

Synthesis of Porphyrins β -Tetrasubstituted by Flexible Hydrocarbon Chains

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Abstract—The free base 2,4-bis-(1'-dodecynyl)-deuteroporphyrin IX dioctylester, **6a**, its Zn(II)complex, **Zn-6a**, its Cu(II)complex, **Cu-6a**, its Ni(II)complex, **Ni-6a** and a number of related compounds have been prepared. The synthesis of **6a** involves as key steps the palladium-catalyzed coupling of β -diiodoporphyrin with dodecyne, and the acid-catalyzed esterification of the two propionic acid groups of deuteroporphyrin with *n*-octanol. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

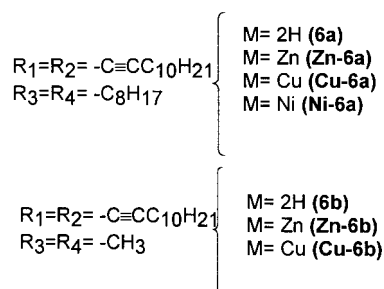
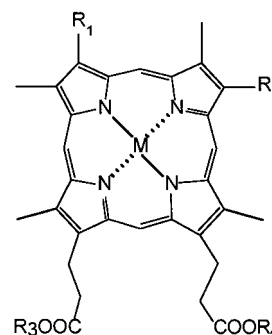
Porphyrins and phthalocyanines peripherally substituted with a number of flexible hydrocarbon chains are of interest in areas as diverse as: (1) the formation of supramolecular stacks¹ and crystals^{1g,2} suitable for energy and/or charge migration; (2) lipid porphyrins³ which, after incorporation into phospholipid vesicles, are of interest as models for biomimetic reactions;⁴ (3) monolayer formation and the study of aggregation and intermolecular interactions within films, as models for a number of biological and photobiological processes;^{5,6} and (4) phototherapeutic agents for the photodynamic therapy of tumors.⁷

As model compounds in which to examine these aspects, porphyrins peripherally substituted by four to eight, identical or not, flexible chains have most often been used,^{1–5,7,8} although a lower number of these substituents is sufficient to study monolayer formation.^{5,6}

These porphyrins and phthalocyanines are usually prepared from the correspondingly substituted pyrroles or phthalonitriles.^{1,2,5} In a number of cases, the flexible side chains substitute the aromatic rings at the *meso* position of the porphyrins.⁸ Alternatively, chemical modification of functional groups present in derivatives of porphyrins of the heme family have been utilized.^{3,6,7,9}

Here, the latter strategy has been used to synthesize a number of hemin **1** derivatives with two to four long flexible chains, with or without a central metal atom. Thus, two dodecynyl residues have been introduced at the (C₂ and C₄) beta positions in a synthetic sequence, which involves

as key step the palladium-catalyzed coupling of the precursor 2,4-diiododeuteroporphyrin IX with dodecyne. In addition, one or two *n*-octyl groups have been introduced both by acid-catalyzed esterification of one or both propionic acid groups of deuteroporphyrin with *n*-octanol, and by nucleophilic substitution of the corresponding porphyrin propionate(s) with *n*-octyl bromide and iodide.



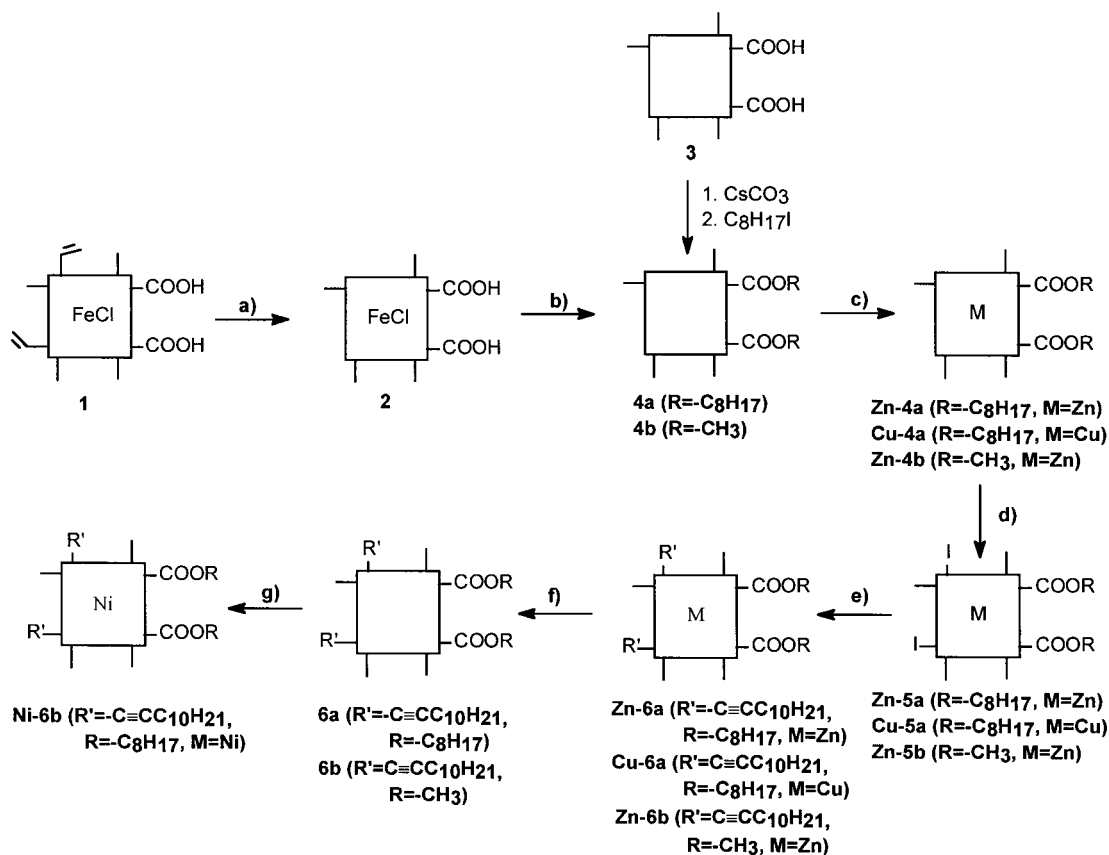
Results and Discussion

We have aimed to develop synthetic strategies to convert porphyrins of the naturally occurring, commercially

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Scheme 1. (a) resorcinol; (b) ROH, FeSO₄·7H₂O, HCl_(g); (c) M(OAc)₂ in MeOH; (d) 1. Hg(OAc)₂, 2. NaBr, 3. I₂; (e) 1-Dodecyne, PdCl₂(PPh₃)₂, CuI; (f) TFA; (g) Ni(acac)₂.

available, heme type into derivatives with up to four flexible chains of about the same length and distributed in an approximately symmetrical fashion around the periphery of the porphyrin macrocycle. We started from the easily accessible deuteroporphyrin-IX **3** (Scheme 1), with two beta unsubstituted positions (at C2 and C4) and two propionic acid groups at C6 and C7. Our strategy was to couple two C12 fragments to the 2,4-positions and two C8 fragments to the propionic acid groups. Various metals (Zn, Cu and Ni) were also inserted to various porphyrinic structures.

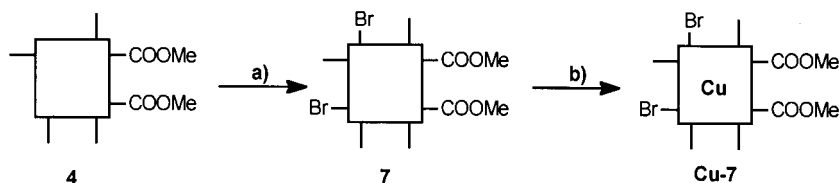
The metal free porphyrin **6a** and its zinc(II) and copper(II) complexes **Zn-6a** and **Cu-6a**, with four flexible alkyl chains in these positions, were synthesized from commercial hemin **1** following the sequence indicated in Scheme 1. Essentially, this sequence includes preparing deuteroporphyrin-IX dioctyl ester **4a**, iodination of **Zn-4a** or **Cu-4a** to the metallated 2,4-diiodo derivative **Zn-5a** or **Cu-5a**, and metal-mediated cross-coupling (Heck reaction) between the zinc(II) or the copper(II) complex and dodecyne to give the 2,4-bis(dodecynyl) derivative **Zn-6a** or **Cu-6a**, respectively. The demetallation of both porphyrins, **Zn-6a** and **Cu-6a**, which was carried out using different conditions (see below), yielded the metal-free porphyrin **6a**. At the same time this last porphyrin **6a** was metallated with Ni, through standard procedures, to give the molecule **Ni-6a**.

Alternatively, the same sequence of synthetic steps was followed using the corresponding dimethyl esters (i.e. via **1**→**Zn-4b**→**Zn-5b**→**Zn-6b**→**6b**). The two strategies are

connected via a transesterification reaction which converts the 2,4-bis-(1'-dodecynyl)-deuteroporphyrin-IX dimethyl ester **6b** to the corresponding di-*n*-octyl ester **6a**.

Deuteroporphyrin-IX dioctyl ester **4a** was obtained in good yield from deuterohemin-IX **2** by simultaneous demetalation and esterification.¹⁰ Alternatively, deuteroporphyrin-IX **3** was first converted into its dicesium salt and the latter was reacted with iodoctane to yield the diester **4a** in addition to the corresponding monoester, which can subsequently be separated by flash chromatography. This procedure results in a lower yield of diester (40%) than the HCl-catalyzed esterification from **2** (80%) but is experimentally easier. When broomooctane was used as an alternative alkylating agent, similar results were obtained.

Iodination of **4a** was successfully carried out as previously reported by Smith et al.,^{11a} in a two-step procedure which involves preparation of zinc(II)-deuteroporphyrin-IX dioctyl ester **Zn-4a** and reaction of its 2,4-bis(chloromercurio) derivative¹² with iodine to afford zinc(II)-2,4-diiododeuteroporphyrin-IX dioctyl ester **Zn-5a**. The same synthetic route was followed to obtain **Cu-5a**. This procedure is clearly superior to direct iodination of **4a** with iodine as previously reported by Bonnett et al.,^{11b} since, in our hands, the latter procedure always yielded difficult mixtures to separate mixtures of the mono- and diiodo derivatives. Similar behaviour is reported by van Lier et al.,¹³ who failed to obtain pure diiododeuteroporphyrin-IX dimethyl ester following Bonnett's description.



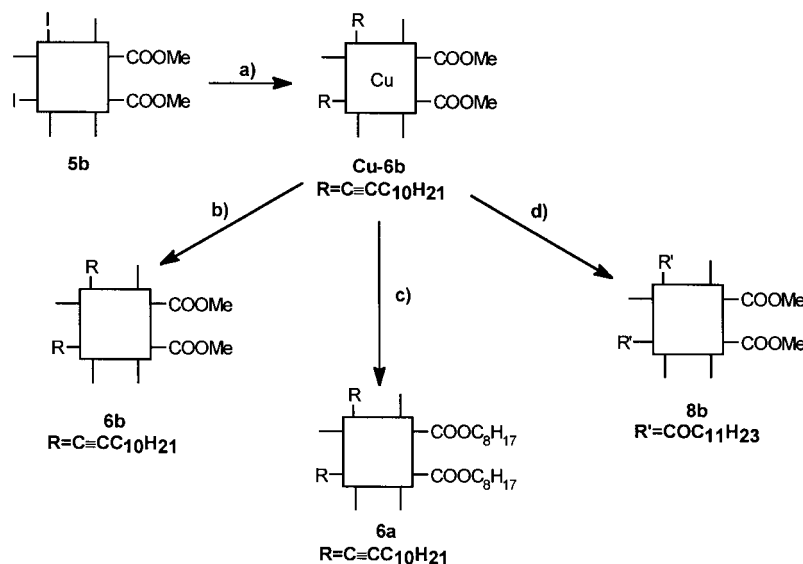
Scheme 2. (a) NBS; (b) 1-dodecyne, CuI, PdCl₂(PPh₃)₂.

We also attempted to prepare the zinc(II)-2,4-diiodo porphyrin **Zn-5a** by direct iodination of the zinc(II)-deuteroporphyrin precursor **Zn-4a** using Bonnett's conditions for the metal free compound.^{11b} Although a zinc(II)-porphyrin should in principle be more reactive towards electrophiles than the corresponding metal free porphyrin, in our case this attempt was unsuccessful since, at the high temperature of the reaction (ca 180°C), the zinc(II) complex **Zn-4a** was completely demetallated, affording the free porphyrin.

For the insertion of two dodecynyl residues into the 2,4-positions of our deuteroporphyrin, we applied the metal-mediated cross-coupling (Heck) reaction successfully used by van Lier et al., to couple a number of alkynes to several monobromo, dibromo and monoiodoporphyrins.¹³ In particular, we prepared the zinc(II)-2,4-bis(dodecynyl)deuteroporphyrin dioctyl ester **Zn-6a** by coupling 1-dodecyne with the zinc(II)-diiodo derivative **Zn-5a**. The use of a metallated porphyrin in this reaction is advisable since when the process is carried out from metal-free porphyrins, the products are invariably the corresponding Cu(II) complexes, and these are much more difficult to demetallate than the zinc(II) complexes. In fact, the strong acid conditions required lead to the simultaneous hydration of the triple bonds at C-2, C-4 (see below). The copper(II) porphyrin **Cu-6a** is also synthesized by the reaction of 1-dodecyne and the copper(II) derivate **Cu-5a**. **Ni-6a** complex was prepared by metallation of the metal free compound **6a**.

In the general procedure described by van Lier, the reaction was carried out in dry triethylamine and, occasionally, dimethylformamide. We found the process extremely sensitive to the presence of water in the amine. In this way, the coupling reaction was first performed with a large excess of the catalyst PdCl₂(PPh₃)₂ (stoichiometric amounts) and the 1-dodecyne (around 5 equiv.). The porphyrins **Zn-6b** and **Cu-6a** were obtained quantitatively in these conditions. The optimum conditions for the synthesis of **Zn-6a** from **Zn-5a** were also studied. The best results, with nearly quantitative yields, required the use of only anhydrous triethylamine and 1.5 equiv. of dodecyne and 20% of the catalyst PdCl₂(PPh₃)₂; however, our yields decreased to 70% when the amount of the diiodo substrate was larger.

The target compound, i.e. the metal-free porphyrin **6a** was obtained quantitatively from **Zn-6a** by brief treatment with trifluoroacetic acid at room temperature. Following essentially the same strategy we also converted deuteroporphyrin-IX dimethyl ester **4b** into its 2,4-bis(dodecynyl) derivative **6b** (Scheme 1). Basically, the arguments given above for the synthetic sequence involving the dioctyl esters are also applicable to the dimethyl esters. In the latter case, however, this conversion was also attempted via the 2,4-dibromodeuteroporphyrin dimethyl ester **7**. In principle, this method should be superior to the one via the diiodo derivative **Zn-5b**, because, in contrast to **Zn-5b**, the dibromo porphyrin **7** can be obtained pure and with good yield by direct bromination of deuteroporphyrin dimethyl ester **4b**.^{11b}



Scheme 3. (a) PdCl₂(PPh₃)₂, 1-dodecyne, CuI; (b) MeOH:CH₂Cl₂ (4:1), HCl_(g), rt, 36 h; (c) *n*-octanol:CH₂Cl₂ (4:1), HCl_(g), rt, 36 h; (d) H₂SO₄ conc. rt, 2 h.

Table 1. Electronic absorption spectra and emission spectra of deuteroporphyrin-IX derivatives in CH₂Cl₂

Porphyrin	Soret: λ (nm) (ϵ , cm ⁻¹ M ⁻¹)	Q bands: λ (nm) (ϵ , cm ⁻¹ M ⁻¹)	λ_{em} (nm) ^a	ϕ_f (%) ^b
4a	398 (179200)	496 (12500), 528 (6600), 565 (4900), 619 (2700)	621, 687	99
Zn-4a	400 (292000)	530 (13200), 566 (16100)	570, 623	97
Cu-4a	397 (393600)	523 (17600), 559 (27300)	570, 685	≅0
Zn-5a	407 (211800)	536 (10300), 573 (13700)	577, 628	5,5
Cu-5a	403 (327700)	529 (15500), 566 (26600)	583, 690	≅0
6a	408 (210000)	507 (17800), 544 (17000), 577 (9900), 633 (7900)	634, 703	97
Zn-6a	413 (253400)	542 (13700), 579 (22300)	542, 632	92
Cu-6a	409 (260500)	535 (11700), 573 (26100)	570, 797	≅0
Ni-6a	402 (210300)	526 (12800), 562 (40300)	570, 633	≅0
4b	398 (152000)	496 (12000), 529 (7000), 566 (5300), 619 (3300)	621, 687	100
Zn-4b	400 (344000)	530 (14600), 566 (18000)	570, 623	100
5b	404 (156000)	502 (12400), 536 (9600), 571 (6000), 625 (3500)	624, 688	3,4
Zn-5b	407 (211800)	536 (10300), 573 (13700)	577, 626	5,5
6b	408 (150000)	508 (12600), 543 (12000), 576 (7000), 632 (5200)	634, 697	93
Zn-6b	413 (230100)	539 (13000), 580 (21400)	583, 637	101
7	402 (168000)	500 (14000), 534 (9500), 570 (6500), 624 (4000)	625, 692	4,6
Zn-7	405 (280000)	535 (14000), 571 (17000)	573, 625	4,1

^a λ_{exc} =400 nm.^b ϕ_f related to **4b** for demetallated porphyrins and **Zn-4b** for metallated porphyrins.

Unfortunately, in our hands, the 2,4-dibromodeuteroporphyrin ester **7** failed to undergo the coupling reaction with dodecyne, and the product obtained was the Cu(II) complex of the starting 2,4-dibromoporphyrin, **Cu-7** (Scheme 2). This result contrasts with the finding by van Lier et al.,¹³ of smooth coupling of a number of alkynes to the Ni(II) and Cu(II) complexes of 2-bromoheptaethylporphyrin. Starting from the zinc(II) complex of 2,4-dibromodeuteroporphyrin-IX dimethyl ester, **Zn-7**, did not improve the results as the starting material was recovered unreacted.

We also attempted the cross-coupling reaction of 1-dodecyne and the metal-free 2,4-diiodoporphyrin **5b** (Scheme 3). The Cu(II) complex of the expected 2,4-bis(dodecynyl)porphyrin, **Cu-6b**, was obtained in 89% yield.

Removal of Cu(II) from **Cu-6b** to yield the metal-free 2,4-bis(dodecynyl)deuteroporphyrin-IX dimethyl ester **6b** was achieved under carefully chosen conditions (MeOH: CH₂Cl₂, 4:1; HCl(g); RT; 36 h). When the Cu(II) was removed from **Cu-6b** using the same conditions, but replacing MeOH with *n*-octanol, transesterification took place simultaneously with demetallation, and the metal-free 2,4-bis-(1'-dodecynyl)-deuteroporphyrin-IX dioctyl ester **6a** was obtained in 67% yield. This led us to connect the two synthetic routes of Scheme 1. In the stronger conditions generally used for removal of Cu(II) (conc. H₂SO₄, RT, 2 h),¹⁴ demetallation of **Cu-6b** was accomplished but the hydration of the two triple bonds of the compound occurred and the 2,4-biscarbonyl porphyrin **8b** was obtained. Analogously, demetallation of the porphyrin **Cu-6a** was carried out using the same conditions (conc. H₂SO₄, RT, 2 h) to give the 2,4-biscarbonyl porphyrin **8a**. The formation of two carbonyl groups at the 2,4-positions of deuteroporphyrin opens the door to the possibility of introducing additional flexible chains, for instance, via Grignard or Wittig reactions, to the porphyrin periphery.

It can be concluded that a new synthetic strategy for the preparation of β -tetraalkylsubstituted porphyrins has been reported. This new method can be summed up in two steps: a palladium-catalyzed reaction between a metal complex of

2,4-diododeuteroporphyrin-IX dimethylester with a alkyne of the desired chain length, followed by a transesterification reaction to obtain the desired diester.

Optical properties

UV-vis and fluorescence spectroscopy were used to monitor the course of the present reactions (Table 1). Essentially, the insertion of halogen atoms in the periphery of a porphyrin results in slight red-shifts in the Soret and Q bands (ca 2 nm for each bromine and ca 3 nm for each iodine) of the absorption spectrum and in similar shifts of the emission bands, as well as in a much greater reduction in the fluorescence quantum yield (to less than 5% of the original value¹⁵). On the other hand, insertion of a metal into the porphyrin results in the well-known reduction from four to two Q bands in the UV-vis spectrum¹⁶ and in the red shift for both Q and B bands. The effect of the different metals on the absorption spectra can be observed in the expected red shift for both Q and b bands along the series Ni(II) < Cu(II) < Zn(II).

For copper and nickel porphyrins, the fluorescence quantum yield is almost imperceptible. It has been described that copper porphyrins, due to their paramagnetic behavior, can show only phosphorescence with relatively short lifetime.¹⁷ The study of several Ni complexes suggests that these complexes do not emit.^{18,19}

The UV-vis and fluorescence spectra in CH₂Cl₂ of the 2,4-bis-(1'-dodecynyl)porphyrin dimethyl esters (metal free **6b** and zinc(II) complex **Zn-6b**) and dioctyl esters (respectively, **6a**, **Zn-6a**) are nearly identical, indicating an imperceptible effect on the structure and state of aggregation by the alkyl chains esterifying the two propionic acid groups of the porphyrin. In contrast, these spectra show large red-shifts (ca 13 nm) relative to those of deuteroporphyrin dimethyl ester **4b** and of mesoporphyrin dimethyl ester (with ethyl groups at C2, C4). The emission bands are also similarly shifted, but the fluorescence quantum yields remain invariant. These shifts probably reflect the electronic

effect of the two triple bonds upon the Π electron system of the macrocycle.

Experimental

Reagents and solvents used for the synthesis were obtained commercially (Aldrich) and were of the highest chemical grade available. Unless otherwise indicated, all were used without further purification. Dimethylformamide (99.8%, Merck) was for residue analysis. It was argon saturated by several cycles of vacuum and argon saturation immediately before use. Absolute tetrahydrofuran was obtained from the commercial material (Normasolv, Barcelona, Spain) by refluxing over LiAlH_4 for 15 min, then distilling from this hydride immediately before use. Similarly, triethylamine (>99%, Merck) and 1,2-dichlorobenzene (>99%, Aldrich) were dried by refluxing over CaH_2 for 15 min, then distilling. Pyridine (>99%, Aldrich) was kept over solid KOH for 24 h and later distilled immediately before use. For the fluorescence experiments, reagent grade CH_2Cl_2 (Normasolv) freshly distilled from K_2CO_3 was used. Immediately before sample preparation, the CDCl_3 used in the NMR measurements was filtered through a short column of basic Al_2O_3 (Act. I, from Merck) and the first few drops were discarded. *N*-bromosuccinimide (Aldrich) was crystallized from water (60 g in 400 ml) and the crystals were washed twice in cold water; mp: 172–176°C.

Deuteroporphyrin-IX dimethyl ester **4b** was obtained from hemin (Aldrich) using the resorcinol (Aldrich, crystallized from benzene; 30 g in 180 ml; mp: 108–109°C) melt procedure, as described by Caughey et al.,¹⁰ 2,4-Dibromodeuteroporphyrin-IX dimethyl ester **2a** was prepared by bromination of **1a** with a 2.2 molar excess of *N*-bromosuccinimide, as reported.^{11b} The Zn-2,4-diiododeuteroporphyrin-IX dimethyl ester **Zn-5b** was prepared from **Zn-4b** in a two-step sequence via the zinc(II) bis-bromomercurated porphyrin, as reported.^{11a}

Analytical thin-layer chromatography (TLC) was carried out either on pre-coated silica gel 60 (230–400 mesh) or on type E neutral alumina plates containing fluorescent indicator (UV 254 nm), and preparative TLC on silica gel 60 plates (0.5 mm width), both from Merck. Flash column chromatography (CC) was carried out either on SDS (France) silica gel 60 (230–400 mesh) or on neutral or activity I basic alumina (Merck, 70–230 mesh). Reactions and sample manipulations were carried out in dim light under argon.

Melting points (not corrected) were determined on a Kofler–Reichert micro hot-stage apparatus. Infrared spectra were obtained on a Perkin–Elmer 681 or a Fourier-Transform Nicolet instrument. UV–vis spectra were recorded on a Perkin–Elmer Lambda 5 or UV/Vis/NIR Cary 5E instrument. Stationary fluorescence spectra were obtained on an SLM-Aminco (Bowman) Series 2 spectrofluorimeter and were determined using air-saturated solutions of absorbance equal to 0.1 at the maximum corresponding to the Soret band (400 nm). Integration of the complete fluorescence spectrum and comparison to deuteroporphyrin dimethyl ester **4b** and to zinc(II)-deuteroporphyrin dimethyl

ester **Zn-4b** yielded the relative fluorescence quantum yields of the metal free porphyrins and their metal complexes, respectively. ^1H and ^{13}C NMR spectra were run on a Varian-Gemini XL-200 (200 MHz) or a Varian-Unity 300 (300 MHz) spectrometer in deuteriochloroform (99.9% d_1 , Merck) or DMSO- d_6 (Merck). Mass spectra were recorded on a triple-quadrupole VG-QUATPRO (Fisons Instruments) spectrometer equipped for FAB(+) analysis with a Capillaritron Frasor, using Xe as the inert gas and nitrobenzyl alcohol (NBA) as the matrix. All spectroscopic measurements were carried out at room temperature.

Zinc-2,4-bis(dodecynyl)deuteroporphyrin-IX dimethyl ester (Zn-6b). Zinc-2,4-diiododeuteroporphyrin-IX dimethyl ester **Zn-5b** (20 mg, 0.023 mmol) was dissolved in 40 ml of dried Et_3N and CuI (10 mg, 0.053 mmol), Pd (II)-bis-triphenylphosphine chloride (20 mg, 0.028 mmol), 1-dodecyne (41 mg, 0.247 mmol) and dried DMF (30 ml), in order to make CuI soluble, were added to the mixture. It was stirred, under an inert atmosphere, for 36 h at room temperature. The solvent was removed and the residue was solved in CH_2Cl_2 , washed in H_2O and purified by column chromatography on SiO_2 . The zinc-2,4-bis-(1'-dodecynyl)-deuteroporphyrin-IX dimethyl ester **Zn-6b** was eluted by CH_2Cl_2 -hexane 10%; the violet amorphous solid **Zn-6b** was obtained (21 mg, 0.023 mmol, 100%). Mp: 130–133°C. TLC (SiO_2 ; CH_2Cl_2 - CH_3OH , 50:1) $R_f=0.61$; IR (KBr, ν , cm^{-1}): 2927 (vib asym methyls β), 2855 (vib sym methyls β), 1736 (ester CO); ^1H NMR (CDCl_3 , δ , ppm): 9.94; 9.92; 9.47; 9.43 (s, H_{meso} , 4H); 4.29; 4.23 (2t, $J=7.5$ Hz, $-\text{CH}_2-\text{CH}_2-\text{COO}-$, 4H); 3.71; 3.64; 3.62 (3s, CH_3 -ring, 12H); 3.56; 3.44 (2s, $-\text{COO}-\text{CH}_3$, 6H); 3.14; 3.10 (2t, $J=7$ Hz, $-\text{CH}_2-\text{C}\equiv\text{C}-$, 4H); 3.06; 3.05 (2t, $J=7.5$ Hz, $-\text{CH}_2-\text{CH}_2-\text{COO}-$, 4H); 2.08 (m, $-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{C}-$, 4H); 1.94 (m, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{C}-$, 4H); 1.35–1.21 (m, $-(\text{CH}_2)_6-$, 24H); 0.91; 0.90 (2t, $-\text{CH}_2-\text{CH}_3$, 6H); ^{13}C NMR (CDCl_3 , δ , ppm): 173.50 (CO); 148.00–136.00 ($\text{C}_{\alpha,\beta}$); 98.70–97.00 (C_{meso}); 100.20 ($-\text{C}\equiv\text{C}-\text{CH}_2-$); 75.70 ($-\text{C}\equiv\text{C}-\text{CH}_2-$); 51.58 ($-\text{COO}-\text{CH}_3$); 36.77 ($-\text{CH}_2-\text{CH}_2-\text{COO}-$); 32.02 ($-\text{CH}_2-\text{C}\equiv\text{C}-$); 29.43; 29.49; 29.60; 29.88; ($-\text{CH}_2-$); 21.68 ($-\text{CH}_2-\text{CH}_2-\text{COO}-$); 20.67; 22.75 ($-\text{CH}_2-$); 14.21; 14.11 ($-\text{CH}_2-\text{CH}_3$); 12.21 (CH_3 -ring); UV–Vis (CH_2Cl_2 , λ , nm (ϵ , $\text{cm}^{-1}\text{M}^{-1}$): 413 (230100), 539 (13000), 580 (21400). Fluorescence (CH_2Cl_2 , $\lambda_{\text{exc}}=400$ nm): λ_{em} (nm)=583, 637; $\phi_f^i=101\%$; MS (FAB+) M+H: 928.36 (100%, ^{64}Zn), 930.62 (63%, ^{66}Zn).

2,4-Bis(dodecynyl)deuteroporphyrin-IX dimethyl ester (6b). **Zn-6b** (12 mg, 0.013 mmol) was dissolved in CH_2Cl_2 (25 ml) and TFA (0.5 ml) was added. The mixture was stirred for 2 min. The violet solution was then washed in water until pH 7. The organic layer was dried with anhydrous Na_2SO_4 and after rotary evaporation, the crude product was purified by column chromatography on silica gel using a solvent mixture of CH_2Cl_2 - CH_3OH (60:1). The dark-red amorphous solid **6b** (6 mg, 0.007 mmol, 64%) was obtained. Mp: 89–93°C. TLC (SiO_2 ; CH_2Cl_2 - CH_3OH , 50:1) $R_f=0.68$; IR (KBr, ν , cm^{-1}): 3310 (st NH), 2927 (vib asym methyls β), 2855 (vib sym methyls β), 1736 (ester CO); ^1H NMR (CDCl_3 , δ , ppm): 10.23; 9.99 (2s, H_{meso} , 4H); 4.38 (m, $-\text{CH}_2-\text{CH}_2-\text{COO}-$, 4H); 3.72; 3.71

(2s, CH₃-ring, 6H); 3.65 (s, -COO-CH₃, 6H); 3.62; 3.61 (2s, CH₃-ring, 6H); 3.27 (m, -CH₂-CH₂-COO-, 4H); 2.99 (t, *J*=7.5 Hz, -CH₂-C≡C-, 4H); 2.04 (m, -CH₂-CH₂-C≡C-, 4H); 1.88 (m, -CH₂-CH₂-CH₂-C≡C-, 4H); 1.31 (m, -(CH₂)₆-, 24H); 0.89 (t, -CH₂-CH₃, 6H); ¹³C NMR (CDCl₃, δ, ppm): 173.45 (CO); 148.00–136.00 (C_{α,β}); 100.78 (-C≡C-CH₂-); 98.43; 97.19; 97.53; 95.93 (C_{meso}); 75.34 (-C≡C-CH₂-); 53.36; 51.64 (-COO-CH₃); 36.75 (-CH₂-CH₂-COO-); 31.90 (-CH₂-C≡C-); 30.84; 29.71; 29.42; 29.96; 29.24 (-CH₂-); 20.45 (-CH₂-CH₂-COO-); 22.66; 21.69 (-CH₂-); 14.06(-CH₂-CH₃); 12.76; 11.52 (CH₃-ring); UV-vis (CH₂Cl₂, λ, nm): 408 (150000), 508 (12600), 543 (12000), 576 (7000); 632 (5200); Fluorescence (CH₂Cl₂, λ_{exc}=400 nm); λ_{em}(nm)=634, 697; φ_f^r=93%; MS (FAB+): M+H: 867.5 (100%); Anal. Calcd for C₅₆H₇₄N₄O₄: C, 77.56; H, 8.60; N, 6.46. Found: C, 77.41; H, 8.44; N, 6.68.

Deuteroporphyrin-IX dioctyl ester (4a). A solution containing Deuterohemin-IX (1 g, 1.67 mmol), *n*-octanol (500 ml), FeSO₄·7H₂O (8 g, 28.78 mmol) was saturated with HCl (g) for 8 h. The solution was then stirred for 14 h at room temperature. The crude material was washed with water, 10% aqueous ammonia, and again water. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed by evaporation. This yielded 1.073 g of a red solid which was chromatographed on silica gel with CH₂Cl₂ as eluant. **4a** (976 mg, 1.33 mmol, 80%), which is a powdered red solid, was eluted from the column. Mp: 114–118°C. TLC (SiO₂; CH₂Cl₂) R_f=0.81; IR (KBr, ν, cm⁻¹): 3313 (st NH), 2927 (vib asym methyls β), 2855 (vib sym methyls β); 1732 (CO ester); ¹H NMR (CDCl₃, δ, ppm): 10.17; 10.14; 10.09; 10.05 (4s, H_{meso}, 4H); 9.09 (s, H_{2,4}, 2H); 4.43 (t, *J*=7.6 Hz, -CH₂-CH₂-COO-, 4H); 4.03 (t, *J*=6.8 Hz, -CH₂OCO-, 2H); 3.77; 3.74; 3.68; 3.64 (4s, CH₃-ring, 12H); 3.29 (t, *J*=7.6 Hz, -CH₂-CH₂-COO-, 4H); 0.97 (m, -(CH₂)₆-, 24H); 0.76 (t, *J*=6.8 Hz, -(CH₂)₆-CH₃, 6H); -3.81 (s, NH, 2H); ¹³C NMR (CDCl₃, δ, ppm): 173.26 (CO); 148.00–136.00 (C_{α,β}); 128.70 (C_{2,4}); 100.20; 99.44; 97.09; 96.11 (C_{meso}); 64.79 (-CH₂-OCO-); 37.11 (-CH₂-CH₂-COO-); 31.59 (-CH₂CH₂OCO-); 28.99; 28.92; 28.89; 25.70; 22.46 (-CH₂-); 21.91 (-CH₂-CH₂-COO-); 13.97 (-CH₂-CH₃); 11.70; 11.67 (CH₃-ring); UV-vis (CH₂Cl₂, λ, nm): 398 (179200), 496 (12500), 528 (6600), 565 (4900), 619 (2700); Fluorescence (CH₂Cl₂, λ_{exc}=400 nm); λ_{em}(nm)=621, 687; φ_f^r=99%; MS (FAB+): M+H: 735.4 (100%); Anal. Calcd for C₄₆H₆₂N₄O₄: C, 75.17; H, 8.50; N, 7.62. Found: C, 75.15; H, 8.70; N, 7.33.

Zinc-deuteroporphyrin-IX dioctyl ester (Zn-4a). Deuteroporphyrin-IX dioctyl ester **4a** (970 mg, 1.32 mmol) was dissolved in CH₂Cl₂ (260 ml) and a saturated solution of Zn(OAc)₂·2H₂O in CH₃OH (32 ml). The mixture was stirred under reflux for 20 min. This crude was washed three times in water, dried over anhydrous Na₂SO₄ and evaporated to dryness. 960 mg of pink solid was purified on silica gel. The powdered pink solid **Zn-4a** (776 mg, 0.974 mmol, 74%) was eluted by CH₂Cl₂. Mp: 146–148°C. TLC(SiO₂; CH₂Cl₂-CH₃OH 10:1) R_f=0.93; (SiO₂; CH₂Cl₂) R_f=0.34; IR (KBr, ν, cm⁻¹): 2927 (vib asym methyls β), 2855 (vib sym methyls β); 1736 (CO ester); ¹H NMR (CDCl₃, δ, ppm): 9.44; 9.26 (s, H_{meso}, 4H); 8.73;

8.63 (2s, H_{2,4}, 2H); 4.15; 4.07 (2t, *J*=7.5 Hz, -CH₂-CH₂-COO-, 4H); 3.93; 3.91 (2t, *J*=6.9 Hz, -CH₂-OCO-, 4H); 3.54; 3.45; 3.41; 3.26 (4s, CH₃-ring, 12H); 3.04; 2.99 (2t, *J*=7.5 Hz, -CH₂-CH₂-COO-, 4H); 0.89 (m, -CH₂-, 24H); 0.70 (t, *J*=6.9 Hz, -CH₂-CH₃, 6H); ¹³C NMR (CDCl₃, δ, ppm): 173.30 (CO); 147.72; 147.44; 147.14; 146.39; 146.19; 146.04; 140.22; 139.65; 138.45; 138.03; 136.42; 136.16 (C_{α,β}); 128.44; 128.66 (C_{2,4}); 100.22; 99.49; 96.65; 95.64 (C_{meso}); 64.66; 64.63 (-CH₂-OCO-); 37.11 (-CH₂-CH₂-COO-); 31.54, 29.70; 28.95; 28.89; 28.44; 25.64; 22.42 (CH₃- (CH₂)₆-); 21.70; 21.62 (-CH₂-CH₂-COO-); 13.95 (CH₃- (CH₂)₇-); 13.49; 13.40; 11.49; 11.34 (CH₃-ring); UV-vis (CH₂Cl₂, λ, nm): 400 (292000), 530 (13200), 566 (16100); Fluorescence (CH₂Cl₂, λ_{exc}=400 nm); λ_{em}(nm)=570,623; φ_f^r=97%; MS (FAB+): M+H: 796.6 (100%, ⁶⁴Zn).

Zinc-2,4-diiododeuteroporphyrin-IX dioctyl ester (Zn-5a). Zinc-deuteroporphyrin-IX dioctyl ester **Zn-4a** (159 mg, 0.188 mmol) was dissolved in THF (20 ml) and 250 mg of Hg(OAc)₂ (250 mg, 0.784 mmol) dissolved in CH₃OH (3.3 ml) and, Ac₂O (1.4 ml) was added. This solution was stirred at 60°C for 5 h. The mixture was then cooled to room temperature and saturated solution of NaBr (17 ml) was added. The stirring was maintained for 30 min. The organic layer was then washed with water, dried over anhydrous Na₂SO₄ and evaporated. This yielded **zinc-2,4-bis(bromomercurio)deuteroporphyrin-IX dioctyl ester** (211 mg, 0.156 mmol, 83%). Mp: 210–213°C. TLC (SiO₂; CH₂Cl₂-CH₃OH 10:1) R_f=0.91; IR (KBr, ν, cm⁻¹): 2927 (vib asym methyls β), 2857 (vib sym methyls β); 1736 (ester CO); UV-vis (CH₂Cl₂, λ, nm (ε/ε′)): 387 (10.6); 406 (13.76); 540 (1); 574 (1.10).

Zinc-2,4-bis(bromomercurio)deuteroporphyrin-IX dioctyl ester (161 mg, 0.12 mmol) was dissolved in anhydrous THF (18 ml) and CH₂Cl₂ (43 ml). I₂ (89 mg, 0.351 mmol) in CH₂Cl₂ (87 ml) was added and the mixture stirred for 15 min at room temperature. The organic layer was washed in water, dried over Na₂SO₄ and evaporated. A powdered red solid **Zn-5a** was obtained (111 mg, 0.106 mmol, 56%). Mp: 196–200°C. TLC (SiO₂; CH₂Cl₂) R_f=0.38; IR (KBr, ν, cm⁻¹): 2927 (vib asym methyls β), 2857 (vib sym methyls β), 1734 (ester CO); ¹H NMR (CDCl₃, δ, ppm): 8.92; 8.80; 8.51; 8.41 (s, H_{meso}, 4H); 4.11; 4.08 (2t, *J*=7.5 Hz, -CH₂-CH₂-COO-, 4H); 3.94; 3.91 (2t, *J*=6.9 Hz, -CH₂-OCO-, 4H); 3.37; 3.18; 3.15; 3.10 (4s, CH₃-ring, 12H); 2.97; 2.92 (2t, *J*=7.5 Hz, -CH₂-CH₂-COO-, 4H); 0.97–0.79 (m, -(CH₂)₆-CH₃, 24H); 0.67 (t, *J*=6.9 Hz, CH₃-CH₂-, 6H); ¹³C NMR (CDCl₃, δ, ppm): 173.30 (CO); 146.56–128.94 (C_{α,β}); 64.61 (-CH₂-OCO-); 37.09 (-CH₂-CH₂-COO-); 31.48; 29.63; 28.89; 28.37; 25.58; 22.35 (-CH₂-); 21.50 (-CH₂-CH₂-COO-); 13.89 (CH₃-CH₂-); 13.50; 13.44; 11.48; 11.38 (CH₃-ring); UV-vis (CH₂Cl₂, λ, nm): 407 (211800), 536 (10300), 573 (13700); Fluorescence (CH₂Cl₂, λ_{exc}=400 nm); λ_{em}(nm)=577, 626; φ_f^r=5.5%; MS (FAB+): M+H: 1047.8 (100%, ⁶⁴Zn), 1050.1 (67%, ⁶⁶Zn); Anal. Calcd for ZnC₄₆H₅₈N₄O₄I₂: C, 52.60; H, 5.58; N, 5.33. Found: C, 52.58; H, 5.65; N, 5.42.

Zinc-2,4-bis(dodecynyl)deuteroporphyrin-IX dioctyl ester (Zn-6a). **Zn-5a** (50 mg, 0.048 mmol), PdCl₂(PPh₃)₂ (10 mg, 0.014 mmol), CuI (19 mg, 0.1 mmol) and 1-dode-

cyne (20 mg, 0.120 mmol) were dissolved in anhydrous Et₃N (6 ml). The mixture was stirred at room temperature, under argon atmosphere for one day. The Et₃N was removed by evaporation and the dark residue was dissolved in CH₂Cl₂, washed four times with water and the CH₂Cl₂ was evaporated off. The residue was purified on SiO₂, eluted with CH₂Cl₂:hexane (10%). The amorphous pink solid **Zn-6a** was obtained (53 mg, 0.047 mmol, 98%). Mp: 56°C, CCPA (SiO₂, CH₂Cl₂) R_f: 0.66; IR (KBr, ν , cm⁻¹): 2927 (vib asym methyls β), 2857 (vib sym methyls β); 1736 (ester CO); ¹H NMR (CDCl₃, δ , ppm): 9.73; 9.70; 9.14; 9.13 (4s, H_{meso}, 4H); 4.29; 4.15 (2t, J=7.8 Hz, -CH₂-CH₂-COO-, 4H); 3.93; 3.91 (2t, J=6.9 Hz, -COO-CH₂-, 4H); 3.66; 3.53; 3.51; 3.33 (4s, CH₃-ring, 12H); 3.08; 3.07 (t, J=7.2 Hz, -CH₂-C≡C-, 4H); 3.08; 3.00 (t, J=7.8 Hz, -CH₂-CH₂-COO-, 4H); 2.12 (m, -CH₂-CH₂-C≡C-, 4H); 1.96 (m, -CH₂-CH₂-CH₂-C≡C-, 4H); 1.25 (m, -CH₂-, 48H); 0.82 (m, -CH₂-CH₃ dodecyn alkyl chains, 48H); 0.69 (m, -CH₂-CH₃ octyl chains, 6H); ¹³C NMR (CDCl₃, δ , ppm): 173.20 (CO); 147.71; 147.39; 146.47; 146.20; 142.23; 141.36; 138.62; 138.13; 136.88; 136.38; 131.86; 128.25; 123.91; 123.80 (C_{α,β}); 100.00 (-C≡C-(CH₂)₉-); 98.59; 97.57; 96.93; 95.72 (C_{meso}); 75.50 (-C≡C-(CH₂)₉-); 64.50 (-COO-CH₂-); 36.94 (-CH₂-CH₂-COO-); 31.94 (-C≡C-CH₂-); 31.44 (-C≡C-CH₂-CH₂-); 29.79; 29.52; 29.42; 29.35; 28.77; 28.30; 25.49; 22.68; 22.33 (-CH₂-); 20.59 (-CH₂-CH₂-COO-); 14.21 (-CH₂-CH₃); 13.87 (CH₃-ring); UV-vis (CH₂Cl₂, λ , nm): 413 (253400), 542 (13700), 579 (22300); fluorescence (CH₂Cl₂, λ_{exc} =400 nm); λ_{em} (nm)=542, 632; ϕ_f^r =92%; MS (FAB+) M+H: 1126.7 (100%, ⁶⁴Zn), 1128.7 (46%, ⁶⁶Zn).

2,4-Bis(dodecynyl)deuteroporphyrin-IX dioctyl ester (6a). In analogy to the synthesis of **6b**, **Zn-6a** (56 mg, 0.050 mmol), was demetallated to give the amorphous dark-red solid **6a** (52 mg, 0.049 mmol, 98%). Mp: 81–82°C; CCPA (SiO₂/CH₂Cl₂) R_f: 0.35; IR (KBr, ν , cm⁻¹): 3310 (NH st), 2925 (vib asym methyls β), 2855 (vib sym methyls β), 1733 (ester CO); ¹H NMR (CDCl₃, δ , ppm): 10.17; 9.92; 9.89 (3s, H_{meso}, 4H); 4.36 (m, -CH₂-CH₂-COO-, 4H); 4.02 (t, J=6.6 Hz, -COOCH₂-, 4H); 3.72; 3.69; 3.62; 3.57 (4s, CH₃-ring, 12H); 3.24 (m, -CH₂-C≡C-, 4H); 3.01 (t, J=7 Hz, -CH₂-CH₂-COO-, 4H); 2.04 (m, -CH₂-CH₂-C≡C-, 4H); 1.89 (m, -CH₂-CH₂-CH₂-C≡C-, 4H); 1.38–0.94 (m, -CH₂-, 48H); 0.90 (t, J=6.6 Hz, -CH₂-CH₃ dodecyn alkyl chains, 6H); 0.76 (t, J=6.6 Hz, -CH₂-CH₃ octyl chains, 6H); -3.90 (s, NH, 2H); ¹³C NMR (CDCl₃, δ , ppm): 173.12 (CO); 144.69; 142.14; 141.38; 138.57; 137.14; 136.8; 123.99; 123.99 (C_{α,β}); 100.80 (-C≡C-CH₂-); 98.50; 97.61; 97.24; 96.19 (C_{meso}); 75.46; 75.41 (-C≡C-CH₂-); 64.78 (-COOCH₂-); 37.06 (-CH₂-CH₂-COO-); 31.97 (-CH₂-C≡C-); 31.59 (-CH₂-CH₂-C≡C-); 29.79; 29.49; 29.43; 29.35; 29.32; 28.98; 28.91; 28.45; 25.69; 22.73; 22.46; 21.84 (-CH₂-); 20.52 (-CH₂-CH₂-COO-); 14.13; 13.98 (-CH₂-CH₃); 12.84; 11.63 (CH₃-ring); UV-vis (CH₂Cl₂, λ , nm): 408 (210000), 544 (17000), 507 (17800), 577 (9900), 633 (7900); Fluorescence (CH₂Cl₂, λ_{exc} =400 nm); λ_{em} (nm)=634, 703; ϕ_f^r =97%; MS (FAB+): M+H: 1064.2 (100%), Anal. Calcd for C₇₀H₁₀₂N₄O₄: C, 79.05; H, 9.68; N, 5.27. Found: C, 79.08; H, 9.72; N, 5.32.

Copper-deuteroporphyrin-IX dioctyl ester (Cu-4a). Deuteroporphyrin-IX dioctyl ester **4a** (111 mg, 0.151 mmol) was dissolved in CH₂Cl₂ (15 ml) and saturated solution of Cu(AcO)₂ in MeOH (15 ml) was added. The resulting mixture was stirred and heated at reflux for 1 h. The solution was poured into water and the organic layer was separated and dried over anhydrous Na₂SO₄. After evaporation of the solvent, the copper porphyrin was purified by silica flash chromatography, with CH₂Cl₂ as eluent, to give the powdered red solid **Cu-4a** (99 mg, 0.124 mmol, 83%). Mp: 153–155°C. TLC (SiO₂; CH₂Cl₂) R_f=0.30; IR (KBr, ν , cm⁻¹): 2925 (vib asym methyls β), 2856 (vib sym methyls β); 1735 (CO ester); UV-vis (CH₂Cl₂, λ , nm): 397 (393600), 523 (17600), 559 (27300); Fluorescence (CH₂Cl₂, λ_{exc} =400 nm); λ_{em} : 570, 685; ϕ_f^r ≅0%; MS (FAB+): M+H: 796.6 (100%, Cu⁶³); 798.7 (46%, Cu⁶⁵).

Copper-2,4-diiododeuteroporphyrin-IX dioctyl ester (Cu-5a). In analogy to the preparation of **Zn-5a**, copper-deuteroporphyrin-IX dioctyl ester **Cu-4a** (99 mg, 0.124 mmol) gave Copper(II)-2,4-bis(bromomercurio)-deuteroporphyrin-IX dioctyl ester (150 mg, 0.111 mmol, 89%). Mp: 272–275°C. TLC (SiO₂; CH₂Cl₂:MeOH(50:1)) R_f=0.92; IR (KBr, ν , cm⁻¹): 2927 (vib asym methyls β), 2856 (vib sym methyls β); 1737 (CO ester); UV-vis (CH₂Cl₂, λ , nm): 387 (79000), 402 (83000), 528 (6500), 572 (9800).

The iodination of copper(II)-2,4-bis(bromomercurio)-deuteroporphyrin-IX dioctyl ester (150 mg, 0.111 mmol) yielded the powdered red solid **Cu-5a** (107 mg, 0.102 mmol, 92%). Mp: 203–205°C. TLC (SiO₂; CH₂Cl₂) R_f=0.55; IR (KBr, ν , cm⁻¹): 2927 (vib asym methyls β), 2856 (vib sym methyls β); 1735 (CO ester), 589 (C–I, st); UV-vis (CH₂Cl₂, λ , nm): 403 (327700), 529 (15500), 566 (26600); Fluorescence (CH₂Cl₂, λ_{exc} =400 nm); λ_{em} (nm)=583, 690; ϕ_f^r ≅0%; MS (FAB+): M+H: 1047.4 (100%, Cu⁶³); 1049.4 (52%, Cu⁶⁵).

Copper-2,4-bis-(1'-dodecynyl)-deuteroporphyrin-IX dioctyl ester (Cu-6a). In the same way that **Zn-6b** was obtained, **Cu-5a** (50 mg, 0.048 mmol) were converted to the amorphous bright-red solid **Cu-6a** (53 mg, 0.035 mmol, 99%). Mp: 87–88°C. TLC (SiO₂; CH₂Cl₂) R_f=0.47; IR (KBr, ν , cm⁻¹): 2925 (vib asym methyls β), 2856 (vib sym methyls β); 1733 (CO ester); UV-vis (CH₂Cl₂, λ , nm): 409 (260500), 535 (11700), 573 (26100); Fluorescence (CH₂Cl₂, λ_{exc} =400 nm); λ_{em} =570, 797; ϕ_f^r ≅0%; MS (FAB+): M+H: 1124.0 (100%, Cu⁶³); 1126.0 (55%, Cu⁶⁵).

Nickel-2,4-bis-(1'-dodecynyl)-deuteroporphyrin-IX dioctyl ester (Ni-6a). 2,4-bis-(1'-dodecynyl)-deuteroporphyrin-IX dioctyl ester **6a** (25 mg, 0.024 mmol) and Ni(acac)₂^{7d} (30 mg, 0.117 mmol) were dissolved in CHCl₃ (3 ml). The solution was stirred under reflux. After 40 h, the solvent was evaporated off and the crude material was purified by chromatography on SiO₂ **Ni-6a** (20 mg, 0.018 mmol, 77%), an amorphous red solid, was eluted with CH₂Cl₂:MeOH (100:0.2). Mp: 60–62°C. TLC (SiO₂/CH₂Cl₂) R_f: 0.33; IR (KBr, ν , cm⁻¹): 2927 (vib asym methyls β), 2856 (vib sym methyls β); 1733 (ester CO); ¹H NMR (CDCl₃, δ , ppm): 9.70; 9.34; 9.28 (s, H_{meso}, 4H);

4.13 (m, $-CH_2-CH_2-COO-$, 4H); 3.99 (m, $-COOCH_2-$, 4H); 3.53; 3.44; 3.43; 3.31 (4s, CH_3 -ring, 12H); 3.06 (m, $-CH_2-C\equiv C-$, 4H); 2.98 (t, $J=7$ Hz, $-CH_2-CH_2-COO-$, 4H); 2.03 (m, $-CH_2-CH_2-C\equiv C-$, 4H); 1.87 (m, $-CH_2-CH_2-CH_2-C\equiv C-$, 4H); 1.38–0.94 (m, $-CH_2-$, 48H); 0.91 (t, $J=7$ Hz, $-CH_2-CH_3$ dodecyl alkyl chains, 6H); 0.77 (t, $J=7$ Hz, $-CH_2-CH_3$ octyl chains, 6H); ^{13}C NMR ($CDCl_3$, δ , ppm): 173.16 (CO); 142.14; 141.79; 141.41; 140.93; 140.69; 140.55; 139.31; 138.99; 137.51; 137.16; 130.88; 128.82; 124.31 ($C_{\alpha,\beta}$); 100.23 ($-C\equiv C-CH_2-$); 99.12; 98.08; 97.68; 96.22 (C_{meso}); 75.28; 75.20 ($-C\equiv C-CH_2-$); 64.71 ($-COOCH_2$); 36.90 ($-CH_2-CH_2-COO-$); 31.98 ($-CH_2-C\equiv C-$); 31.60 ($-CH_2-CH_2-C\equiv C-$); 29.79; 29.69; 29.50; 29.43; 29.39; 29.31; 29.00; 28.94; 28.44; 25.67; 22.73; 22.46; 21.73 ($-CH_2-$); 20.48 ($-CH_2-CH_2-COO-$); 14.13; 13.97 ($-CH_2-CH_3$); 12.78; 12.73; 11.54; 11.46 (CH_3 -ring); UV–Vis (CH_2Cl_2 , λ , nm): 402 (210300), 526 (12800), 562 (40300); Fluorescence (CH_2Cl_2 , $\lambda_{exc}=400$ nm); $\lambda_{em}(nm)=570, 633$; $\phi_f^r=0\%$; MS (FAB+): M+H: 1119.8 (Ni^{58} , 100%).

2,4-Bis-(1'-oxododecyl)-deuteroporphyrim-IX dioctyl ester (8a). The metallated porphyrin **Cu-6a** (28 mg, 0.025 mmol) was dissolved in concentrated H_2SO_4 (20 ml). The mixture was stirred for 2 h at room temperature. The crude material was poured into cold water (100 ml) and K_2CO_3 was added until a dark-brown solid precipitated. This solid was dissolved and extracted with CH_2Cl_2 . The organic layer was washed twice with water, dried over anhydrous Na_2SO_4 and evaporated to dryness. The product was purified by chromatography on SiO_2 , using CH_2Cl_2 : MeOH (0.5%) as eluant, and was obtained an amorphous dark-red solid **8a** (19 mg, 0.017 mmol, 69%). Mp: 61–63°C; CCPA (SiO_2 ; $CH_2Cl_2-CH_3OH$, 50:1) R_f : 0.84; IR (KBr, ν , cm^{-1}): 3310 (NH st), 2927 (vib asym methyls β), 2856 (vib sym methyls β), 1735 (ester CO), 1652 (ketone CO); 1H NMR ($CDCl_3$, δ , ppm): 10.66; 10.50; 9.86; 9.84 (4s, H_{meso} , 4H); 4.32 (t, $J=8.1$ Hz, $-CH_2-CH_2-COO-$, 4H); 4.00; 3.99 (2t, $J=8.1$ Hz, $-COOCH_2-$, 4H); 3.86; 3.83 (2s, CH_3 -ring, 6H); 3.62 (m, $-CO-CH_2-$, 4H); 3.57 (s, CH_3 -ring, 6H); 3.23; 3.21 (2t, $J=8.1$ Hz, $-CH_2-CH_2-COO-$, 4H); 2.17 (m, $-CO-CH_2-CH_2-$, 4H); 1.67–0.94 (m, $-CH_2-$, 56H); 0.87 (t, $J=8.1$ Hz, $-CH_2-CH_3$ dodecyl alkyl chains, 6H); 0.75 (t, $J=8.1$ Hz, $-CH_2-CH_3$ octyl chains, 6H); –3.66 (s, NH, 2H); ^{13}C NMR ($CDCl_3$, δ , ppm): 203.04 (CO ketone); 173.10 (CO ester); 154.05–125.59 ($C_{\alpha,\beta}$); 102.32; 100.03; 97.87 96.17 (C_{meso}); 64.81 ($-COOCH_2-$); 45.56 ($COCH_2$); 36.84 ($-CH_2-CH_2-COO-$); 31.89–22.41 ($-CH_2-$); 25.66 ($CO-CH_2$); 21.50 ($-CH_2-CH_2-COO-$); 14.07; 13.94 ($-CH_2-CH_3$); 11.72; 11.57 (CH_3 -ring); UV–Vis (CH_2Cl_2 , λ , nm): 415 (119920), 512 (10800), 548 (7150), 581 (5690), 634 (2700); Fluorescence (CH_2Cl_2 , $\lambda_{exc}=400$ nm); $\lambda_{em}(nm)=640, 691$; $\phi_f^r=27.5\%$; MS (FAB+): M+H: 1100.98(100%); Anal. Calcd for $C_{70}H_{106}N_4O_6$: C, 76.46; H, 9.72; N, 5.09. Found: C, 76.45; H, 9.86; N, 4.89.

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