 (4.03), 656 (3.49). IR: ν_{max}/cm^{-1} 3337 (w, NH), 2922 (m), 2852 (m), 1723 (m), 1557 (m), 1520 (m, NO_2), 1427 (s), 1359 (m, NO_2), 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-tetrakis(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.[57]

Tin(II) chloride dihydrate $SnCl_2{\cdot}2H_2O$ (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 N_2 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 × 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-tetrakis(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 $CHCl_3$.

δ_H(300 MHz; $CDCl_3$; 25 °C) -2.85 (2 H, very br s, internal NH), 1.49 (24 H, t, *J* = 7.1 Hz, CH_3), 4.29–4.44 (16 H, m, CH_2), 7.68 (1 H, s, 3-H_β), 8.12–8.31 (16 H, m, $(EtO)_2OP\text{-}Ph$), 8.41 (1 H, d, *J* = 4.9 Hz, 18-H_β), 8.63 (1 H, d, *J* = 4.9 Hz, 7-H_β), 8.66 (1 H, d, *J* = 4.9 Hz, 17-H_β), 8.72 (1 H, d, *J* = 4.9 Hz, 8-H_β), 8.74 (2 H, AB system, 12,13-H_β) ppm, NH_2 protons are not observed. δ_P(121 MHz; $CDCl_3$; 25 °C) 17.88 (1 P), 18.87 (1 P), 18.92 (1 P), 18.98 (1 P) ppm. HRMS (ESI+): *m/z* calcd for $(C_{60}H_{68}N_5O_{12}P_4)^+$: 1174.38094; found: 1174.38164 $[M+H]^+$. λ_{max}($CHCl_3$)/nm (log ε) 403 (5.26), 524 (3.98), 593 (3.64), 652 (3.62) 672 (3.13). IR: ν_{max}/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), 956 (s), 788 (s), 765 (s),717 (s), 579 (s).

2-Amino-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (2H-2g) was obtained from **2H**-**4g** (39 mg, 0.038 mmol) in (20 mg, 53%) yield as a purple solid after purification by silica gel column chromatography using degassed hexane/CH_2Cl_2 (7:3) mixture.

δ_H(300 MHz; $CDCl_3$; 25 °C) -2.78 (2 H, very br s, internal NH), 4.65 (2 H, br s, NH_2), 7.82 (1 H, s, 3-H_β), 8.61 (1 H, d, *J* = 4.8 Hz, 18-H_β), 8.74 (1 H, d, *J* = 4.8 Hz, 7-H_β), 8.77–8.83 (2 H, m, 8,17-H_β), 8.81 and 8.85 (2 H, AB system, J_{AB} = 4.8 Hz, 12,13-H_β) ppm. δ_F(282 MHz; $CDCl_3$; 25 °C) -161.83 – -161.43 (6 F, m), -159.81 – -159.56 (2 F, m), -152.11 (1 F, t, *J* = 20.8 Hz), -151.64 (1 F, t, *J* = 20.8 Hz), -151.60 (1 F, t, *J* = 20.8 Hz), -149.92 (1 F, t, *J* = 20.8 Hz), -136.74 – -136.50 (6 F, m), -135.64 – -135.46 (2 F, m). HRMS (ESI+): *m/z* calcd for $(C_{44}H_1F_{20}N_5Na)^+$: 1012.05873; found: 1012.05694 $[M+Na]^+$. λ_{max}($CHCl_3$)/nm (log ε) 401 (5.08), 517 (4.06), 590 (3.68), 645 (3.61), 673 (3.54). IR: ν_{max}/cm^{-1} 3475 (w, NH), 3391 (w, NH), 3311 (w), 2923 (m), 2853 (m), 1729 (m), 1648 (m), 1612 (m), 1515 (s), 1496 (s), 1346 (m), 1319 (m), 1261 (w), 1215 (w), 1143 (m), 1082 (m), 1025 (m), 987 (s), 919 (s), 850 (w), 804 (m), 756 (s), 723 (m), 705 (m).

Procedure for the preparation of 2-(COOH(CH_2)$_2$CONH)-5,10,15,20-tetrakis(4-diethoxyphosphorylphenyl)porphyrin (2H-5e).[88]

Succinic anhydride (185 mg, 1.85 mmol) was added to a solution of **2H-2e** (43 mg, 0.037 mmol) in CH_2Cl_2 (15 mL) under N_2 atmosphere. The reaction mixture was stirred at reflux until complete conversion of the amine according to TLC (24 h). Then the reaction mixture was evaporated under reduced pressure. The residue was chromatographed on a silica gel eluting with a CH_2Cl_2/MeOH (9:1) mixture to afford **2H-5e** (35

mg, 74%) as a purple solid and **2H-6e** (7 mg, 16%) as a brown solid.

2H-5e δ_H(300 MHz; $CDCl_3$; 25 °C) -2.89 (2 H, br s, internal NH), 1.49 (24 H, t, *J* = 6.9 Hz, CH_3), 2.27–2.34 (2 H, m, CH_2), 2.65–2.73 (2 H, m, CH_2), 4.27–4.45 (16 H, m, (O-CH_2), 7.62 (1 H, s, NH), 8.10-8.37 (16 H, m, $(EtO)_2$OP-Ph), 8.57 (1 H, d, *J* = 4.9 Hz, H_β), 8.70 (1 H, d, *J* = 4.9 Hz, H_β), 8.73(2 H, s, H_β), 8.75-8.82 (2 H, 2 d, *J* = 5.0 Hz, H_β), 9.21 (1 H, s, 3-H_β) ppm. δ_P(121 MHz; $CDCl_3$; 25 °C) 17.48 (1 P), 18.65 (2 P), 18.67 (1 P) ppm. HRMS (ESI+): *m/z* calcd for $(C_{64}H_{72}N_5O_{15}P_4)^+$: 1274.39699; found: 1274.39907 $[M+H]^+$; *m/z* calcd for $(C_{64}H_{71}N_5NaO_{15}P_4)^+$: 1296.37893; found: 1296.37956 $[M+Na]^+$. λ_{max}($CHCl_3$)/nm (log ε) 423 (5.43), 519 (4.32), 550 (3.86), 593 (3.83), 648 (3.40). IR: ν_{max}/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-dioxo-5,10,15,20-tetraarylchlorins 2H-6a-d,f.[45]

To the crude 2-aminotetraarylporphyrin **2H-2** silica gel (525 mg) and CH_2Cl_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/CH_2Cl_2 (3:2) (**2H-6a, 2H-6b, 2H-6c, 2H-6f**) or CH_2Cl_2/methanol (99.8:0.2) mixtures (**2H-6d**). The yield of **2H-6** was calculated using to the amount of **2H-4** introduced in the reduction (total yield for two steps).

2,3-Dioxo-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, 0.15 mmol).

δ_H(300 MHz; $CDCl_3$; 25 °C) -2.01 (2 H, br s, internal NH), 2.65 (6 H, s, CH_3), 2.67 (6 H, s, CH_3), 7.48 (4 H, d, *J* = 8.0 Hz, Tol_{meta}), 7.52 (4 H, d, *J* = 8.0 Hz, Tol_{meta}), 7.76 (4 H, d, *J* = 8.0 Hz, Tol_{ortho}), 7.99 (4 H, d, *J* = 8.0 Hz, Tol_{ortho}), 8.56 (2 H, s, 12,13-H), 8.60 (2 H, dd, *J* = 5.0 Hz, ^4J = 1.3 Hz, 8,17-H_β), 8.74 (2 H, dd, *J* = 5.0 Hz, ^4J = 1.3 Hz, 7,18-H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{48}H_{37}N_4O_2)^+$: 701.29110; found: 701.29076 $[M+H]^+$. λ_{max}($CHCl_3$)/nm (log ε) 407 (5.11), 477 (4.17), very broad band stretching from 575 nm to 800 nm centered at about 670 nm. IR: ν_{max}/cm^{-1} 3361 (w, NH), 2956 (m), 2921 (m), 2854 (m), 1725 (vs, C=O), 1505 (m), 1456 (m), 1407 (w), 1378 (m), 1346 (m), 1266 (s), 1248 (m), 1222 (m), 1181 (m), 1109 (m), 1101 (m), 1089 (s), 1065 (m), 1042 (m), 1020 (m), 994 (m), 980 (m), 966 (m), 836 (m), 821 (w), 793(s), 724 (s), 688 (s).

2,3-Dioxo-5,10,15,20-tetramesitylchlorin (2H-6b) was obtained as a brown solid in 80% (300 mg) yield from the crude **2H-2b** prepared from **2H-4b** (380 mg, 0.46 mmol).

δ_H(300 MHz; $CDCl_3$; 25 °C) -1.79 (2 H, br s, internal NH), 1.77 (12 H, s, CH_{3ortho}), 1.85 (12 H, s, CH_{3ortho}), 2.57 (6 H, s, CH_{3para}), 2.58 (6 H, s, CH_{3para}), 7.21 (4 H, br s, Mes), 7.23 (4 H, br s, Mes), 8.36 (2 H, s, 12,13-H_β), 8.44 (2 H, dd, *J* = 4.9 Hz, ^4J = 1.7 Hz, 8,17-H_β), 8.54 (2 H, dd, *J* = 4.9 Hz, ^4J = 1.7 Hz, 7,18-H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{56}H_{52}N_4NaO_2)^+$: 835.39825; found: 835.40188 $[M+Na]^+$. λ_{max}($CHCl_3$)/nm (log ε) 406 (5.21), 479 (4.17), very broad band stretching from 575 nm to 800 nm centered at about 670 nm. IR: ν_{max}/cm^{-1} 3354 (w, NH), 2913 (m), 2852 (m), 1724 (s, C=O), 1615 (m), 1535 (m), 1455 (m), 1407 (w), 1373 (w), 1339 (m), 1287 (w), 1267 (m), 1249 (w), 1215 (m), 1187 (s), 1060 (m), 1035 (m), 1019 (m), 993 (m), 981 (m), 969 (m), 947 (m), 850 (m), 828 (m), 803 (s), 756 (s), 719 (s), 689 (s), 667 (m).

2,3-Dioxo-5,10,15,20-tetrakis(4-bromophenyl)chlorin (2H-6c) was obtained as a brown solid in 64% (160 mg) yield from the crude **2H-2c** prepared from **2H-4c** (254 mg, 0.29 mmol).

δ_H(300 MHz; $CDCl_3$; 25 °C) -2.14 (2 H, br s, internal NH), 7.74 and 7.82 (8 H, AB system, *J* = 8.4 Hz, Br-Ph), 7.88 and 7.97 (8 H, AB system, *J* = 8.4 Hz, Br-Ph), 8.54 (2 H, s, 12,13-H_β), 8.60 (2 H, dd, *J* = 5.1 Hz, ^4J = 1.4 Hz, 8,17-H_β), 8.74 (2 H, dd, *J* = 5.1 Hz, ^4J = 1.4 Hz, 7,18-H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{44}H_{25}B_{r4}N_4O_2)^+$: 956.87055; found: 956.87435 $[M+H]^+$. λ_{max}($CHCl_3$)/nm (log ε) 406 (5.09), 471 (4.12), 566 (3.58), 602 (3.55), 655 (3.61). IR: ν_{max}/cm^{-1} 3354 (w, NH), 2956 (m), 2924 (m), 2857 (m), 1721 (s, C=O), 1585 (w), 1486 (m), 1464 (m), 1408 (w), 1392 (m), 1346 (m), 1266 (s), 1248 (s), 1116 (m), 1100 (s), 1071 (m), 1044 (m), 1013 (s), 995 (m), 978 (m), 964 (m), 875 (m), 838 (m), 799 (s), 729 (s), 713 (m), 692 (m), 685 (m), 676(m).

2,3-Dioxo-5,10,15,20-tetrakis(4-methylcarboxyphenyl)-chlorin (2H-6d) was obtained as a brown solid in 70% (61 mg) yield from the crude **2H-2d** prepared from **2H-4d** (89 mg, 0.1 mmol).

δ_H(300 MHz; $CDCl_3$; 25 °C) -2.11 (2 H, br s, internal NH), 4.06 (6 H, s, CH_3), 4.08 (6 H, s, CH_3), 7.96 (4 H, d, *J* = 8.4 Hz, $MeCO_2$-Ph_{meta}), 8.18 (4 H, d, *J* = 8.4 Hz, $MeCO_2$-Ph_{meta}), 8.37 (4 H, d, *J* = 8.4 Hz, $MeCO_2$-Ph_{ortho}), 8.41 (4 H, d, *J* = 8.4 Hz, $MeCO_2$-Ph_{ortho}), 8.51 (2 H, s, 12,13-H_β), 8.56 (2 H, dd, *J* = 5.0 Hz, ^4J = 1.4 Hz, 8,17-H_β), 8.71 (2 H, dd, *J* = 5.0 Hz, ^4J = 1.4 Hz, 7,18-H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{52}H_{36}N_4NaO_{10})^+$: 899.23236; found: 899.23386 $[M+Na]^+$. λ_{max}($CHCl_3$)/nm (log ε) 406 (5.26), 471 (4.28). IR: ν_{max}/cm^{-1} 3351 (w, NH), 2953 (m), 2926 (m), 2856 (m), 1716 (s, CO), 1607 (m), 1566 (w), 1454 (m), 1432 (m), 1404 (m), 1383 (w), 1349 (w), 1267 (s), 1191 (m), 1176 (m), 1100 (s), 1067 (m), 1043 (m), 1020 (m), 996 (w), 978 (m), 963 (m), 864 (m), 821 (m), 798 (m), 759 (m), 713 (s), 678 (m), 631 (m).

2,3-Dioxo-5,10,15,20-tetrakis(2,6-dichlorophenyl)chlorin (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).

δ_H(600 MHz; $CDCl_3$; 25 °C) -1.94 (2 H, br s, internal NH), 7.66 (2 H, t, *J* = 8.3 Hz, Cl_2Ph_{para}), 7.69 (2 H, t, *J* = 8.3 Hz, Cl_2Ph_{para}), 7.73 (4 H, d, *J* = 8.3 Hz, Cl_2Ph_{meta}), 7.77 (4 H, d, *J* = 8.3 Hz, Cl_2Ph_{meta}), 8.42 (2 H, s, 12,13-H_β), 8.55 (2 H, dd, *J* = 4.8 Hz, ^4J = 1.5 Hz, 8,17-H_β), 8.64 (2 H, dd, *J* = 4.8 Hz, ^4J = 1.5 Hz, 7,18-H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{44}H_{21}Cl_8N_4O_2)^+$: 916.91672; found: 916.91873 $[M+H]^+$.

$\lambda_{max}(CHCl_3)$/nm (log ε) 404 (5.27), 469 (4.26), very broad band stretching from 630 nm to 800 nm centered at about 695 nm. IR: ν_{max}/cm-1 3356 (w, NH), 2922 (w), 2849 (w), 1729 (s, C=O), 1557 (m), 1528 (m), 1427 (s), 1343 (m), 1293 (m), 1220 (m), 1191 (m), 1152 (m), 1090 (m), 1063 (m), 1038 (m), 995 (m), 966 (s), 881 (m), 834 (w), 800 (s), 774 (s), 708 (s), 674 (s), 648 (m).

2,3-Dioxo-5,10,15,20-tetrakis(4-diethoxyphosphorylphenyl)-chlorin (2H-6e)

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 CH_2Cl_2, 0.0166 mmol) was added to a solution of porphyrin **2H-2e** (15 mg, 0.0128 mmol) in degassed CH_2Cl_2 (3 mL) under N_2 atmosphere. The reaction mixture was stirred at r.t. when monitored by MALDI spectrometry. After 2 h the reaction mixture was diluted with CH_2Cl_2 (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 CH_2Cl_2/MeOH (99:1) mixture as eluent. The product **2H-6e** (15 mg, 99%) was obtained as a brown solid.

δ_H(300 MHz; $CDCl_3$; 25 °C) -2.12 (2 H, br s, internal NH), 1.47 (12 H, t, *J* = 7.1 Hz, CH_3), 1.49 (12 H, t, *J* = 7.1 Hz, CH_3), 4.25-4.43 (16 H, m, CH_2), 7.99 (4 H, dd, *J* = 8.3 Hz, J_{HP}= 4.1 Hz, $(EtO)_2OP\text{-}Ph_{ortho}$), 8.09–8.23 (12 H, m, 4 H $(EtO)_2OP\text{-}Ph_{ortho}$ and 8 H $(EtO)_2OP\text{-}Ph_{meta}$), 8.51 (2 H, s, 12,13-$H_\beta$), 8.56–8.60 (2 H, br d, *J* = 5.0 Hz, 8,17-H_β), 8.71–8.75 (2 H, br d, *J* = 5.0 Hz, 7,18-H_β) ppm. δ_P(121 MHz; $CDCl_3$; 25 °C) 18.26 (2 P), 18.75 (2 P) ppm. HRMS (ESI+): *m/z* calcd for $(C_{60}H_{64}N_4NaO_{14}P_4)^+$: 1211.32617; found: 1211.32397 $[M+Na]^+$. $\lambda_{max}(CHCl_3)$/nm (log *ε*) 404 (5.18), 524 (3.98), 562 (3.92), 600 (3.84), 652 (3.88). IR: ν_{max}/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-diethoxyphosphorylphenyl)chlorin (2H-7e).

Silica gel (57 mg) was added to a solution of 2-aminoporphyrin **2H-2e** (15 mg, 0.0128 mmol) in CH_2Cl_2 (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 $CHCl_3$/MeOH (50:1) mixture as a rose-violet solid. Yield 33% (5 mg).

δ_H(500 MHz; $CDCl_3$; 25 °C) 1.24 (6 H, t, *J* = 7.1 Hz, CH_3), 1.25 (6 H, t, *J* = 7.1 Hz, CH_3), 1.27 (12 H, t, *J* = 7.1 Hz, CH_3), 4.06–4.16 (16 H, m, CH_2), 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, H_β), 8.31 (1 H, d, *J* = 4.7 Hz, H_β), 8.34 (1 H, d, *J* = 4.7 Hz, H_β), 8.47 (1 H, d, *J* = 4.7 Hz, H_β), 8.55 and 8.59 (2 H, AB system, *J* = 4.4 Hz, H_β) ppm. NH protons are not observed. δ_P(202 MHz; $CDCl_3$; 25 °C: 18.76 (1 P), 18.81 (1 P), 18.96 (1 P), 19.22 (1 P) ppm. HRMS (ESI+): *m/z* calcd for $(C_{59}H_{65}N_4O_{14}P_4)^+$: 1177.34422; found: 1177.34304 $[M+H]^+$; *m/z* calcd for $(C_{59}H_{64}N_4NaO_{14}P_4)^+$: 1199.32617; found: 1199.32381 $[M+Na]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 281 (3.62), 419 (4.89), 520 (3.51), 558 (3.51), 590 (3.29), 644 (3.08). IR: ν_{max}/cm^{-1} 3337 (w, NH), 2980 (m), 2930 (m), 1772 (s, C=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.[45]

2,3-Dioxo-5,10,15,20-tetraarylchlorin **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/CH_2Cl_2 (1:1) (**2H-14**, **2H-15**) or CH_2Cl_2/MeOH (99:1) (**2H-16**-**19)** mixture to afford imidazoporphyrins **2H-14-19.**

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

δ_H(300 MHz; $CDCl_3$; 25 °C) -2.92 (2 H, br s, internal NH), 2.70 (6 H, s, CH_3), 2.75 (3 H, s, CH_3), 2.81 (3 H, s, CH_3), 7.55 (4 H, br d, *J* = 7.8 Hz, Tol_{meta}), 7.59 (4 H, br s, 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_{ortho}), 8.14 (2 H, d, *J* = 7.8 Hz, Tol_{ortho}), 8.15 (2 H, d, *J* = 7.8 Hz, Tol_{ortho}), 8.54 (1 H, br s, imidazole NH), 8.79 (2 H, s, H_β), 8.90 (1 H, d, *J* = 4.8 Hz, H_β), 8.93 and 8.96 (2 H, AB system, J_{AB} = 4.8 Hz, H_β), 8.96 (1 H, d, *J* = 4.8 Hz, H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{55}H_{42}BrN_6)^+$: 865.26488; found: 865.26391 $[M+H]^+$. $\lambda_{max}(CHCl_3)$/nm (log *ε*) 421 (5.25), 518 (4.15), 552 (3.83), 588 (3.77), 647 (3.25). IR: ν_{max}/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)-1*H*-imidazo[4,5-*b*]-5,10,15,20-tetramesitylporphyrin (2H-14b) was obtained from 2,3-dioxo-5,10,15,20-tetramesitylchlorin (**2H-6b**) and 4-bromobenzaldehyde (**8**) in 64% (62 mg) yield.
δ_H(300 MHz; $CDCl_3$; 25 °C) -2.70 (2 H, br s, internal NH), 1.84 (6 H, s, CH_{3ortho}), 1.85 (6 H, s, CH_{3ortho}), 1.86 (6 H, s, CH_{3ortho}), 1.87 (6 H, s, CH_{3ortho}), 2.62 (6 H, s, CH_{3para}), 2.67 (3 H, s, CH_{3para}), 2.74 (3 H, s, CH_{3para}), 7.27 (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, J_{AB} = 8.4 Hz, Br-Ph), 8.29 (1 H, br s, imidazole NH), 8.58 (2 H, s, H_β), 8.73 (1 H, d, J = 4.8 Hz, H_β), 8.76–8.79 (2 H, 2d, J = 4.8 Hz, H_β), 8.84 (1 H, d, J = 4.5 Hz, H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{63}H_{57}BrN_6)^+$: 977.38009; found: 977.38819 $[M+H]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 304 (4.30), 419 (5.44), 516 (4.25), 548 (3.75), 587 (3.82), 645 (3.24). IR: ν_{max}/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)-1*H*-imidazo[4,5-*b*]-5,10,15,20-tetrakis(4-methylcarboxyphenyl)porphyrin (2H-14d) was obtained from 2,3-dioxo-5,10,15,20-tetrakis(4-methylcarboxyphenyl)-chlorin (**2H-6d)** (50 mg, 0.057 mmol) and 4-bromobenzaldehyde (**8**) in 69% (41 mg) yield.
δ_H(600 MHz; $CDCl_3$; 25 °C) -2.95 (2 H, br s, internal NH), 4.10 (6 H, s, CH_3), 4.13 (3 H, s, CH_3), 4.17 (3 H, s, CH_3), 7.53 and 7.59 (4 H, AB system, J_{AB} = 8.4 Hz, Br-Ph), 8.28 (4 H_A, AB system, J_{AB} = 8.3 Hz, $MeCO_2$-Ph_{ortho}), 8.33 (2 H, d, J = 7.9 Hz, $MeCO_2$-Ph_{ortho}), 8.36 (2 H, d, J = 7.9 Hz, $MeCO_2$-Ph_{ortho}), 8.43 (4 H_B, AB system, J_{AB} = 8.3 Hz, $MeCO_2$-Ph_{meta}), 8.49 (2 H, d, J = 7.9 Hz, $MeCO_2$-Ph_{meta}), 8.60 (3 H, br d, J = 7.9 Hz, imidazole NH and $MeCO_2$-Ph_{metha}), 8.73 (2 H, s, 12,13-H_β), 8.81 (1 H, d, J = 4.8 Hz, 7-H_β), 8.88 (2 H, br s, H_β), 8.90 (1 H, d, J = 4.8 Hz, H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{59}H_{42}BrN_6O_8)^+$: 1041.22420; found: 1041.22460 $[M+H]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 291 (4.48), 421 (5.51), 517 (4.33), 550 (3.90), 588 (3.90), 645 (3.39). IR: ν_{max}/cm^{-1} 3437 (w, NH), 2957 (m), 2928 (m), 2859 (m), 1718 (s, C=O), 1605 (m), 1504 (w), 1463 (m), 1433 (m), 1407 (m), 1382 (m), 1265 (s), 1247 (s), 1165 (w), 1113 (s), 1100 (s), 1019 (m), 995 (w), 961 (m), 874 (m), 818 (m), 795 (m), 764 (m), 729 (s).

2-(4-Bromophenyl)-1*H*-imidazo[4,5-*b*]-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (2H-14f) was obtained from 2,3-Dioxo-5,10,15,20-tetrakis(2,6-dichlorophenyl)chlorin (**2H-6f**) (18 mg, 0.02 mmol) and 4-bromobenzaldehyde (**8**) in 51% (11 mg) yield.
δ_H(600 MHz; $CDCl_3$; 25 °C) -2.72 (2 H, br s, internal NH), 7.59 and 7.60 (4 H, AB system, J_{AB} = 8.7 Hz, Br-Ph), 7.69 (2 H, t, J = 8.4 Hz, Cl_2Ph_{para}), 7.74 (1 H, t, J = 8.4 Hz, Cl_2Ph_{ortho}), 7.79 (4 H, d, J = 8.4 Hz, *o*-Cl_2Ph_{meta}), 7.82 (2 H, d, J = 8.4 Hz, *o*-Cl_2Ph_{meta}), 7.89 (1 H, t, J = 8.4 Hz, *o*-Cl_2Ph_{ortho}), 7.97 (2 H, d, J = 8.4 Hz, *o*-Cl_2Ph_{meta}), 8.50 (1 H, br s, imidazole NH), 8.61 (2 H, s, 12,13-H_β), 8.76-8.82 (3 H, br s, H_β), 8.87 (1 H, d, J = 4.8 Hz, H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{51}H_{26}BrCl_8N_6)^+$: 1080.89051; found: 1080.89326 $[M+H]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 288 (3.96), 418 (5.29), 514 (4.25), 588 (3.81), 642 (3.49).

2-(4-Nitrophenyl)-1*H*-imidazo[4,5-*b*]-5,10,15,20-tetratolylporphyrin (2H-15a) was obtained from 2,3-dioxo-5,10,15,20-tetratolylchlorin (**2H-6a)** (119 mg, 017 mmol) and 4-nitrobenzaldehyde (**9**) in 55% (78 mg) yield.
δ_H(300 MHz; $CDCl_3$; 25 °C) -2.94 (2 H, br s, internal NH), 2.70 (6 H, s, CH_3), 2.77 (3 H, s, CH_3), 2.84 (3 H, s, CH_3), 7.54 (4 H, br d, J = 7.8 Hz, Tol_{meta}), 7.62 (2 H, d, J = 7.8 Hz, Tol_{meta}), 7.75 (2 H, d, J = 7.8 Hz, Tol_{meta}), 7.83 (2 H d, J = 8.7 Hz, Ph), 8.09 (4 H, d, J = 7.8 Hz, Tol_{ortho}), 8.15 (4 H, d, J = 7.8 Hz, Tol_{ortho}), 8.32 (2 H, d, J = 8.7 Hz, Ph), 8.65 (1 H, s, imidazole NH), 8.77 (2 H, s, 12,13-H_β), 8.92 and 8.98 (2 H, AB system, J = 5.0 Hz, H_β), 8.95 and 8.98 (2 H, AB system, J = 5.0 Hz, H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{55}H_{42}N_7O_2)^+$: 832.33945; found: 832.33894 $[M+H]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 424 (5.38), 519 (4.33), 554 (3.98), 587 (3.93), 647 (3.35). IR: ν_{max}/cm^{-1} 3430 (w, NH), 3325 (w, NH), 2956 (m), 2924 (s), 2855 (m), 1722 (s), 1601 (m), 1517 (m, NO_2), 1457 (m), 1408 (m), 1378 (m, NO_2), 1344 (s), 1328 (m), 1267 (s), 1248 (s), 1182 (m), 1165 (m), 1102 (m), 1019 (m), 996 (m), 978 (m), 966 (m), 853 (m), 799 (s), 753 (m), 730 (s), 667 (m), 660 (m).

2-(4-Carboxyphenyl)-1*H*-imidazo[4,5-*b*]-5,10,15,20-tetramesitylporphyrin (2H-16b) was obtained from 2,3-dioxo-5,10,15,20-tetramesitylchlorin (**2H-6b**) and 4-carboxybenzaldehyde (**10**) in 53% (52 mg) yield.
δ_H(300 MHz; $CDCl_3$; 25 °C) -2.69 (2 H, br s, internal NH), 1.85 (s, 24 H, m, CH_{3ortho}), 2.62 (6 H, s, CH_{3para}), 2.68 (3 H, s, CH_{3para}), 2.76 (3 H, s, CH_{3para}), 7.27 (4 H, s, Mes), 7.33 (2 H, s, Mes), 7.49 (2 H, s, Mes), 7.79 (2 H, d, J = 8.5 Hz, HO_2C-Ph), 8.18 (2 H, d, J = 8.5 Hz, HO_2C-Ph), 8.39 (1 H, br s, imidazole NH), 8.57 (2 H, s, H_β), 8.73 and 8.80 (2 H, AB system, J_{AB} = 4.6 Hz, H_β), 8.78 and 8.85 (2 H, AB system, J_{AB} = 4.6 Hz, H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{64}H_{59}N_6O_2)^+$: 943.46940; found: 943.46891 $[M+H]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 421 (5.37), 516 (4.23), 548 (3.78), 587 (3.82), 647 (3.34). IR: ν_{max}/cm^{-1} 3418 (w, NH), 3323 (w, NH), 2951 (w), 2917 (m), 2854 (m), 1687 (s, C=O), 1683 (m), 1611 (m), 1568 (w), 1447 (m), 1377 (m), 1284 (m), 1242 (m), 1215 (m), 1170 (m), 1150 (m), 1107 (w), 1031 (w), 1015 (m), 996 (m), 969 (m), 948 (m), 851 (m), 826 (m), 799 (s), 776 (m), 725 (s), 708 (s).

2-(4-Carboxyphenyl)-1*H*-imidazo[4,5-*b*]-5,10,15,20-tetrakis(4-bromophenyl)porphyrin (2H-16c) was obtained from 2,3-dioxo-5,10,15,20-tetrakis(4-bromophenyl)chlorin (**2H-6c**) (27 mg, 0.028 mmol) and 4-carboxybenzaldehyde (**10**) in 56% (17 mg) yield.
δ_H(300 MHz; DMSO; 25 °C) -3.06 (2 H, br s, internal NH), 7.90–8.20 (20 H, m, Br-Ph and HO_2C-Ph), 8.77 (2 H, br s, 12,13-H_β), 8.74–8.83 (2 H, m, 7,18-H_β), 8.88 (2 H, m, 8,17-H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{52}H_{31}Br_4N_6O_2)^+$: 1086.92365; found: 1086.92570 $[M+H]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 420 (5.50), 517 (4.29), 551 (3.93), 588 (3.89), 649 (3.59). IR: ν_{max}/cm^{-1} 3450 (w, NH), 3300 (w, NH), 2961 (m), 2920 (m), 2851 (m), 1692 (s, C=O), 1610 (m), 1555(m), 1470 (m), 1375 (m), 1259 (s), 1202

(m), 1165 (m), 1094 (m), 1069 (m), 1011 (s), 976 (m), 963 (m), 793 (s), 750 (m), 725 (m), 680 (w).

2-(4-Carboxyphenyl)-1*H*-imidazo[4,5-*b*]-5,10,15,20-tetrakis(4-diethoxyphosphorylphenyl)porphyrin (2H-16e) was obtained from 2,3-dioxo-5,10,15,20-tetrakis(4-diethoxyphosphoryl-phenyl)chlorin (**2H-6e**) (34 mg, 0.029 mmol) and 4-carboxybenzaldehyde (**10)** in 50% (19 mg) yield.

δ_H(300 MHz; $CDCl_3$; 25 °C) -2.97 (2 H, br s, internal NH), 1.46–1.56 (24 H, m, CH_3), 4.30–4.46 (16 H, m, CH_2), 7.66 (2 H, d, *J* = 7.7 Hz, HO_2C-Ph), 8.04 (2 H, d, *J* = 7.7 Hz, HO_2C-Ph), 8.22 (6 H, dd, J_{PH} = 12.9 Hz, *J* = 7.8 Hz, $(EtO)_2OP$-Ph_{meta}), 8.27–8.43 (10 H, m, 2H $(EtO)_2OP$-Ph_{meta} and 8H $(EtO)_2OP$-Ph_{ortho}), 8.73 (2 H, s, 12,13-H_β), 8.92 (4 H, br s, 7,8,17,18-H_β) ppm. δ_P(121 MHz; $CDCl_3$; 25 °C) 17.95 (1 P), 18.73 (2 P), 19.62 (1 P) ppm. HRMS (ESI+): *m/z* calcd for $(C_{68}H_{71}N_6O_{14}P_4)^+$: 1319.39732; found: 1319.39772 $[M+H]^+$; *m/z* calcd for $(C_{68}H_{70}N_6NaO_{14}P_4)^+$: 1341.37927; found: 1341.37905 $[M+Na]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 421 (5.35), 517 (4.20), 549 (3.82), 587 (3.82), 645 (3.41). IR: ν_{max}/cm^{-1} 3418 (w, NH), 3323 (w, NH), 2956 (m), 2924 (m), 2852 (m), 1716 (m), 1699 (m, C=O), 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-Diethoxyphosphorylphenyl)-1*H*-imidazo[4,5-*b*]-5,10,15,20-tetramesitylporphyrin (2H-17b) was obtained from 2,3-dioxo-5,10,15,20-tetramesitylchlorin (**2H-6b**) (292 mg, 0.36 mmol) and 4-diethoxyphosphorylbenzaldehyde (**11)** in 71% (264 mg) yield.

δ_H(300 MHz; $CDCl_3$; 25 °C) -2.69 (2 H, br s, internal NH), 1.83 (6 H, s, CH_{3ortho}), 1.85 (12 H, s, CH_{3ortho}), 1.86 (6 H, s, CH_{3ortho}), 2.61 (6 H, s, CH_{3para}), 2.67 (3 H, s, CH_{3para}), 2.75 (3 H, s, CH_{3para}), 4.04–4.25 (4 H, m, CH_2), 7.26 (4 H, br s, Mes), 7.32 (2 H, s, Mes), 7.48 (2 H, s, Mes), 7.78 (2 H, dd, *J* = 8.3 Hz, J_{PH} = 3.8 Hz, $(EtO)_2OP$-Ph_{ortho}), 7.90 (2 H, dd, J_{PH} = 12.7 Hz, *J* = 8.3 Hz, $(EtO)_2OP$-Ph_{meta}), 8.36 (1 H, br s, imidazole NH), 8.57 (2 H, s, 12,13-H_β), 8.72 and 8.78 (2 H, AB system, J_{AB} = 4.8 Hz, 17,18-H_β), 8.78 and 8.84 (2 H, AB system, J_{AB} = 4.8 Hz, 8,7-H_β) ppm. δ_P(121 MHz; $CDCl_3$; 25 °C) 18.31 (1 P, s) ppm. HRMS (ESI+): *m/z* calcd for $(C_{67}H_{68}N_6O_3P)^+$: 1035.50850; found: 1035.50934 $[M+H]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 421 (5.35), 517 (4.22), 548 (3.75), 587 (3.77), 647 (3.24). IR: ν_{max}/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 (s).

Imidazo[4,5-*b*]porphyrin (2H-18a) was obtained from 2,3-dioxo-5,10,15,20-tetratolylchlorin (**2H-6a**) (70 mg, 0.1 mmol) and 4'-(4-formylphenyl)-2,2':6',2''-terpyridine (**12**) in 49% (50 mg) yield.

δ_H(300 MHz; $CDCl_3$; 25 °C) -2.91 (2 H, br s, internal NH), 2.70 (6 H, s, CH_3), 2.80 (3 H, s, CH_3), 2.87 (3 H, s, CH_3), 7.38 (2 H, ddd, ^3J = 7.6 Hz, ^3J = 4.8 Hz, ^4J = 1.2 Hz, terpyridine 5, 5'' H), 7.55 (4 H, d, *J* = 7.9 Hz, Tol_{meta}), 7.65 (2 H, d, *J* = 7.9 Hz, Tol_{meta}), 7.77 (2 H, d, *J* = 7.9 Hz, Tol_{meta}), 7.87 (2 H, d, *J* = 8.6 Hz, Ph), 7.90 (2 H, ddd, ^3J = 7.9 Hz, ^3J = 7.6 Hz, ^4J = 1.8 Hz, terpyridine 4, 4'' H), 8.05 (2 H, d, *J* = 8.6 Hz, Ph), 8.10 (4 H, d, *J* = 7.9 Hz, Tol_{ortho}), 8.17 (2 H, d, *J* = 7.9 Hz), 8.19 (2 H, d, *J* = 7.9 Hz, Tol_{ortho}), 8.66 (1 H, br s, imidazole NH), 8.70 (2 H, ddd, ^3J = 8.0 Hz, ^4J = 1.1 Hz, ^5J = 1.0 Hz, terpyridine 3, 3'' H), 8.77 (2 H, ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz, terpyridine 6, 6'' H), 8.79 (2 H, s, terpyridine 3', 5' H), 8.82 (2 H, s, H_β), 8.93 and 8.97 (2 H, AB system, *J* = 4.8 Hz, H_β), 8.93 and 8.98 (2 H, AB system, *J* = 4.8 Hz, H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{70}H_{52}N_9)^+$: 1018.43402; found: 1018.43379 $[M+H]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 422 (5.12), 518 (3.95), 552 (3.64), 588 (3.57), 648 (3.27). IR: ν_{max}/cm^{-1} 3444 (w, NH), 3330 (w, NH), 2954 (w), 2922 (m), 2852 (m), 1717 (m), 1604 (m), 1584 (m), 1568 (m), 1467 (m), 1390 (m), 1268 (m), 1246 (m), 1214 (m), 1181 (m), 1115 (m), 1038 (m), 1019 (m), 979 (m), 966 (m), 853(m), 791 (s), 752 (s), 732 (s), 667 (m), 660 (m).

Imidazo[4,5-*b*]porphyrin 2H-18b was obtained from 2,3-dioxo-5,10,15,20-tetramesitylchlorin (**2H-6b**) (81 mg, 0.1 mmol) and 4'-(4-formylphenyl)-2,2':6',2''-terpyridine (**12**) in 48% (54 mg) yield.

δ_H(300 MHz; $CDCl_3$; 25 °C) -2.66 (2 H, br s, internal NH), 1.85-1.91 (24 H, m, CH_{3ortho}), 2.63 (6 H, s, CH_{3para}), 2.73 (3 H, s, CH_{3para}), 2.82 (3 H, s, CH_{3para}), 7.28 (4 H, br s, Mes), 7.37 (2H, br s, Mes), 7.40 (2 H, ddd, ^3J = 7.4 Hz, ^3J = 4.8 Hz, ^4J = 1.2 Hz, terpyridine 5, 5'' H), 7.53 (2 H, br s, Mes), 7.88 (2 H, d, *J* = 8.6 Hz, Ph), 7.92 (2 H, ddd, ^3J = 7.5 Hz, ^3J = 8.0 Hz, ^4J = 1.8 Hz, terpyridine 4, 4'' H), 8.07 (2 H, d, *J* = 8.6 Hz, Ph), 8.42 (1 H, br s, imidazole NH), 8.60 (2 H, s, terpyridine 3',5' H), 8.72 (2 H, ddd, ^3J = 8.0 Hz, ^4J = 1.1 Hz, ^5J = 1.0 Hz, terpyridine 3, 3'' H), 8.75 and 8.82 (2 H, AB system, *J* = 4.8 Hz, H_β), 8.79 (2 H, ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.9 Hz, terpyridine 6, 6'' H), 8.80 and 8.87 (2 H, AB system, *J* = 4.8 Hz, H_β), 8.84 (2 H, s, 12,13-H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{78}H_{68}N_9)^+$: 1130.55922; found: 1130.55895 $[M+H]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 421 (5.39), 517 (4.26), 548 (3.81), 587 (3.84), 646 (3.47). IR: ν_{max}/cm^{-1} 3415 (w, NH), 3309 (w, NH), 2920 (m), 2852 (m), 1719 (m), 1604 (m), 1584 (m), 1567 (m), 1467 (m), 1443 (m), 1390 (m), 1378 (m), 1266 (m), 1247 (m), 1214 (m), 1170 (m), 1149 (m), 1115 (m), 1102 (m), 1037 (m), 1017 (m), 994 (m), 970 (m), 947 (m), 851 (m), 827 (m), 793 (s), 729 (s), 709 (m), 692 (m), 660 (m).

Imidazo[4,5-*b*]porphyrin 2H-19a was obtained from 2,3-dioxo-5,10,15,20-tetratolylchlorin (**2H-6a**) (70 mg, 0.1 mmol) and 4'-formylbenzo-15-crown-5 (**13**) in 50% (49 mg) yield.

δ_H(300 MHz; $CDCl_3$; 25 °C) -2.90 (2 H, br s, internal NH), 2.70 (6 H, s, CH_3), 2.73 (3 H, s, CH_3), 2.80 (3 H, s, CH_3), 3.77-3.88 (8 H, m, CH_2), 3.91–3.97 (2 H, m, CH_2), 4.01–4.07 (2 H, m, CH_2), 4.16–4.22 (2 H, m, CH_2), 4.26-4.32 (2 H, m, CH_2), 6.92 (1 H, d, *J* = 8.2 Hz, Ph), 7.09 (1 H, dd, ^3J = 8.2, ^4J = 2.0 Hz, Ph), 7.54 (1 H, d, ^4J = 2.0 Hz, Ph), 7.55 (4 H, d, *J* = 7.9 Hz, Tol_{meta}), 7.62 (2 H, d, *J* = 8.0 Hz, Tol_{meta}), 7.72 (2 H, d, *J* = 8.0 Hz, Tol_{meta}), 8.11 (4 H, d, *J* = 7.9 Hz, Tol_{ortho}), 8.15 (2 H, d, *J* = 8.0 Hz, Tol_{ortho}), 8.19 (2 H, d, *J* = 8.0 Hz, Tol_{ortho}), 8.53 (1 H, br s, imidazole NH), 8.81 (2 H, s, 12,13-H_β), 8.91 and 8.96 (2 H, AB system, *J* = 4.9 Hz, H_β), 8.94 and 9.00 (2 H, AB system, J_{AB} = 4.9 Hz, H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{63}H_{57}N_6O_5)^+$: 977.43850; found: 977.43951 $[M+H]^+$; *m/z* calcd for $(C_{63}H_{56}N_6NaO_5)^+$: 999.42044; found: 999.41570 $[M+Na]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 420 (5.44), 518

(4.26), 552 (3.91), 588 (3.84), 647 (3.55). IR: ν_{max}/cm^{-1} 3439 (w, NH), 3316 (w, NH), 2920 (m), 2853 (m), 1721 (m), 1607 (w), 1448 (m), 1406 (w), 1350 (w), 1267 (s), 1247 (m), 1217 (m), 1182 (m), 1161 (m), 1136 (m), 1115 (m), 1053 (m), 1021 (m), 996 (m), 977 (m), 964 (m), 935 (m), 881 (w), 826 (m), 796 (s), 752 (m), 729 (s), 648 (m).

[2-(4-Carboxyphenyl)-1*H*-imidazo[4,5-*b*]-5,10,15,20-tetramesitylporphyrinato]zinc (Zn-16b) was prepared by metallation of **2H-16b** (86 mg, 0.09 mmol) by $Zn(OAc)_2$ (5 equiv) in $CHCl_3$/MeOH (9:1) in 85% (78 mg) yield.
δ_H(300 MHz; $CDCl_3$; 25 °C) 1.84 (12 H, 2, CH_{3ortho}), 1.85 (12 H, 2, CH_{3ortho}), 2.62 (6 H, s, CH_{3para}), 2.65–2.80 (6 H, 2 br s, CH_{3para}), 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$_\beta$), 8.73-8.88 (4 H, br s, 7,8,17,18-H$_\beta$) ppm. HRMS (ESI+): *m/z* calcd for $(C_{64}H_{57}N_6O_2Zn)^+$: 1005.38290; found: 1005.38351 $[M+H]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 429 (5.39), 552 (4.20), 590 (3.90), 620 (3.56). IR: ν_{max}/cm^{-1} 3410 (w, NH), 2915 (m), 2851 (m), 1721 (s), 1692 (s), 1610 (s), 1572(w), 1434 (m), 1375 (w), 1257 (s), 1190 (m), 1097 (m), 993 (s), 951 (w), 852 (w), 796 (m), 752 (m), 724 (m), 555 (w).

[2-(4-Carboxyphenyl)-1*H*-imidazo[4,5-*b*]-5,10,15,20-tetrakis(4-diethoxyphosphoryl)porphyrinato]zinc (Zn-16e) was prepared by metallation of **2H-16e** (66 mg, 0.05 mmol) by $Zn(OAc)_2$ (5 equiv) in $CHCl_3$/MeOH (9:1) in 89% (61 mg) yield.
δ_H(500 MHz; $CDCl_3$/MeOH (2:1); 25 °C) 1.30 (12 H, t, J = 7.1 Hz, CH_3), 1.33 (12 H, t, J = 7.1 Hz, CH_3), 4.09–4.28 (16 H, m, CH_2), 7.63 (2 H, d, J = 8.4 Hz, HO_2C-Ph), 7.91 (2 H, d, J = 8.4 Hz, HO_2C-Ph), 7.95 (4 H, dd, J_{PH} = 13.2 Hz, J = 7.9 Hz, $(EtO)_2OP$-Ph$_{meta}$), 8.07 (4 H, dd, J_{PH} = 13.2 Hz, J = 7.9 Hz, $(EtO)_2OP$-Ph$_{meta}$), 8.14 (4 H, dd, J_{PH} = 4.0 Hz, J = 8.2 Hz, $(EtO)_2OP$-Ph$_{ortho}$), 8.23 (4 H, dd, J_{PH} = 4.0 Hz, J = 8.2 Hz, $(EtO)_2OP$-Ph$_{ortho}$), 8.57 (2 H, d, J = 4.8 Hz, H$_\beta$), 8.59 (2 H, s, H$_\beta$), 8.64 (2 H, d, J = 4.8 Hz, H$_\beta$) ppm. δ_P(121 MHz; $CDCl_3$/MeOH (2:1); 25 °C) 23.52 ppm. HRMS (ESI-): *m/z* calcd for $(C_{68}H_{67}N_6O_{14}P_4Zn)^-$: 1379.29627; found: 1379.29754 $[M-H]^-$. λ_{max} (CH_2Cl_2)/nm (log ε) 318 (3.91), 430 (4.90), 560 (3.74), 598 (3.53). IR: ν_{max}/cm^{-1} 3354 (br, OH), 2977 (m), 2926 (m), 1700 (w), 1599 (m), 1475 (w), 1440 (w), 1389 (m), 1333 (w), 1228 (m), 1160 (m), 1130 (m), 1096 (w), 1013 (s), 938 (s), 763 (s), 725 (s), 637 (w), 578 (s), 455 (m).

Sulfonation of carboxylic acid 2H-5 and M-16.

Porphyrin carboxylic acids were linked with β-Ala(SO_3H) (**20**) according to the two-step procedure consisting of their transformation into reactive *N*-hydroxysuccinimidyl (NHS) esters followed by aminolysis by β-Ala(SO_3H) (**20**).

Step I – General procedure for the preparation of N-hydroxysuccinimide esters M-22.

To a solution of porphyrin carboxylic acid **M-16** (10 µmol) in 200 µL of *N*-methyl-2-pyrrolidone (NMP) were sequentially added a solution of TSTU (10 µmol, 1 equiv) in 100 µL of NMP and 2.0 M solution of DIEA in NMP (25 µL, 50 µmol, 5 equiv). The resulting reaction mixture was stirred at r.t. for 30 min. The reaction progress was monitored by ESI-MS and the reactions were stopped after a full consumption of the starting acid. The NHS esters were characterized by ESI-MS.

2H-22b: LRMS (ESI+): *m/z* calcd for $(C_{68}H_{62}N_7O_4)^+$: 1040.49; found: 1040.55 $[M+H]^+$.
Zn-22b: LRMS (ESI+): *m/z* calcd for $(C_{68}H_{60}N_7O_4Zn)^+$: 1102.40; found: 1102.55 $[M+H]^+$.
Zn-22e: MS (ESI-): *m/z* calcd for $(C_{72}H_{71}N_7O_{16}P_4Zn)$: 1477.32; found: 1478.40 $[M+1]^-$, LRMS (ESI+): *m/z* calcd for $(C_{72}H_{71}N_7O_{16}P_4Zn)$: 1477.32; found: 1502.33 $[M+Na+1]^+$.

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 **2H-21e** was formed in the intermolecular acylation reaction. The reaction mixture was subjected to column chromatography on silica gel using gradual CH_2Cl_2/MeOH (0-5%) system as an eluent. Yield 42% (9 mg).
δ_H(300 MHz; $CDCl_3$; 25 °C) -2.83 (2 H, br s, internal NH), 1.46–1.54 (24 H, m, CH_3), 2.86 (4 H, s, CH_2-CH_2), 4.27–4.44 (16 H, m, CH_2), 8.11 (2 H, dd, J_{PH} = 13.1 Hz, J = 8.1 Hz, $(EtO)_2OP$-Ph$_{meta}$), 8.17 (2 H, dd, J_{PH} = 13.1 Hz, J = 8.1 Hz, $(EtO)_2OP$-Ph$_{meta}$), 8.19 (2 H, dd, J_{PH} = 13.1 Hz, J = 8.1 Hz, $(EtO)_2OP$-Ph$_{meta}$), 8.20 (2 H, dd, J_{PH} = 13.1 Hz, J = 8.1 Hz, $(EtO)_2OP$-Ph$_{meta}$), 8.22 (2 H, dd, J = 8.2 Hz, J_{PH} = 3.9 Hz, $(EtO)_2OP$-Ph$_{ortho}$), 8.28 (2 H, dd, J = 8.2 Hz, J_{PH} = 3.9 Hz, $(EtO)_2OP$-Ph$_{ortho}$), 8.31 (4 H, 2dd, J = 8.2 Hz, J_{PH} =3.9 Hz, $(EtO)_2OP$-Ph$_{ortho}$), 8.61 (1 H, s, 3-H$_\beta$), 8.62 (1 H, d, J = 5.0 Hz, 8-H$_\beta$), 8.71 and 8.72 (2 H, AB system, J_{AB} = 4.9 Hz, 17,18-H$_\beta$), 8.78 (1 H, d, J = 5.0 Hz, 7-H$_\beta$), 8.85 (2 H, br s, 12,13-H$_\beta$) ppm. δ_P(121 MHz; $CDCl_3$; 25 °C) 17.83 (1 P), 18.52 (1 P), 18.60 (2 P) ppm. HRMS (ESI+): *m/z* calcd for $(C_{64}H_{70}N_5O_{14}P_4)^+$: 1256.38642; found: 1256.38851 $[M+H]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 421 (5.59), 518 (4.12), 550 (3.72), 594 (3.59), 647 (3.50). IR: ν_{max}/cm^{-1} 3400 (br, OH), 3328 (w, NH), 2964 (m), 2931 (m), 2874 (m), 1717 (s, C=O), 1683 (s, C=O), 1600 (m), 1475 (m), 1444 (m), 1389 (s), 1349 (m), 1238 (s, P=O), 1163 (m, P–O), 1128 (s), 1047 (s), 1016 (s), 960 (s, P–O), 796 (s), 761 (s), 581 (s).

Step II – General procedure for sulfonation of esters M-22.

To the solution of TBA salt of β-Ala(SO_3H) (**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 semi-preparative RP-HPLC.

2H-3b (purification by RP-HPLC with system A followed by three freeze-drying processes)
δ_H(300 MHz; $CDCl_3$; 25 °C) -2.71 (2 H, br s, internal NH), 1.83 (12 H, s, CH_{3ortho}), 1.84 (12 H, s, CH_{3ortho}), 2.61 (6 H, s, CH_{3para}), 2.69 (6 H, s, CH_{3para}), 3.87–4.09 (2 H, m, CH_2), 4.29-4.46 (1 H, m, CH), 7.25 (4 H, s, Mes), 7.38 (4 H, s, Mes), 7.73 (2 H, d, J = 8.3 Hz, Ph$_{meta}$), 7.87 (1 H, br s, NH), 7.92 (2 H, d, J = 8.3 Hz,

Ph_{ortho}), 8.29 (1 H, br s, imidazole NH), 8.56 (2 H, s, 12,13-H_β), 8.73 and 8.78 (4 H, 2 AB systems, J = 4.8 Hz, 7,8,17,18-H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{67}H_{64}N_7O_6S)^+$: 1094.46333; found: 1094.46406 $[M+H]^+$; *m/z* calcd for $(C_{67}H_{63}N_7NaO_6S)^+$: 1116.44527; found: 1116.44535 $[M+Na]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 421 (5.26), 515 (4.06), 550 (3.71), 589 (3.68), 648 (3.54). IR: ν_{max}/cm^{-1} 3416 (w, OH), 3330 (w, NH), 2955 (s), 2921 (s), 2853 (s), 1646 (m, C=O), 1611 (m), 1550 (m), 1456 (m), 1377 (m), 1214 (m, S=O), 1169 (m), 1038 (m, S=O), 969 (w), 947 (w), 852 (w), 801 (s), 753 (s), 664 (w).

Zn-3b (purification by RP-HPLC with system B followed by three freeze-drying processes)
δ_H(300 MHz; $CDCl_3$; 25 °C) 1.82 (12 H, s, CH_{3ortho}), 1.84 (12 H, s, CH_{3ortho}), 2.61 (6 H, s, CH_{3para}), 2.71 (6 H, s, CH_{3para}), 3.85–4.00 (2 H, m, CH_2), 4.25–4.41 (1 H, m, CH), 7.25 (4 H, s, Mes), 7.38 (4 H, br s, Mes), 7.77 (2 H, d, J = 7.1 Hz, Ph_{meta}), 7.87–7.98 (3 H, m, 2 H Ph_{ortho} + 1 H NH), 8.06 (1 H, s, imidazole NH), 8.67 (2 H, s, 12,13-H_β), 8.71–8.77 (2 H, br s, H_β), 8.77–8.84 (2 H, br s, H_β) ppm. HRMS (ESI+): *m/z* calcd for $(C_{67}H_{62}N_7O_6SZn)^+$: 1156.37683; found: 1156.37844 $[M+H]^+$; *m/z* calcd for $(C_{67}H_{61}N_7NaO_6SZn)^+$: 1178.35877; found: 1178.35803 $[M+Na]^+$. $\lambda_{max}(CHCl_3)$/nm (log ε) 314 (4.54), 428 (5.72), 552 (4.41), 590 (4.09). IR: ν_{max}/cm^{-1} 3416 (br, OH), 2966 (m), 2917 (m), 2852 (m), 1724 (s), 1646 (s, C=O), 1611 (s), 1550 (w), 1552 (m), 1474 (m), 1453 (m), 1376 (w), 1327 (w), 1227 (w, S=O), 1189 (s), 1085 (w), 1037 (s, S=O), 992 (s), 877 (w), 854 (m), 830 (m), 796 (m), 753 (m), 726 (m), 623 (w), 557 (w).

Zn-3e (purification by RP-HPLC with system C followed by three freeze-drying processes)
δ_H(300 MHz; $CDCl_3$; 25 °C) 1.34–1.47 (24 H, m, CH_3), 3.85–3.93 (2 H, m, CH_2), 4.01–4.09 (1 H, m CH), 4.18-4.37 (16 H, m, CH_2), 7.68 and 7.74 (4 H, AB system, J_{AB} = 8.4 Hz, HNCO-Ph), 8.04 (4 H, dd, J_{PH} = 13.0 Hz, J = 7.9 Hz, $(EtO)_2OP$-Ph_{meta}), 8.09–8.20 (4 H, m, $(EtO)_2OP$-Ph_{meta}), 8.20-8.27 (4 H, m, $(EtO)_2OP$-Ph_{ortho}), 8.27–8.34 (4 H, m, $(EtO)_2OP$-Ph_{ortho}), 8.66–8.76 (6 H, m, H_β) ppm. δ_P(121 MHz; $CDCl_3$; 25 °C) 23.52 (3 P, br s), 23.59 (1 P, br s) ppm. HRMS (ESI): *m/z* calcd for $(C_{71}H_{74}N_7O_{18}P_4SZn)^+$: 1532.30475; found: 1532.30150 $[M+H]^+$; *m/z* calcd for $(C_{71}H_{73}N_7NaO_{18}P_4SZn)^+$: 1554.28669; found: 1554.28440 $[M+Na]^+$. λ_{max}(PBS buffer)/nm 315, 406, 443, 563, 601. IR: ν_{max}/cm^{-1} 3366 (br, OH), 2981 (m), 2934 (m), 2903 (m), 1644 (m, C=O), 1598 (s), 1548 (w), 1525 (w), 1476 (w), 1441 (w), 1389 (m), 1227 (s, S=O), 1190 (s), 1161 (m), 1129 (m), 1044 (m), 1012 (s, S=O), 958 (s), 789 (m), 761 (m), 717 (m), 634 (w), 580 (m), 454 (w).

Acknowledgements

Marie-José Penouilh and Fanny Picquet are warmly acknowledged for technical support. Financial support from the CNRS, the Burgundy University, the Council of the Russian President (grant for young scientists MK-272.2014.3) are acknowledged. This work was carried out in the frame of the International Associated French–Russian (LIA) Laboratory of Macrocycle Systems and Related Materials (LAMREM) of CNRS and RAS. Prof R. Guilard acknowledges support from the French Academy of Sciences (Emile Jungfleisch Award). Prof. A. Romieu thanks the Institut Universitaire de France (IUF) and the Burgundy region ("FABER" programme, PARI Action 6, SSTIC 6 "Imagerie, instrumentation, chimie et applications biomédicales") for financial support.[89]

References

1 J.-H. Chou, M. E. Kosal, H. S. Nalwa, N. A. Rakow and K. S. Suslick, in *The Porphyrin Handbook*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, vol. 6, pp. 43.
2 J. A. A. W. Elemans, R. van Hameren, R. J. M. Nolte and A. E. Rowan, *Adv. Mater.*, 2006, **18**, 1251.
3 S. J. Lee and J. T. Hupp, *Coord. Chem. Rev.*, 2006, **250**, 1710.
4 S. Mohnani and D. Bonifazi, *Coord. Chem. Rev.*, 2010, **254**, 2342.
5 J. P. Celli, B. Q. Spring, I. Rizvi, C. L. Evans, K. S. Samkoe, S. Verma, B. W. Pogue and T. Hasan, *Chem. Rev.*, 2010, **110**, 2795.
6 P. D. Harvey, C. Stern and R. Guilard, in *Handbook of Porphyrin Science* World Scientific Publishing, Singapore, 2011, vol. 11, pp. 1.
7 M. K. Panda, K. Ladomenou and A. G. Coutsolelos, *Coord. Chem. Rev.*, 2012, **256**, 2601.
8 M. Q. Simões Mário, M. B. Neves Cláudia, M. G. Pires Sónia, M. G. P. M. S. Neves and A. S. Cavaleiro José, *Pure Appl. Chem.*, 2013, **85**, 1671.
9 Q. Zha, X. Rui, T. Wei and Y. Xie, *CrystEngComm*, 2014, **16**, 7371.
10 D. V. Konarev, S. S. Khasanov and R. N. Lyubovskaya, *Coord. Chem. Rev.*, 2014, **262**, 16.
11 M. da Vicente and K. M. Smith, *Curr. Org. Synth.*, 2014, **11**, 3.
12 M. G. H. Vicente, in *The Porphyrin Handbook*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, vol. 1, pp. 149.
13 L. Jaquinod, in *The Porphyrin Handbook*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, vol. 1, pp. 201.
14 E. V. Vinogradova, Y. Y. Enakieva, S. E. Nefedov, K. P. Birin, A. Y. Tsivadze, Y. G. Gorbunova, A. G. Bessmertnykh-Lemeune, C. Stern and R. Guilard, *Chem. Eur. J.*, 2012, 15092.
15 J.-i. Setsune, *J. Porphyrins Phthalocyanines*, 2004, **8**, 93.
16 H. Shinokubo and A. Osuka, *Chem. Commun.*, 2009, 1011.
17 M. O. Senge, *Chem. Commun.*, 2011, **47**, 1943.
18 H. Yorimitsu and A. Osuka, *Asian J. Org. Chem.*, 2013, **2**, 356.
19 H. J. Shine, A. G. Padilla and S.-M. Wu, *J. Org. Chem.*, 1979, **44**, 4069.
20 A. Giraudeau, H. J. Callot, J. Jordan, I. Ezhar and M. Gross, *J. Am. Chem. Soc.*, 1979, **101**, 3857.
21 J. E. Baldwin, M. J. Crossley and J. DeBernardis, *Tetrahedron*, 1982, **38**, 685.
22 M. M. Catalano, M. J. Crossley, M. M. Harding and L. G. King, *J. Chem. Soc., Chem. Commun.*, 1984, 1535.
23 M. G. H. Vientte, M. G. P. M. S. Neves, J. S. Cavaleiro, H. K. Hombrecher and D. Koll, *Tetrahedron Lett.*, 1996, **37**, 261.
24 A. Sen and V. Krishnan, *Tetrahedron Lett.*, 1996, **37**, 5421.
25 Q. Huang, Z. Pan, P. Wang, Z. Chen, X. Zhang and H. Xu, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 3030.
26 G. D. Bajju, N. Singh and Deepmala, *Chem. Sci. Trans.*, 2014, **3**, 314.
27 P. Wyrębek and S. Ostrowski, *J. Porphyrins Phthalocyanines*, 2007, **11**, 822.

28 M. Chen and H. Scheer, *J. Porphyrins Phthalocyanines*, 2013, **17**, 1.
29 J. L. Worlinsky, G. Zarate, M. Zeller, M. Ghandehari, G. Khalil and C. Brückner, *J. Porphyrins Phthalocyanines*, 2013, **17**, 836.
30 V. I. Vaz Serra, S. M. G. Pires, C. M. A. Alonso, M. G. P. M. S. Neves, A. C. Tomé and J. A. S. Cavaleiro, *Top. Heterocycl. Chem.*, 2014, **33**, 35.
31 J. E. Baldwin and J. F. DeBernardis, *J. Org. Chem.*, 1977, **42**, 3986.
32 H. K. Hombrecher, V. M. Gherdan, S. Ohm, J. A. S. Cavaleiro, M. d. Graça, P. M. S. Neves and M. d. Fátima Condesso, *Tetrahedron*, 1993, **49**, 8569.
33 E. Tsuchida, T. Komatsu, S.-i. Kumamoto, K. Ando and H. Nishide, *J. Chem. Soc., Perkin Trans. 2*, 1995, 747.
34 D.-M. Shen, C. Liu and Q.-Y. Chen, *Eur. J. Org. Chem.*, 2007, **2007**, 1419.
35 S. Weimin, S. Qi, W. Yucheng, L. Lihong and T. Jingchao, *J. Heterocycl. Chem.*, 2010, **47**, 1221.
36 M. E. Lipińska, D. M. D. Teixeira, C. A. T. Laia, A. M. G. Silva, S. L. H. Rebelo and C. Freire, *Tetrahedron Lett.*, 2013, **54**, 110.
37 A. Beeby, R. S. Dickins, S. FitzGerald, L. J. Govenlock, C. L. Maupin, D. Parker, J. P. Riehl, G. Siligardi and J. A. G. Williams, *Chem. Commun.*, 2000, 1183.
38 T. Hasobe, Y. Kashiwagi, M. A. Absalom, J. Sly, K. Hosomizu, M. J. Crossley, H. Imahori, P. V. Kamat and S. Fukuzumi, *Adv. Mater.*, 2004, **16**, 975.
39 M. Espinosa, S. Pacheco and R. Rodriguez, *J. Non-Cryst. Solids*, 2007, **353**, 2573.
40 P. Wyrębek, A. Osuch-Kwiatkowska, Z. Pakulski, S. Jarosz and S. Ostrowski, *J. Porphyrins Phthalocyanines*, 2013, **17**, 384.
41 K. Wang, Q. Jin, X. Zhang and S.-H. Song, *J. Korean Chem. Soc.*, 2013, **57**, 246.
42 A. R. M. Soares, M. V. Martínez-Díaz, A. Bruckner, A. M. V. M. Pereira, J. P. C. Tomé, C. M. A. Alonso, M. A. F. Faustino, M. G. P. M. S. Neves, A. C. Tomé, A. M. S. Silva, J. A. S. Cavaleiro, T. Torres and D. M. Guldi, *Org. Lett.*, 2007, **9**, 1557.
43 J. C. J. M. D. S. Menezes, A. M. V. M. Pereira, M. G. P. M. S. Neves, A. M. S. Silva, S. M. Santos, S. T. Martinez, B. V. Silva, Â. C. Pinto and J. A. S. Cavaleiro, *Tetrahedron*, 2012, **68**, 8330.
44 S. P. Lopes, J. C. J. M. D. S. Menezes, S. Hackbarth, D. C. G. A. Pinto, M. A. F. Faustino, A. M. S. Silva, M. G. P. M. S. Neves, B. Röder and J. A. S. Cavaleiro, *Tetrahedron Lett.*, 2013, **54**, 5253.
45 M. J. Crossley and J. A. McDonald, *J. Chem. Soc., Perkin Trans. 1*, 1999, 2429.
46 M. J. Crossley, P. Thordarson and R. A. S. Wu, *J. Chem. Soc., Perkin Trans. 1*, 2001, 2294.
47 D. Curiel, K. Ohkubo, J. R. Reimers, S. Fukuzumi and M. J. Crossley, *Phys. Chem. Chem. Phys.*, 2007, **9**, 5260.
48 M.-L. Yu, S.-M. Wang, K. Feng, T. Khoury, M. J. Crossley, F. Yang, J.-P. Zhang, C.-H. Tung and L.-Z. Wu, *J. Phys. Chem. C*, 2011, **115**, 23634.
49 S.-H. Lee, A. G. Larsen, K. Ohkubo, Z.-L. Cai, J. R. Reimers, S. Fukuzumi and M. J. Crossley, *Chem. Sci.*, 2012, **3**, 257.
50 Y. Kashiwagi, K. Ohkubo, J. A. McDonald, I. M. Blake, M. J. Crossley, Y. Araki, O. Ito, H. Imahori and S. Fukuzumi, *Org. Lett.*, 2003, **5**, 2719.
51 H. Hayashi, A. S. Touchy, Y. Kinjo, K. Kurotobi, Y. Toude, S. Ito, H. Saarenpää, N. V. Tkachenko, H. Lemmetyinen and H. Imahori, *ChemSusChem*, 2013, **6**, 508.
52 J. R. Reimers, L. K. McKemmish, R. H. McKenzie and N. S. Hush, *Phys. Chem. Chem. Phys.*, 2015, **17**, 24641.
53 M. J. Crossley and L. G. King, *J. Chem. Soc., Chem. Commun.*, 1984, 920.
54 M. J. Crossley, L. G. King, I. A. Newsom and C. S. Sheehan, *J. Chem. Soc., Perkin Trans. 1*, 1996, 2675.
55 A. M. V. M. Pereira, C. M. A. Alonso, M. G. P. M. S. Neves, A. C. Tomé, A. M. S. Silva, F. A. A. Paz and J. A. S. Cavaleiro, *J. Org. Chem.*, 2008, **73**, 7353.
56 A. M. V. M. Pereira, M. G. P. M. S. Neves, J. A. S. Cavaleiro, J.-P. Gisselbrecht, C. Jeandon and R. Ruppert, *J. Porphyrins Phthalocyanines*, 2011, **15**, 575.
57 V. Promarak and P. L. Burn, *J. Chem. Soc., Perkin Trans. 1*, 2001, 14.
58 T. Kopke, M. Pink and J. M. Zaleski, *Chem. Commun.*, 2006, 4940.
59 J. R. McCarthy, H. A. Jenkins and C. Brückner, *Org. Lett.*, 2003, **5**, 19.
60 D. Wagner, D. Gertner and A. Zilkha, *Tetrahedron Lett.*, 1968, 4479.
61 A. Romieu, D. Brossard, M. Hamon, H. Outaabout, C. Portal and P.-Y. Renard, *Bioconjugate Chem.*, 2008, **19**, 279.
62 S. L. Niu, G. Ulrich, R. Ziessel, A. Kiss, P.-Y. Renard and A. Romieu, *Org. Lett.*, 2009, **11**, 2049.
63 S. L. Niu, C. Massif, G. Ulrich, R. Ziessel, P.-Y. Renard and A. Romieu, *Org. Biomol. Chem.*, 2010, **9**, 66.
64 A. Romieu, T. Bruckdorfer, G. Clavé, V. Grandclaude, C. Massif and P.-Y. Renard, *Org. Biomol. Chem.*, 2011, **9**, 5337.
65 T. Traoré, G. Clavé, L. Delacour, N. Kotera, P.-Y. Renard, A. Romieu, P. Berthault, C. Boutin, N. Tassali and B. Rousseau, *Chem. Commun.*, 2011, **47**, 9702.
66 C. Massif, S. Dautrey, A. Haefele, R. Ziessel, P.-Y. Renard and A. Romieu, *Org. Biomol. Chem.*, 2012, **10**, 4330.
67 S.-L. Niu, C. Massif, G. Ulrich, P.-Y. Renard, A. Romieu and R. Ziessel, *Chem. Eur. J.*, 2012, **18**, 7229.
68 W. Bannwarth and R. Knorr, *Tetrahedron Lett.*, 1991, **32**, 1157.
69 R. Knorr, A. Trzeciak, W. Bannwarth and D. Gillessen, *Tetrahedron Lett.*, 1989, **30**, 1927.
70 A. Romieu, C. Massif, S. Rihn, G. Ulrich, R. Ziessel and P.-Y. Renard, *New J. Chem.*, 2013, **37**, 1016.
71 A. Romieu, D. Tavernier-Lohr, S. Pellet-Rostaing, M. Lemaire and P.-Y. Renard, *Tetrahedron Lett.*, 2010, **51**, 3304.
72 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.
73 R. W. Wagner, D. S. Lawrence and J. S. Lindsey, *Tetrahedron Lett.*, 1987, **28**, 3069.
74 C. B. Nielsen and F. C. Krebs, *Tetrahedron Lett.*, 2005, **46**, 5935.
75 J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney and A. M. Marguerettaz, *J. Org. Chem.*, 1987, **52**, 827.
76 R. Kumar, P. Yadav, A. Kumar and M. Sankar, *Chem. Lett.*, 2015, **44**, 914.
77 N. K. Boaen and M. A. Hillmyer, *Macromolecules*, 2003, **36**, 7027.
78 M. Dommaschk, F. Gutzeit, S. Boretius, R. Haag and R. Herges, *Chem. Commun.*, 2014, **50**, 12476.
79 S. Thies, C. Bornholdt, F. Köhler, F. D. Sönnichsen, C. Näther, F. Tuczek and R. Herges, *Chem. Eur. J.*, 2010, **16**, 10074.
80 M. N. Patel, D. S. Gandhi and P. A. Parmar, *Spectrochim. Acta A*, 2011, **84**, 243.
81 J.-P. Collin, A. Harriman, V. Heitz, F. Odobel and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1994, **116**, 5679.
82 I. Abe, K. Hayashi, M. Kitagawa and T. Urahata, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1473.
83 A. M. Brouwer, *Pure Appl. Chem.*, 2011, **83**, 2213.

84 S. Eu, S. Hayashi, T. Umeyama, Y. Matano, Y. Araki and H. Imahori, *J. Phys. Chem. C*, 2008, **112**, 4396.
85 F. R. Kooriyaden, S. Sujatha, B. Varghese and C. Arunkumar, *J. Fluorine Chem.*, 2015, **170**, 10.
86 R. Beavington, P. A. Rees and P. L. Burn, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2847.
87 S. Yang, B. Sun, Z. Ou, D. Meng, G. Lu, Y. Fang and K. M. Kadish, *J. Porphyrins Phthalocyanines*, 2013, **17**, 857.
88 J. G. Hardy, D. J. Mouser, N. Arroyo-Curras, S. Geissler, J. K. Chow, L. Nguy, J. M. Kim and C. E. Schmidt, *J. Mater. Chem. B*, 2014, **2**, 6809.
89 C. M. Carcel, J. K. Laha, R. S. Loewe, P. Thamyongkit, K.-H. Schweikart, V. Misra, D. F. Bocian and J. S. Lindsey, *J. Org. Chem.*, 2004, **69**, 6739.

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)