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# Formation, structure, and reactivity of *meso*-tetraaryl-chlorolactones, -porpholactams, and -chlorolactams, porphyrin and chlorin analogues incorporating oxazolone or imidazolone moieties†‡

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Reaction of known *meso*-tetraarylporpholactone free bases **3**, made from the corresponding porphyrins, with hydrazine produces three products: It converts the lactone functional group into an *N*-aminolactam moiety, generating porphyrin-like *N*-aminoporpholactams **8**. It also reduces regioselectively the β,β′-double bond of the pyrrolic moiety opposite to the imidazolone in both the starting material and the *N*-aminoporpholactam, thus forming the chlorin-like chlorolactones **7** and *N*-aminochlorolactams **9**. An equivalent set of reaction products is also derived from the reaction of porpholactones **3** with tosylhydrazide. Reductive N–N cleavage of the *N*-aminoporpholactams **8** generated the parent porpholactams **10**. The molecular structures of all key compounds were shown by single crystal X-ray diffraction to be essentially planar. Porpholactam **10a** can be converted in two steps (enolization and halogenation α to the imine, followed by reductive removal of the halogen) to known imidazoloporphyrin **5a**, thus constituting the third independent pathway to replace a β-carbon of a tetraphenylporphyrin by a nitrogen. All these transformations show the flexibility of our 'porphyrin breaking and mending' strategy toward the synthesis of novel porphyrin and chlorin analogues incorporating non-pyrrolic heterocycles that carry functionalities at their periphery.

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## Introduction

The synthesis of chlorins (2,3-dihydroporphyrins) has received considerable attention in recent years because they possess UV-visible spectra that are generally red-shifted and endowed with strongly enhanced $\lambda_{max}$ absorbance bands when compared to the spectra of the corresponding porphyrins.[1,2] These properties are utilized in nature where chlorins are the most prominent photosynthetic pigments.[3,4] Chlorins promise also to be of use in a number of technical (light harvesting)[5,6] and biomedical applications (*e.g.*, tumor imaging and photodynamic therapy).[3,7] Particularly chromophores that allow a facile modulation of their optical or solubility properties are of interest.

Efficient and scaleable total syntheses of chlorins have recently been described by the group of Lindsey.[8] Alternatively, chlorins can be made from porphyrins by removing one of the β,β′-double bonds from macrocycle conjugation. For instance, 1,3-dipolar cycloadditions, Diels–Alder reactions, and reductions have been used to accomplish this.[9] The classic reductant is diimide.[10,11] This reduction results in the most straight forward formation of chlorins but, for notable exceptions,[11] these unsubstituted chlorins and bacteriochlorins tend to be unstable with respect to reversion (oxidation) to the parent porphyrin.

We described the formal oxidation of *meso*-tetraarylporphyrins, such as **1**, with $OsO_4$ to form the corresponding dihydroxychlorins, such as **2**. The chlorin diols are a versatile class of chlorins that are relatively stable toward air oxidation (Scheme 1).[12–15]

We also described multiple ways in which the diol functionality in **2** can be used as a synthetic handle toward the generation of a range of other porphyrin- and chlorin-like chromophores.[14,18,19] For instance, oxidation of chlorin **2**

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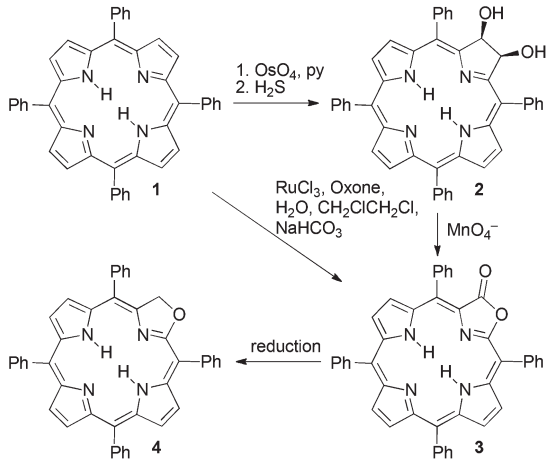
‡Electronic supplementary information (ESI) available: $^1H$, $^{13}C$ NMR, UV-vis, and IR spectra of all novel compounds and experimental details to the crystal structure determination of **7a**, **8c**, **9c**, and **15a**, including their CIF files. CCDC 919810–919813. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ob40138c




**Scheme 1** Synthesis of porpholactone **3** and oxazolochlorin **4** along the 'porphyrin breaking and mending strategy'.[16,17]

generates porpholactone **3** in which a pyrrole was formally replaced by an oxazolone moiety.[14,15,17,20] Alternative syntheses for porpholactones are known, several of which appeared well before our reports.[20–22] A recently described ruthenium-catalyzed oxidation strategy also makes porpholactones available from the corresponding porphyrins in a single efficient step.[23] The lactone moiety in the free base porpholactones mimics the electronic properties of the β,β′-double bond. Thus, their UV-visible spectra are very similar to those of the corresponding porphyrin (Fig. 1A).[17,22]

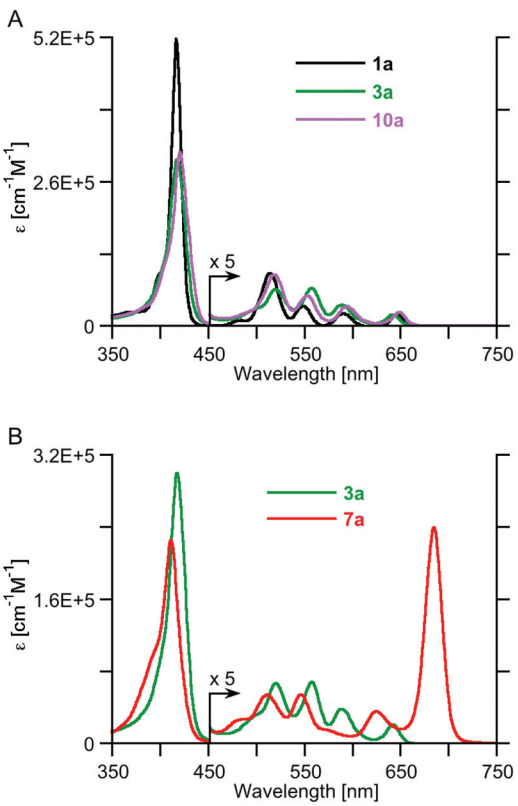
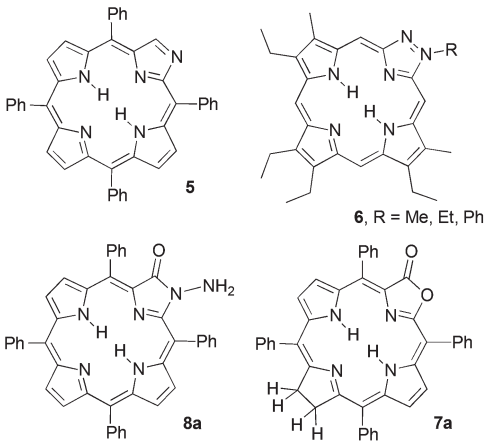



**Fig. 1** UV-visible spectra ($CH_2Cl_2$) of the porphyrinoids indicated.

Porpholactones found utility as catalysts,[24] or were used as sensor dyes in pressure-sensing paints.[25,26] A porpholactone metal complex also served as a high pH-sensing chromophore.[15] Only relatively few organic transformations of porpholactones were reported to date. We described the reduction of porpholactones to generate oxazolochlorins, such as the oxidatively sensitive parent compound **4**.[17,27] More robust α-alkylated oxazolochlorins (and oxazolobacteriochlorins) can be generated from porpholactone **3** by alkylation reactions.[28] The alkylation reactions using Grignard reagents, hydride reductions, and the reaction with hydroxide and methoxide, the fundamental reaction on which the high pH sensor relies,[15] show the susceptibility of the lactone carbonyl to nucleophilic attack.




Applying our 'porphyrin breaking and mending strategy' to dihydroxychlorin **2**, other heterocycles could also be introduced.[12,14,16,19,29–31] For instance, a β-carbon of a porphyrin can also be replaced in a multi-step sequence with a nitrogen atom, generating imidazoloporphyrin **5**.[16]

Porphyrin analogues that maintain the principle porphyrinoid macrocycle structure but in which one (or two) C or N atoms were exchanged for other heteroatoms have become a widely investigated class of porphyrinoids.[32–34] The β-functionalities of porphyrins in general,[35] and those of the pyrrole-modified porphyrins in particular, potentially enable their application in sensing and molecular recognition applications.[15,25,36] Aside from the N-confused porphyrins, a class of carbaporphyrins carrying a 2,4-linked pyrrole pointing its nitrogen to the outside and a β-carbon to the inside,[34,37] the introduction of nitrogens to the β-positions of (aza-)porphyrins is, however, relatively rare. We are aware of only one other true porphyrin analogue containing β-nitrogens, pyrazoloporphyrin **6**,[38] prepared by total synthesis.[39]

In a preliminary report we described the reaction of porpholactone **3** with hydrazine, generating *N*-aminoporpholactams, such as **8a**.[31] Incidentally, the reaction of the porpholactones with hydrazine also led to a reduction of the porpholactones to form the novel chlorin-like chromophores, such as chlorolactone **7a**.[31] The reduction of porpholactam **8a** to the corresponding chlorolactam was observed as well.[31]

We will disclose here the details of these transformations, the structures of the novel chromophores, as determined by single crystal X-ray diffractometry, and their reactivity. We will further detail the consequences of the modifications on the optical properties of these compounds, and we will report on an alternative route toward imidazoloporphyrins by step-wise manipulation of porpholactams, thus establishing a third independent pathway toward this intriguing pyrrole-modified porphyrin class.[16]

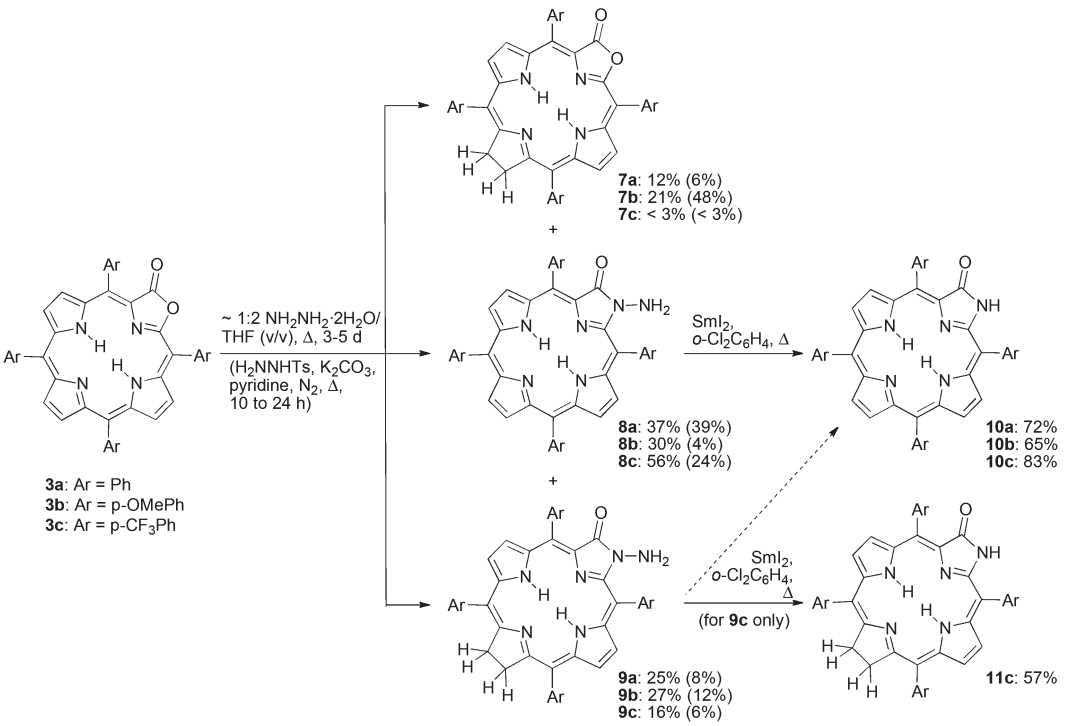
## Results and discussion

### Reaction of porpholactones with hydrazine hydrate

Reaction of porpholactones **3** with a large stoichiometric excess of hydrazine hydrate in THF (~1 : 2 v/v) at refluxing temperatures forms, over the course of 3–5 days, one minor (in 12% yield) and two major products (in 37% and 25% yields) of the compositions $C_{43}H_{30}N_4O_2$ (**7a**), $C_{43}H_{30}N_6O$ (**8a**) and $C_{43}H_{32}N_6O$ (**9a**), respectively (compositions determined by ESI+ HR-MS) (Scheme 2). The composition of product **7a** suggested that a two-hydrogen reduction of starting porpholactone **3a** ($C_{43}H_{28}N_4O_2$) had taken place. Indeed, the UV-vis spectrum of product **7a** is, in contrast to the porphyrin-like spectrum of porpholactone **3a**, 46 nm red-shifted ($\lambda_{max}$ = 686 nm) and chlorin-like (Fig. 1B). The $^1$H NMR spectrum of **7a** identifies four non-equivalent pyrrolidine β-protons (4.06–3.98 ppm), while the retention of the lactone moiety was indicated by its IR ($\nu_{C=O}$ at 1757 cm$^{-1}$) and $^{13}$C NMR (quaternary carbon at 170 ppm) spectra. The absence of isomers of this novel chromophore and the chemical shift similarity of the four sp$^2$-hybridized β-protons suggests that a regioselective reduction had taken place at the pyrrolic moiety opposite of the oxazolone moiety. The structure of **7a** could be confirmed by single crystal X-ray diffractometry (see below). We suggest to name this chromophore chlorolactone, reflecting its chlorin-like optical properties and the presence of the lactone moiety.

A pronounced effect of the *meso*-aryl substituents on the outcome of the reaction of porpholactones **3** with hydrazine (or diimide generated *in situ*, see below) is noticeable. A switch from *meso*-phenyl to the more electron-rich *meso*-4-methoxyphenyl groups (*i.e.*, reacting *meso*-tetrakis(4-methoxyphenyl)-porpholactone **3b**) doubles the yield of the corresponding *meso*-tetrakis(4-methoxyphenyl)chlorolactone **7b** in case of the hydrazine reaction and makes this chlorolactone the main product in the reaction of **3b** with diimide. Inversely, subjecting the relatively less electron-rich *meso*-tetrakis(α,α,α-trifluorotolyl)-substituted porpholactone **3c** to either reduction conditions yields only traces (<3%) of the corresponding chlorolactone **7c**.

There is precedence for a hydrazine-induced reduction of a porphyrin to a chlorin.[40] However, the classic method for the synthesis of hydroporphyrins from porphyrins is using diimide (HN=NH) as the reductant. Diimide is formed by reaction of tosylhydrazide in the presence of base ($K_2CO_3$) at elevated temperatures (reflux temperature of pyridine). Applied to **3a**, this reaction forms chlorolactone **7a** in only 6% yield and also the *N*-aminoporpholactam **8** and -chlorolactam **9** (see




**Scheme 2** Formation of chlorolactones **7**, *N*-aminoporpholactams **8**, *N*-aminochlorolactams **9**, porpholactams **10**, and chlorolactam **11c** by conversion of porpholactones **3**.

below).[41] The reaction with tosylhydrazide is significantly faster (10–24 h) than the reaction with hydrazine hydrate.

The composition of the major product **8** ($C_{43}H_{30}N_6O$ for **8a**) resulting from the reaction of **3** with hydrazine hydrate is suggestive of the take-up of hydrazine by porpholactone **3**, with concomitant loss of water (Scheme 2). $^1$H and $^{13}$C NMR spectroscopic data of the products were indecisive whether a hydrazone or an *N*-aminolactam had formed. IR spectroscopy supported the lactam formulation ($\nu_{C=O}$ at 1686 cm$^{-1}$). This was confirmed by single crystal diffractometry (discussed below; Fig. 4). In essence, the lactone oxygen was replaced by a hydrazinyl moiety.

Interestingly, the O-to-$NNH_2$ exchange had only minor effects on the optical properties of the chromophores as product **8** retains the porphyrin-like spectra of the porpholactones (**8a**: $\lambda_{max}$ = 651 nm, **8b**: $\lambda_{max}$ = 653 nm, **8c**: $\lambda_{max}$ = 651 nm), with only ~8 nm red-shifts of the $\lambda_{max}$ bands (Fig. 2). Again, it appears that the lactam sp$^2$-carbon also effectively mimics the electronic effects of a β,β′-bond. We suggest the trivial name porpholactam for this chromophore. Thus, derivatives **8** are *N*-aminoporpholactams.

The third product **9**, generally formed as the second most abundant product in the hydrazine reactions, possesses a composition that suggested both a lactone-to-lactam conversion and a reduction had taken place ($C_{43}H_{32}N_6O$ for **9a**). As observed for the reduction of porpholactone **3a** to chlorolactone **7a**, the $\nu_{C=O}$ frequency measured for porpholactam **8a** (at 1686 cm$^{-1}$) and its corresponding chlorin analogue **9a** (at 1678 cm$^{-1}$) are close to each other. Parallel to the generation of a red-shifted chlorin-like optical spectrum upon reduction of porpholactone **3** to chlorolactone **7**, reduction of porpholactam **8** to form **9** also generates a chromophore with a chlorin-like optical spectrum (Fig. 2). The UV-vis spectra of *N*-aminochlorolactam **9** (**9a**: $\lambda_{max}$ = 695 nm, **9b**: $\lambda_{max}$ = 695 nm, **9c**: $\lambda_{max}$ = 697 nm) are very similar to the spectra of the corresponding chlorolactones, except for a ~10 nm red-shift, mirroring the relative positions of their corresponding parent compounds. Correspondingly, we name these chromophores chlorolactams. The structure of the *N*-aminochlorolactam **9a** could also be confirmed by X-ray diffractometry (discussed below; Fig. 4).

Perceivably, chlorolactam **9a** can either be formed as the reduction product of **8a** or as the substitution product of chlorolactone **7a**. Indeed, reaction of porpholactam **8a** with hydrazine forms the corresponding chlorolactam. However, isolated chlorolactone **7a** does not undergo any substitution reaction with hydrazine, even after extended reaction times. This may be a consequence of the generally increased HOMO level of chlorins *versus* porphyrins.[2]

Intriguingly, when the reaction of porpholactones **3** with hydrazine is performed under anoxic conditions ($N_2$ atmosphere), little to no chlorolactone **7** and chlorolactam **9** are formed and the major product becomes the *N*-aminolactam **8**. We cannot provide an explanation for this finding except to suggest that this seems to point at an oxidatively or radical-induced step in the reduction of a porphyrinoid with hydrazine.

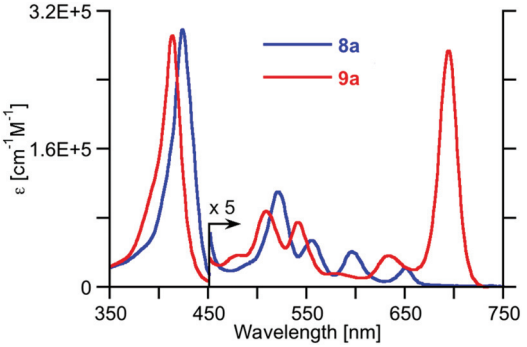



**Fig. 2** UV-visible spectra ($CH_2Cl_2$) of the porphyrinoids indicated.

### N–N cleavage of the *N*-aminolactams

The reductive N–N cleavage of hydrazine derivatives using $SmI_2$ is known.[42] This reaction can also be applied to *N*-aminoporpholactams **8**, generating the parent porpholactams **10** in good yield (Scheme 2). This reaction leads to the expected change in composition ($C_{43}H_{29}N_5O$ for **10a**) with a significant change in the $\nu_{C=O}$ vibrational frequency of the product (1703 cm$^{-1}$). The most diagnostic feature in the $^1$H NMR spectrum of **10a** for the conversion is the replacement of the signals assigned to the $NH_2$-group protons at 4.13 ppm in starting material **8a** by a signal at 9.64 ppm, assigned to the lactam NH group. The UV-visible spectrum of **10** is nearly identical to that of the starting material (Fig. 1A), while that of **11** is chlorin-like (Fig. 3) (**10a**: $\lambda_{max}$ = 649 nm, **10b**: $\lambda_{max}$ = 650 nm; **11c**, $\lambda_{max}$ = 701 nm). Again, suitable crystals for an analysis by single crystal diffractometry confirmed the connectivity of the chromophore (discussed below; Fig. 4).

As this N–N cleavage reaction proceeds only at elevated temperatures (*o*-dichlorobenzene, reflux, bp = 180.5 °C), only the least electron-rich and presumably more oxidation-resistant *N*-amino chlorolactam **9c** could be converted to the corresponding parent chlorolactam **11c**. The more electron-rich derivatives **9a** and **9b** underwent the desired N–N cleavage but concomitantly also oxidized to the corresponding porpholactams.

Theoretically, porpholactams **10** could be derived from lactones **3** by reaction with ammonia. However, we failed to

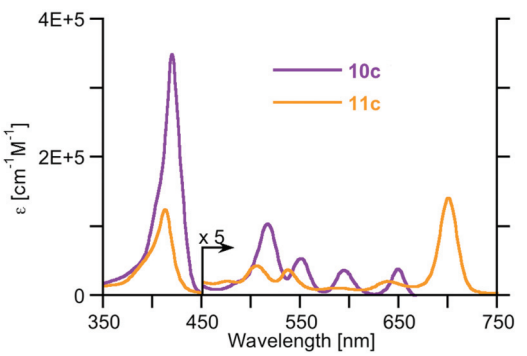



**Fig. 3** UV-visible spectra ($CH_2Cl_2$) of the porphyrinoids indicated.

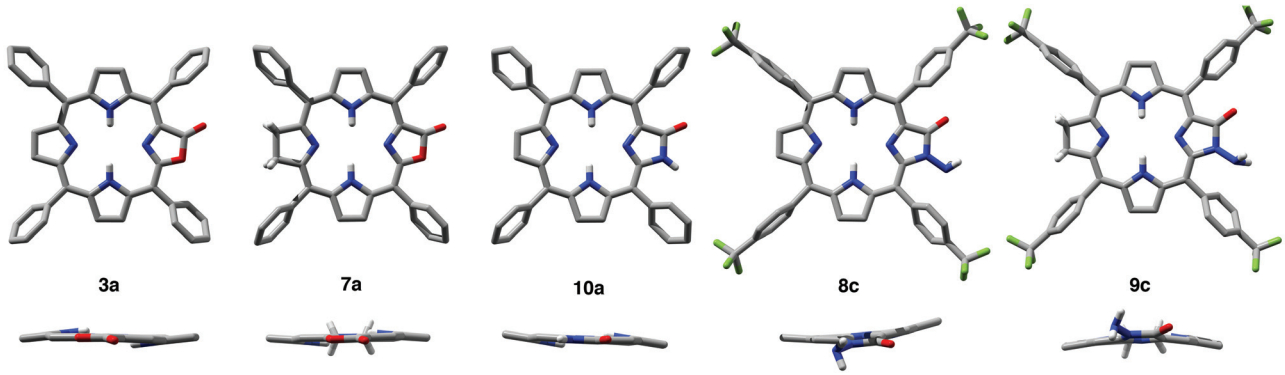


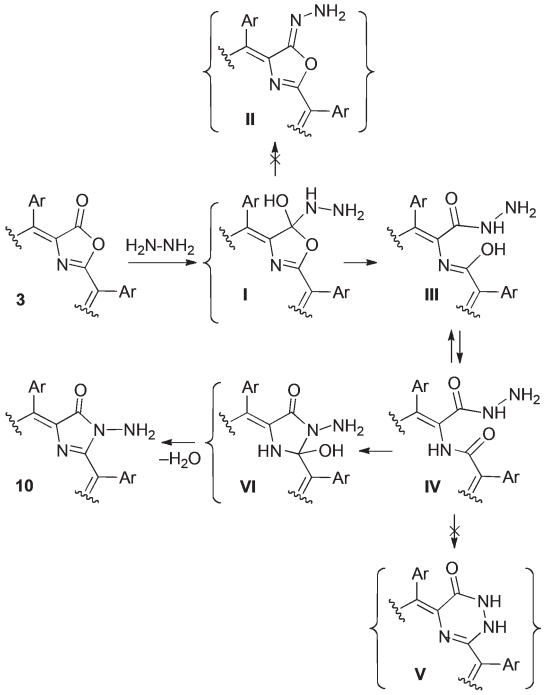

**Fig. 4** Single crystal X-ray structure of porpholactone **3a**[17] (included for comparison), chlorolactone **7a**, porpholactam **10a**,[48] *N*-aminoporpholactam **8c**,[49] and *N*-aminochlorolactam **9c**,[50] top (top) and side (bottom) views. All hydrogen atoms attached to $sp^2$-hybridized carbon positions and all disorder and solvent, when present, have been omitted for clarity; in addition, the phenyl groups were removed in the side views. For details to the crystal structures, see ESI.‡

induce this reaction under a range of conditions (aq. and anhyd. $NH_3$, different solvents, temperatures, slightly elevated pressures, presence of Lewis acids, *etc.*). Perhaps the increased nucleophilicity of hydrazine is required for the substitution reaction to proceed.

### Mechanistic considerations

Over the course of the reaction, we never observed any ring-opened or other intermediates or hydrazones. The propensity of lactones to undergo an aminolysis reaction with hydrazine is well known.[43] Also, one pot, two-step and direct, one-step conversions of lactones to lactams are known; the conversion of the oxazolidinones to imidazolidinones are particularly well studied.[44] Thus, the transformation of lactone **3** to lactam **10** does, in principle, not surprise. On the other hand, the reaction is unusual in several aspects as a more detailed look at a possible mechanism of this reaction will illustrate (Scheme 3).

Many lactones, such as coumarins, react with hydrazine to form ring-opened γ-hydroxyhydrazides.[45] However, considering that the five-membered lactone in **3** is being rigidly held in position by the porphyrinic macrocycle, any ring-opening reaction may be inhibited or prevented. Thus, following the nucleophilic attack of **3** by hydrazine, forming intermediate **I**, the formation of hydrazone **II** would not have been an unreasonable outcome of the reaction. However, this reaction is not observed. Evidently, a ring-opening of intermediate **I** to form **III** did indeed take place. The γ-hydroxy group in **III** thus established is the hydroxy group of the imidol tautomeric form of an amide that can be expected to be in equilibrium with its amide tautomeric form **IV**. Amide **IV** is set up to undergo a condensation reaction with either one of the hydrazide nitrogens. However, this reaction is highly selective as the reaction with the terminal amine group leading to the formation of the six-membered hydro-1,3,4-triazine **V** is not observed. Instead, the five-membered imidazolidinone is formed by reaction of the amidic NH group with the neighboring amidic carbonyl group, thus forming intermediate **VI**. This subsequently dehydrates, thereby reestablishing the porphyrinic π-conjugated




**Scheme 3** Proposed mechanism of the lactone-to-lactam conversion and possible other reactions.

system. We attribute the formation of the five-membered ring to the overwhelming steric preference for five-membered rings within the porphyrinoid macrocycle,[46] though porphyrinoids containing, for example, a pyrazine moiety, are known.[30,47] This reaction highlights that the established chemistry of the oxazolidones with amines is transferable into the context of porphyrin chemistry, even if the reaction mechanism evokes the temporary perturbation of the aromatic ring current. It is reasonable to assume that the porphyrinic ring would more strongly enforce the formation of a five-membered ring product than any unrestricted substrate. Alas, since we are not aware of reports on the reaction of oxazolidones with hydrazine, the latter conclusion must remain speculative.

### Structural characterization of chlorolactones, porpholactam, and chlorolactams

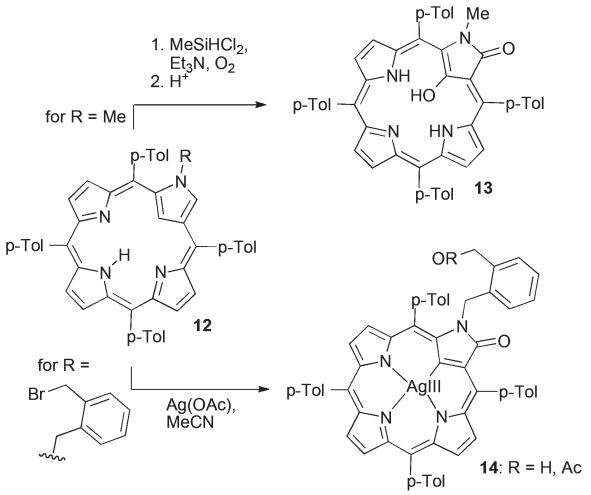
The structures of chlorolactone **7a**, porpholactam **10a**,[31] *N*-aminoporpholactam **8c**, and *N*-aminochlorolactam **9c** were determined by single crystal X-ray diffraction (Fig. 4). The molecular structures of the essentially planar free base porpholactone **3a** was reported previously and is included here as the benchmark compound.[17] The structures confirm the atom connectivities of the novel chromophores but more importantly, they also prove the conformation of the macrocycles (in the solid state) to be all idealized planar. The structure of the phenyl-derivatives **8a** and **9a** are near-identical to the structures of **8c** and **9c** shown,[47,48] highlighting the generality of the findings. In other words, the replacement of a pyrrole by any one or two five-membered heterocycles pyrroline, imidazole, imidazolone, or oxazolone does not disturb the overall planarity of the parent porphyrin. However, as already observed for the porpholactone and imidazoloporphyrin structures,[16,17] the non-pyrrolic moiety is frequently disordered over several positions, somewhat limiting the detailed metric analyses of these macrocycles (for details, see ESI‡).

Nonetheless, some trends and details are discernable. The small deviation from planarity in the solid state conformations of porpholactam **10a** and chlorolactone **7a** are similar to the deviations also observed for *meso*-tetraarylporphyrin free bases **1**.[51] In all cases, the two pyrroles carrying the NH groups are slightly tilted out of plane to minimize the steric interaction of the inner NH groups.

In comparison, the *N*-amino-substituted chromophores **8c** and **9c** are slightly more non-planar, likely because of a larger steric interaction of the *N*-amino group with the flanking phenyl group. The *N*-amino groups in **8c** and **9c** are H-bonded to solvate molecules (EtOH), highlighting their ability to interact with the surroundings, a prerequisite for the utilization of these molecules in, for instance, sensing applications. Hydroporphyrins are generally more conformationally flexible than porphyrins. Correspondingly, chlorin-type chromophore **9c** (and **9a**)[48] is slightly more saddled than porphyrin-type chromophore **8c** (or **8a**).[47] Irrespective of the small deviations from planarity, neither the atom positions and thermal ellipsoids in the structures nor any broadening of the UV-vis spectra of the compounds indicate the presence of a conformationally flexible chromophore.

### Comparison to other porphyrinoids containing a β,β′-lactam moiety

Both the β,β′-reduction of porpholactones as well as the porpholactone-to-porpholactam conversions detailed above have not been, outside of our earlier communication,[31] reported before. Nonetheless, γ-lactams have been reported in a benziporphodimethene,[52] calixphyrin,[53] N-confused hexaphyrin,[54] and N-confused porphyrins.[36,55] They were established by means of (often fortuitous) oxidations of a pyrrolic building block of the macrocycle (Scheme 4). The introduction of the β,β′-lactam moieties in carbaporpholactams **13** and **14** is



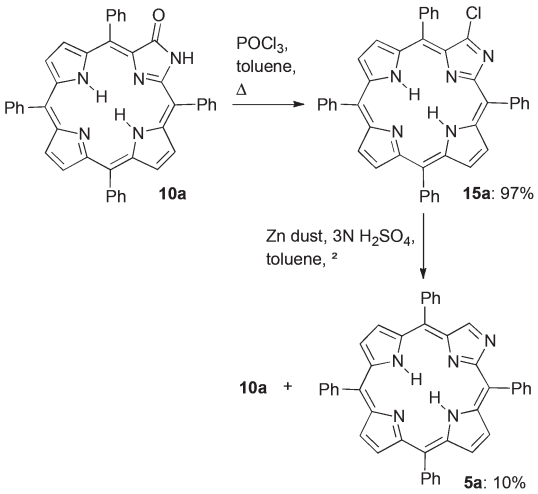

**Scheme 4** Formation of carbaporpholactones **13** and **14** by oxidation of *N*-substituted N-confused porphyrin **12** according to Chmielewski and Latos-Grażyński.[56]

representative of these reactions.[56] Oxidations of *N*-benzylated or *N*-methylated N-confused porphyrin **12**, as its silane complex or free base, using oxygen or silver(I) as oxidant forms the corresponding N-substituted carbaporpholactams **13** and **14**, respectively. Internal *C*-oxidation or a metalation reaction also have taken place.[56] This oxidation sensitivity of the α-carbon of the inverted pyrrole was observed previously during the synthesis of N-confused porphyrins.[55] In comparison, we did not observe any oxidation sensitivity of the porpholactams. Except for the partial structural similarity with the porpho- and chloro-lactams reported here, compounds **13** and **14** are much different because they are subject to very different electronic substituent and conformational effects. Therefore, no similarity in their optical properties with those of the porpho- and chloro-lactams are evident.

### Porpholactam to imidazoloporphyrin conversions

The amide functionality of porpholactam **10a** is susceptible to enolization with concomitant hydroxy-to-chlorine substitution using phosphoryl chloride ($POCl_3$) in refluxing toluene, yielding 3-chloroimidazoloporphyrin **15a** in excellent yield (Scheme 5).

The imine-peak in the $^1$H NMR spectrum is diagnostic for the known parent imidazoloporphyrin **5a**. Chloride **15a** is, naturally, devoid of this diagnostic handle. However, the compound possesses the expected porphyrin-like UV-vis spectrum and the expected composition. 3-Chloroimidazoloporphyrin **15a** also exhibits an optical response to protonation much different from the parent compound **5a** (Fig. 5). Exposure of **15a** to TFA produces a UV-vis spectrum that is reminiscent of a porphyrin protonated at the central nitrogens,[57] whereas parent compound **5a** responded with an unusually red-shifted spectrum we rationalized by outer imine protonation.[16] The difference between the two imidazoloporphyrins is presumably a consequence of the presence of the strongly electron-




**Scheme 5** Conversions of porpholactam **10a** to imidazoloporphyrins.

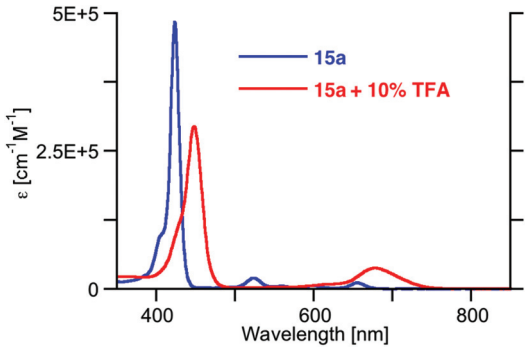



**Fig. 5** UV-visible spectra ($CH_2Cl_2$) of the porphyrinoids indicated.

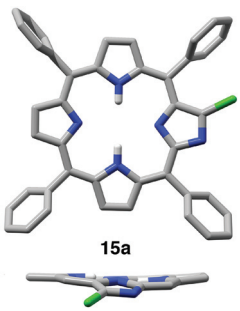



**Fig. 6** Single crystal X-ray structure of the 3-chloroimidazoloporphyrin **15a**, top view (top) and side view (bottom). All hydrogen atoms attached to carbon positions in both views have been omitted for clarity; in addition, the phenyl groups were removed in the side view. For details to the crystal structures, see ESI.‡

withdrawing chlorine substitution next to the imine, rendering it less basic than the inner nitrogens.

The crystal structure analysis of 3-chloroimidazoloporphyrin **15a** ultimately proved its connectivity (Fig. 6). The substituted imidazole moiety is slightly tilted out of the mean chromophore plane, likely as a result of the interaction of the (large) chlorine atom with the flanking phenyl group ($Cl–Ph_{centroid}$ distance 3.37 Å). The crystal structure of the non-chlorinated parent compound, also as its free base, shows no such distortion.[16]

Reduction of chloro-imine **15a** with Zn dust/$H_2SO_4$ formed, in addition to the major hydrolysis product porpholactam **10a**, the known parent imidazoloporphyrin **5a** in low yield.[16] This 6-step pathway to formally replace a β-carbon of tetraphenylporphyrin by a nitrogen is the third and – irrespective of its overall low yield – the best pathway toward imidazoloporphyrins, an intriguing porphyrinoid class combining the $N_4$-core of porphyrins with the peripheral nitrogen of N-confused porphyrins.[16]

## Conclusions

We have shown here that the lactone moiety in porpholactones can be converted to the corresponding lactam by reaction with hydrazine. We have also shown that the reduction of the porpholactones and porpholactams to the corresponding novel chlorin-like chromophores in which the pyrrole opposite of the lactone/lactam functionality is reduced to a pyrroline is possible. We thus demonstrated the formal replacement of a pyrrolic moiety in porphyrins and chlorins by an imidazolone moiety, further highlighting the power of our 'breaking and mending of porphyrin' strategy toward the synthesis of porphyrinoids containing non-pyrrolic heterocycles. While the lactone-to-lactam replacement does not alter the optical properties of the porphyrin or chlorin-like chromophore much, it introduces functionality to the porphyrin periphery that can be further manipulated, as shown by the conversion of the initially formed *N*-aminolactams to lactams and substituted imidazoloporphyrins.

The minor deviations from planarity observed in these novel chromophores presented here are not large enough to affect their optical properties in any major way. This further allows the conclusion to be drawn that all observed differences in the optical properties of the chromophores are entirely due to the atom replacement and substituent effects.

The introduction of functionality to the periphery of the porphyrin is important as it enables the use of these chromophores as, for instance, sensors and will allow further chemical modifications. To a significant portion, the increasing popularity of porpholactones and the immense importance of N-confused porphyrins[33,34,58] are due to their β-functionalities that are part of their macrocycles, a property that distinguishes them sharply from substituted porphyrins or chlorins. With the facile syntheses of porpholactams and the chlorin analogues chlorolactone and chlorolactam described herein, we expect these derivatives over time to gain utility and prominence for their optical properties, stability, and functionality.

## Experimental

### X-Ray single crystal diffractometry

Intensity data for a single crystal of chlorolactone **7a** (0.04 × 0.04 × 0.005 mm, MiTeGen mount with paratone-N oil) were

collected on a D8 goniostat equipped with a Bruker APEXII CCD detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to $\lambda$ = 0.8856 Å. Data collection frames were measured for a duration of 5 s at 0.3° intervals of $\omega$ with a maximum resolution of ~0.60 Å. The data frames were collected using the program APEX2 and processed using the program SAINT within APEX2. The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS.[59]

Single crystals of *N*-aminoporpholactam **8c**, *N*-aminochlorolactam **9c**, and chloro-imidazoloporphyrin **15a** were mounted on MiTeGen micromesh mounts with the help of a trace of mineral oil, mounted on a pin and placed a goniometer head under a stream of cold nitrogen. The data were collected on a Bruker APEX CCD diffractometer with Mo source Kα radiation ($\lambda$ = 0.71073 Å) using $\omega$ scans. The frames were integrated with the Bruker SAINT software package using a narrow frame algorithm. Data were corrected for absorption effects using the multiscan method (SADABS). All structures were solved and refined using the Bruker SHELXTL Software Package until the final anisotropic full-matrix, least-squares refinement on $F^2$ converged.[60]

Data collection and structural parameters for the structure elucidations can be found in Table 1 and the ESI.‡

## Materials and instrumentation

All solvents and reagents (Aldrich, Acros, CIL) were used as received. *meso*-Tetrakisarylporpholactones **3a**, **3b**, and **3c** were synthesized as reported in the literature.[17] Analytical (aluminum backed, silica gel 60, 250 μm thickness) and preparative (20 × 20 cm, glass backed, silica gel 60, 500 or 1000 μm thickness) TLC plates, and basic alumina gel (50–200 μm, pH 10) were used.

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker DRX 400, or Avance 500 instrument. High and low resolution mass spectra were provided by the Mass Spectrometry Facilities at the Department of Chemistry, University of Connecticut. UV-vis spectra were recorded on a Varian Cary 50 spectrophotometer. IR spectra were acquired on a JASCO FT-IR-410 using an ATR (ZnSe) unit.

## *meso*-Tetrakisphenyl-12-oxa-13-oxochlorin (chlorolactone 7a), *meso*-tetrakisphenyl-2-(*N*-amino-aza)-3-oxoporphyrin (*N*-aminoporpholactam 8a), and *meso*-tetrakisphenyl-12-(*N*-amino-aza)-13-oxochlorin (chlorolactam 9a)

*meso*-Tetraphenyl-2-oxa-3-oxoporphyrin **3a** (56 mg, 8.85 × $10^{-5}$ mol) was dissolved in THF (20 mL) and magnetically stirred. Hydrazine hydrate ($N_2H_4{\cdot}2H_2O$, 11 mL) was added and the mixture was heated to reflux for 5 d. When the starting material was consumed (reaction monitored by TLC), the reaction mixture was allowed to cool and was evaporated to dryness by rotary evaporation. The residue was taken up in $CH_2Cl_2$, washed with $H_2O$ (2 × 10 mL), dried over anhyd. $Na_2SO_4$, and reduced by rotary evaporation. The reaction mixture was separated by preparative TLC (silica–$CH_2Cl_2$/2% MeOH), providing **7a** in 12% (7.0 mg) as a red-purple solid, **8a** as a purple solid in 37% (21.0 mg), and **9a** as a purple solid in 25% (15.0 mg) yields. When the reaction was performed under an atmosphere of $N_2$, the formation of **7a** is almost totally suppressed, and **8a** and **9a** were isolated in 81–90% and 3–5% yields, respectively. **7a**: $R_f$ (silica–$CH_2Cl_2$) = 0.50; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.48 (dd, $^3J$ = 5.0, $^4J$ = 1.6 Hz, 1H), 8.24 (dd, $^3J$ = 4.6, $^4J$ = 1.9 Hz, 1H), 8.15 (dd, $^3J$ = 5.0, $^4J$ = 1.5 Hz, 1H), 8.00 and 7.99 (overlapping d, $^3J$ = 7.8 Hz, and s, 2H), 7.93 (dd,

**Table 1** Crystal data[a]

| | 7a | 8c·2EtOH | 9c·2EtOH | 15a |
|---|---|---|---|---|
| Formula | $C_{43}H_{30}N_4O_2$ | $C_{51}H_{38}F_{12}N_6O_3$ | $C_{51}H_{40}F_{12}N_6O_3$ | $C_{43}H_{28}ClN_5$ |
| $M$/g mol$^{-1}$ | 634.71 | 1010.87 | 1012.89 | 650.15 |
| Crystal system | Monoclinic | Triclinic | Triclinic | Monoclinic |
| Space group | $P2/n$ | $P\bar{1}$ | $P\bar{1}$ | $P2(1)/n$ |
| $a$, $b$, $c$/Å | 11.016(3), 6.7826(18), 21.878(6) | 12.801(4), 12.814(4), 14.782(5) | 12.6859(12), 12.9511(12), 14.5378(13) | 14.440(4), 16.901(5), 14.820(4) |
| $\alpha$, $\beta$, $\gamma$ (°) | 90, 101.024(4), 90 | 81.419(5), 75.271(5), 84.415(5) | 81.7260(10), 76.306(2), 84.1850 (10) | 90, 117.629(4), 90 |
| $V$/Å$^3$ | 1604.6(7) | 2314.3(12) | 2290.8(4) | 3204.4(17) |
| $T$/K | 150(2) | 150(2) | 100(2) | 100(2) |
| $Z$ | 2 | 2 | 2 | 4 |
| Reflections measured | 14 751 | 20 289 | 19 920 | 16 647 |
| Unique ($R_{int}$) | 3227 (0.0474) | 8112 (0.0529) | 9252 (0.0261) | 7763 (0.0724) |
| Data/parameters/ restraints | 3227/248/13 | 8112/771/327 | 9252/703/125 | 7763/561/51 |
| Goodness-of-fit on $F^2$ | 1.033 | 1.024 | 1.051 | 0.984 |
| $R(F)$ [all data] | 0.0729 | 0.1336 | 0.0979 | 0.1966 |
| $R(F)$ [$I > 2\sigma(I)$] | 0.0446 | 0.0693 | 0.0674 | 0.0733 |
| w$R(F_2)$ [all data] | 0.1149 | 0.2130 | 0.2038 | 0.2002 |
| w$R(F_2)$ [$I > 2\sigma(I)$] | 0.1028 | 0.1809 | 0.1846 | 0.1599 |
| CCDC number | 919810 | 919811 | 919812 | 919813 |

[a] For details, particularly with respect to the disorder models used, see ESI.

$^3J$ = 4.6, $^4J$ = 1.8 Hz, 1H), 7.89 and 7.88 (overlapping s and d, $^3J$ = 7.6 Hz, 2H), 7.82–7.80 (m, 4H), 7.68–7.65 (m, 12H), 4.06–3.98 (m, 4H), −0.78 (s, 1H, exchangeable with $D_2O$), −1.20 (s, 1H, exchangeable with $D_2O$) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$ neutralized in basic alumina): $\delta$ 170.0, 167.6, 164.2, 152.6, 142.8, 142.1, 141.0, 139.1, 139.0, 138.5, 137.5, 134.8, 133.9, 132.3, 132.2, 131.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 126.6, 125.9, 125.5, 122.9, 121.7, 116.0, 114.6, 104.9, 36.8, 34.7 ppm; UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 412 (5.35), 512 (4.02), 547 (4.02), 625 (3.83), 686 (4.67) nm; HR-MS ($ESI^+$, cone voltage = 30 V, 100% $CH_3CN$, TOF) $m/z$ calcd for $C_{43}H_{31}N_4O_2$ 635.2447 ($[M{\cdot}H]^+$), found 635.2432. **8a**: $R_f$ (silica–$CH_2Cl_2$/2% MeOH) = 0.45; $^1H$ NMR (400 MHz, $CDCl_3$ neutralized in basic alumina): $\delta$ 8.80 (d, $^3J$ = 4.0 Hz, 1H), 8.77 (d, $^3J$ = 4.0 Hz, 1H), 8.71 (d, $^3J$ = 4.0 Hz, 1H), 8.68 (d, $^3J$ = 4.0 Hz, 1H), 8.64 (d, $^3J$ = 4.0 Hz, 1H), 8.58 (d, $^3J$ = 4.0 Hz, 1H), 8.17–8.15 (m, 4H), 8.11–8.09 (m, 2H), 8.04–8.02 (m, 2H), 7.78–7.72 (m, 12H), 4.73 (s, 2H, exchangeable with $D_2O$), −2.08 (s, 1H, exchangeable with $D_2O$), −2.35 (s, 1H, exchangeable with $D_2O$) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 168.3, 156.3, 154.3, 147.4, 141.8, 141.7, 141.4, 140.5, 140.1, 139.2, 138.4, 137.3, 135.5, 134.8, 134.6, 134.4, 133.8, 133.6, 132.8, 129.5, 128.3, 128.23, 128.2, 128.1, 127.8, 127.7, 127.1, 127.0, 127.0, 124.3, 121.4, 118.3, 105.8 ppm; UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 424 (5.47), 522 (4.35), 556 (4.04), 597 (3.93), 651 (3.68) nm; HR-MS ($ESI^+$, cone voltage = 30 V, 100% $CH_3CN$, TOF) $m/z$ calcd for $C_{43}H_{31}N_6O$ 647.2559 ($[M{\cdot}H]^+$), found 647.2603. **9a**: $R_f$ (silica–$CH_2Cl_2$/2% MeOH) = 0.17; $^1H$ NMR (400 MHz, $CDCl_3$ neutralized in basic alumina): $\delta$ 8.43 (dd, $^3J$ = 5.0, $^4J$ = 1.6 Hz, 1H), 8.37 (dd, $^3J$ = 4.7, $^4J$ = 1.8 Hz, 1H), 8.15 (dd, $^3J$ = 4.9, $^4J$ = 1.6 Hz, 1H), 8.02–7.98 (m, 3H), 7.95–7.93 (m, 2H), 7.84–7.82 (m, 4H), 7.72–7.66 (m, 12H), 4.62 (s, 2H, exchangeable with $D_2O$), 4.06 (s, 4H), −1.27 (s, 1H, exchangeable with $D_2O$), −1.51 (s, 1H, exchangeable with $D_2O$) ppm; $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 168.8, 167.4, 164.6, 144.8, 142.8, 142.5, 140.8, 140.4, 140.2, 139.3, 138.7, 134.8, 133.2, 132.4, 132.3, 132.1, 131.3, 128.34, 128.33, 128.1, 127.98, 127.93, 127.8, 127.6, 126.7, 125.7, 125.6, 121.9, 121.7, 115.2, 114.0, 107.8, 36.6, 34.9 ppm; UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 414 (5.46), 509 (4.23), 542 (4.17), 634 (3.88), 695 (4.75) nm; HR-MS ($ESI^+$, cone voltage = 30 V, 100% $CH_3CN$, TOF) $m/z$ calcd for $C_{43}H_{33}N_6O$ 649.2716 ($[M{\cdot}H]^+$), found 649.2735.

### *meso*-Tetrakis(4-methoxyphenyl)-12-oxa-13-oxochlorin (chlorolactone 7b), *meso*-tetrakis(4-methoxyphenyl)-2-(*N*-amino-aza)-3-oxoporphyrin (*N*-aminoporpholactam 8b), and *meso*-tetrakis(4-methoxyphenyl)-12-(*N*-amino-aza)-13-oxochlorin (chlorolactam 9b)

Prepared by reaction of *meso*-tetrakis(4-methoxyphenyl)-2-oxa-3-oxoporphyrin (**3b**) (33 mg, $4.45 \times 10^{-5}$ mol) with $N_2H_4{\cdot}2H_2O$ as described for the preparation of **3a**. Isolated yields for **7b** are 21% (6.9 mg) as a purple solid, for **8b** 30% (8.4 mg) as a purple solid, and for **9b** 27% (11.0 mg) as a purple solid. When the reaction was performed under an atmosphere of $N_2$, only products **8b** and **9b** were isolated in 78% and 3% yields, respectively. **7b**: $R_f$ (silica–$CH_2Cl_2$/2% MeOH) = 0.46; $^1H$ NMR (400 MHz, $CDCl_3$ neutralized with basic alumina): $\delta$ 8.49 (dd, $^3J$ = 5.2, $^4J$ = 1.8 Hz, 1H), 8.27 (dd, $^3J$ = 4.7, $^4J$ = 2.0 Hz, 1H), 8.17 (dd, $^3J$ = 5.0, $^4J$ = 1.9 Hz, 1H), 7.95 (dd, $^3J$ = 4.9 Hz, $^4J$ = 1.9 Hz, 1H), 7.91 (d, 8.6 Hz, 2H), 7.79 (d, 8.6 Hz, 2H), 7.69 (dd, $^3J$ = 8.6, $^4J$ = 2.9 Hz, 4H), 7.22–7.18 (m, 8H), 4.02–4.00 (m, 16H), −0.78 (s, 1H, exchangeable with $D_2O$), −1.21 (s, 1H, exchangeable with $D_2O$) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 170.3, 167.8, 164.6, 159.8, 159.7, 159.5, 159.3, 152.6, 141.3, 139.4, 139.2, 135.2, 135.1, 135.0, 134.4, 133.5, 133.2, 132.9, 130.8, 129.9, 127.9, 126.5, 125.8, 125.5, 122.7, 121.6, 115.4, 113.9, 113.8, 113.7, 113.5, 113.2, 104.6, 55.71, 55.68, 55.66, 55.55, 36.74, 34.73 ppm; UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 416 (5.31), 516 (4.03), 554 (4.13), 625 (3.92), 686 (4.69) nm; HR-MS ($ESI^+$, cone voltage = 30 V, 100% $CH_3CN$, TOF) $m/z$ calcd for $C_{47}H_{39}N_4O_6$ 755.2870 ($[M{\cdot}H]^+$), found 755.2878. **8b**: $R_f$ (silica–$CH_2Cl_2$/2% MeOH) = 0.39; $^1H$ NMR (400 MHz, $CD_2Cl_2$ neutralized with basic alumina): $\delta$ 8.80 (d, $^3J$ = 5.0 Hz, 1H), 8.77 (d, $^3J$ = 4.9 Hz, 1H) 8.71 (d, $^3J$ = 5.0 Hz, 1H), 8.65 (d, $^3J$ = 4.9 Hz, 1H) 8.62 (d, $^3J$ = 4.6 Hz, 1H) 8.57 (d, $^3J$ = 4.6 Hz, 1H) 8.05–8.02 (m, 4H), 7.95 (d, $^3J$ = 8.7, $^4J$ = 2.1 Hz, 2H), 7.87 (d, $^3J$ = 8.7, $^4J$ = 2.3 Hz, 2H) 7.26–7.23 (m, 8H), 4.74 (s, 2H), 4.04–4.02 (m, 12H), −2.08 (s, 1H, exchangeable with $D_2O$), −2.34 (s, 1H, exchangeable with $D_2O$) ppm. $^{13}C$ NMR (100 MHz, $CD_2Cl_2$): $\delta$ 167.7, 160.0, 159.9, 159.8, 159.7, 156.4, 154.4, 147.8, 141.8, 139.6, 138.6, 137.4, 136.0, 135.6, 135.5, 134.6, 134.4, 134.1, 134.0, 133.4, 132.7, 132.6, 129.2, 127.6, 127.5, 126.7, 123.9, 121.0, 117.5, 113.2, 112.9, 112.6, 112.5, 105.2, 55.74, 55.71, 55.6 ppm; UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 429 (5.60), 525 (4.45), 562 (4.24), 600 (4.08), 653 (3.72) nm; HR-MS ($ESI^+$, cone voltage = 30 V, 100% $CH_3CN$, TOF) $m/z$ calcd for $C_{47}H_{39}N_6O_5$ 767.2982 ($[M{\cdot}H]^+$), found 767.2953. **9b**: $R_f$ (silica–$CH_2Cl_2$/5% MeOH) = 0.77; $^1H$ NMR (400 MHz, $CD_2Cl_2$ neutralized with basic alumina): $\delta$ 8.42 (dd, $^3J$ = 5.1, $^4J$ = 1.9 Hz, 1H), 8.31 (dd, $^3J$ = 4.7, $^4J$ = 2.1 Hz, 1H), 8.16 (dd, $^3J$ = 5.1, $^4J$ = 1.9 Hz, 1H), 8.00 (dd, $^3J$ = 4.7, $^4J$ = 2.1 Hz, 1H), 7.87 (d, 8.6 Hz, 2H), 7.78 (d, $^3J$ = 8.6 Hz, 2H), 7.72, 7.70 (two overlapping d, $^3J$ = 8.5 Hz, 4H), 7.21–7.17 (m, 8H), 4.65 (s, 2H), 4.07–4.00 (m, 16H), −1.31 (s, 1H, exchangeable with $D_2O$), −1.55 (s, 1H, exchangeable with $D_2O$) ppm; $^{13}C$ NMR (100 MHz, $CD_2Cl_2$): $\delta$ 169.5, 166.8, 165.1, 159.8, 159.6, 159.5, 159.4, 145.1, 141.0, 139.4, 139.1, 135.1, 135.0, 134.7, 134.1, 133.7, 133.3, 133.1, 132.7, 132.6, 131.7, 127.7, 126.2, 125.4, 121.6, 120.9, 114.6, 113.6, 113.5, 113.2, 112.8, 107.3, 55.67, 55.62, 55.61, 55.55, 36.5, 34.8 ppm; UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 418 (5.10), 512 (3.92), 547 (3.90), 634 (3.60), 695 (4.42) nm; HR-MS ($ESI^+$, cone voltage = 30 V, 100% $CH_3CN$, TOF) $m/z$ calcd for $C_{47}H_{41}N_6O_5$ 769.3138 ($[M{\cdot}H]^+$), found 769.3111.

### *meso*-Tetrakis(4-trifluoromethylphenyl)-12-oxa-13-oxochlorin (chlorolactone 7c), *meso*-tetrakis(4-trifluoromethylphenyl)-2-(*N*-amino-aza)-3-oxoporphyrin (*N*-aminoporpholactam 8c), and *meso*-tetrakis(4-trifluoromethylphenyl)-12-(*N*-amino-aza)-13-oxochlorin (chlorolactam 9c)

Prepared by reaction of *meso*-tetrakis(4-trifluoromethylphenyl)-2-oxa-3-oxoporphyrin (**3c**) (105 mg, $1.16 \times 10^{-4}$ mol) with $N_2H_4{\cdot}2H_2O$ as described for the preparation of **3a**. Isolated yields for **7c** were traces (<3%; identified by MS, but not

further characterized), **8c** 56% (59.3 mg) as a purple solid, and **9c** 16% (16.0 mg) as a purple solid. When the reaction was performed under an atmosphere of $N_2$, only products **8c** and **9c** were isolated in 60–65% and 3–7% yields, respectively. **8c**: $R_f$ (silica–$CH_2Cl_2$/2% petroleum ether 30–60) = 0.54; $^1$H NMR (400 MHz, $CDCl_3$ neutralized with basic alumina): $\delta$ 8.74 (t, $^3J$ = 5.7 Hz, 2H), 8.64 (d, $^3J$ = 5.2 Hz, 1H) 8.62 (d, $^3J$ = 4.8 Hz, 1H), 8.58 (d, $^3J$ = 4.6 Hz, 1H) 8.52 (d, $^3J$ = 4.6 Hz, 1H) 8.28 and 8.26 (two overlapping d, 7.8 Hz, 4H), 8.17 (d, $^3J$ = 7.8 Hz, 2H), 8.12 (d, $^3J$ = 8.0 Hz, 2H) 8.04–7.99 (m, 8H), 4.56 (s, 2H), −2.12 (s, 1H, exchangeable with $D_2O$), −2.38 (s, 1H, exchangeable with $D_2O$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.7, 155.9, 154.1, 147.8, 144.9, 144.1, 143.5, 141.3, 138.9, 138.2, 136.9, 135.5, 134.9, 134.6, 134.4, 133.9, 133.7, 132.9, 130.8, 130.5, 129.5, 128.0, 127.9, 127.1, 124.8, 124.2, 123.2, 122.9, 120.2, 116.9, 104.8 ppm; UV-vis ($CHCl_2$) $\lambda_{max}$ (log $\varepsilon$) 423 (5.44), 519 (4.26), 552 (3.91), 598 (3.81), 651 (3.66) nm; HR-MS (ESI$^+$, cone voltage = 30 V, 100% $CH_3CN$, TOF) $m/z$ calcd for $C_{47}H_{27}F_{12}N_6O$ 919.2055 ($[M{\cdot}H]^+$), found 919.2022. **9c**: $R_f$ (silica–$CH_2Cl_2$) = 0.10; $^1$H NMR (400 MHz, $CDCl_3$ neutralized with basic alumina): $\delta$ 8.36 (dd, $^3J$ = 5.2, $^4J$ = 1.9 Hz, 1H), 8.29 (dd, $^3J$ = 4.7, $^4J$ = 2.1 Hz, 1H), 8.12 (dd, $^3J$ = 5.2, $^4J$ = 1.9 Hz, 1H), 8.08 (d, $^3J$ = 7.8 Hz, 2H), 8.02 (d, $^3J$ = 7.8 Hz, 2H), 7.99–7.93 (m, 13H), 4.44 (s, 2H), 4.06–4.04 (m, 4H), −1.31 (s, 1H, exchangeable with $D_2O$), −1.52 (s, 1H, exchangeable with $D_2O$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.6, 167.9, 164.5, 146.2, 145.1, 143.6, 140.5, 138.9, 138.7, 134.5, 133.2, 132.6, 132.5, 132.4, 131.3, 130.6, 130.3, 129.3, 129.2, 128.2, 126.8, 125.8, 125.5, 124.6, 122.1, 120.3, 114.2, 113.1, 106.9, 36.7, 34.9 ppm; UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 412 (5.43), 503 (4.25), 538 (4.03), 637 (3.95), 697 (4.75) nm; HR-MS (ESI$^+$, cone voltage = 30 V, 100% $CH_3CN$, TOF) $m/z$ calcd for $C_{47}H_{29}F_{12}N_6O$ 921.2211 ($[M{\cdot}H]^+$), found 921.2197.

### *meso*-Tetrakisphenyl-2-aza-3-oxoporphyrin (porpholactam 10a)

*meso*-Tetrakisphenyl-2-(*N*-amino-aza)-3-oxoporphyrin (**8a**) (27 mg, $4.18 \times 10^{-5}$ mol) was dissolved in anhyd. 1,2-dichlorobenzene (10 mL) and magnetically stirred. To this was added $SmI_2$ (2.5 mL of a 0.1 M solution in THF, 6 equiv.) and the mixture was heated to reflux for 14 h. When the starting material was consumed (reaction monitored by TLC), the reaction mixture was allowed to cool and was evaporated to dryness by rotary evaporation. The residue was taken up in $CH_2Cl_2$, filtered and washed with water (2 × 10 mL), and dried over anhydrous $Na_2SO_4$. The crude product was purified by preparative TLC ($CH_2Cl_2$/1% MeOH) to furnish **10a** as a purple solid in 72% (19.0 mg) yield. $R_f$ (silica–$CH_2Cl_2$) = 0.20; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.64 (s, 1H, exchangeable with $D_2O$), 8.80 (d, $^3J$ = 4.0 Hz, 1H), 8.72 (d, $^3J$ = 4.0 Hz, 1H), 8.64 (d, $^3J$ = 4.0 Hz, 1H), 8.61 (d, $^3J$ = 4.0 Hz, 1H), 8.58 (d, $^3J$ = 4.0 Hz, 1H), 8.55 (d, $^3J$ = 4.0 Hz, 1H), 8.14–8.12 (m, 4H), 8.09–8.07 (m, 2H), 7.99–7.97 (m, 2H), 7.81–7.79 (m, 3H), 7.77–7.73 (m, 9H), −1.86 (s, 1H, exchangeable with $D_2O$), −2.13 (s, 1H, exchangeable with $D_2O$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 169.5, 156.4, 153.9, 147.4, 141.9, 141.7, 140.2, 139.9, 139.6, 138.6, 138.3, 136.8, 134.9, 134.5, 134.3, 133.7, 133.4, 132.7, 129.6, 129.2, 128.8, 128.2, 128.1, 127.9, 127.7, 127.1, 126.9, 126.8, 126.4, 124.8, 121.2, 118.0, 103.9, 55.85, 55.74, 55.57 ppm; UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 421 (5.49), 519 (4.28), 554 (4.08), 595 (3.87), 649 (3.84) nm; HR-MS (ESI$^+$, cone voltage = 30 V, 100% $CH_3CN$, TOF) $m/z$ calcd for $C_{43}H_{30}N_5O$ 632.2450 ($[M{\cdot}H]^+$), found 632.2398.

### *meso*-Tetrakis(4-methoxyphenyl)-2-aza-3-oxoporphyrin (porpholactam 10b)

Prepared in 65% yield (19.0 mg) as a purple solid from *N*-aminoporpholactam **8b** (30 mg, $3.91 \times 10^{-5}$ mol) by $SmI_2$ reduction as described for the preparation of **10a**. $R_f$ (silica–$CH_2Cl_2$/2% MeOH) = 0.22; $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 9.76 (s, 1H, exchangeable with $D_2O$), 8.81 (d, $^3J$ = 5.0 Hz, 1H), 8.74 (d, $^3J$ = 5.0 Hz, 1H) 8.65 (d, $^3J$ = 5.0 Hz, 1H), 8.60 (d, $^3J$ = 5.0 Hz, 1H) 8.55 (m, 2H), 8.04–7.97 (m, 6H), 7.84 (d, $^3J$ = 7.8 Hz, 2H), 7.31–7.22 (m, 8H), 4.04 (d, $^3J$ = 7.4 Hz, 12H), −1.87 (s, 1H, exchangeable with $D_2O$), −2.15 (s, 1H, exchangeable with $D_2O$) ppm; $^{13}$C NMR (100 MHz, $CD_2Cl_2$): $\delta$ 169.4, 160.5, 160.0, 159.9, 159.6, 147.9, 140.7, 140.3, 138.6, 136.9, 135.5, 135.4, 134.7, 134.6, 134.2, 133.9, 133.1, 132.0, 130.7, 129.4, 127.8, 126.9, 126.1, 124.5, 120.8, 117.3, 114.2, 112.9, 112.6, 112.5, 103.7, 55.9, 55.7, 55.6 ppm; UV-vis ($CH_2Cl$) $\lambda_{max}$ (log $\varepsilon$) 426 (5.32), 523 (4.22), 559 (4.11), 598 (4.00), 650 (3.84) nm; HR-MS (ESI$^+$, cone voltage = 30 V, 100% $CH_3CN$, TOF) $m/z$ calcd for $C_{47}H_{38}N_5O_5$ 752.2873 ($[M{\cdot}H]^+$), found 752.2798.

### *meso*-Tetrakis(4-trifluoromethylphenyl)-2-aza-3-oxoporphyrin (porpholactam 10c)

Prepared in 83% yield (26.0 mg) as a purple solid from *N*-aminoporpholactam **8c** (32 mg, $3.48 \times 10^{-5}$ mol) by $SmI_2$ reduction as described for the preparation of **10a**. $R_f$ (silica–$CH_2Cl_2$/2% petroleum ether 30–60) = 0.49; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.61 (s, 1H, exchangeable with $D_2O$), 8.79 (d, $^3J$ = 5.0 Hz, 1H), 8.70 (d, $^3J$ = 4.8 Hz, 1H) 8.64 (d, $^3J$ = 5.0 Hz, 1H), 8.57 (d, $^3J$ = 4.6 Hz, 1H), 8.54 (d, $^3J$ = 5.0 Hz, 1H), 8.51 (d, $^3J$ = 4.7 Hz, 1H), 8.28–8.23 (m, 6H), 8.11–8.08 (m, 4H), 8.05–7.98 (m, 6H), −1.88 (s, 1H, exchangeable with $D_2O$), −2.13 (s, 1H, exchangeable with $D_2O$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 169.2, 156.1, 153.7, 147.4, 145.2, 144.9, 142.9, 142.0, 140.1, 139.7, 138.4, 138.1, 136.5, 135.1, 134.5, 134.3, 133.9, 133.7, 132.9, 132.0, 131.7, 131.0, 130.9, 130.7, 130.6, 130.3, 129.7, 128.2, 127.1, 126.6, 126.1, 125.96, 125.93, 125.6, 124.8, 124.7, 124.29, 124.26, 124.14, 124.11, 123.5, 123.4, 123.2, 122.9, 120.1, 116.7, 102.9 ppm; UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 420 (5.54), 517 (4.32), 551 (4.02), 595 (3.86), 650 (3.88) nm; HR-MS (ESI$^+$, cone voltage = 30 V, 100% $CH_3CN$, TOF) $m/z$ calcd for $C_{47}H_{26}F_{12}N_5O$ 904.1946 ($[M]^+$), found 904.1917.

### *meso*-Tetrakis(4-trifluoromethylphenyl)-2-aza-3-oxochlorin (chlorolactam 11c)

Prepared in 57% yield (6.0 mg) as a purple solid from *N*-aminochlorolactam **9c** (~11 mg, $1.16 \times 10^{-5}$ mol) by $SmI_2$ reduction as described for the preparation of **10a**. $R_f$ (silica–$CH_2Cl_2$/2% MeOH) = 0.58; $^1$H NMR (400 MHz, $CDCl_3$ neutralized with basic alumina): $\delta$ 9.41 (s, 1H), 8.35 (d, $^3J$ = 4.8 Hz,

1H), 8.20 (d, $^3J$ = 4.5 Hz, $^4J$ = 1.5 Hz, 1H) 8.15 (d, 7.2 Hz, 3H), 8.05–7.92 (m, 15H), 4.08–4.01 (m, 4H), −1.11 (s, 1H, exchangeable with $D_2O$), −1.44 (s, 1H, exchangeable with $D_2O$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 168.8, 168.7, 163.9, 146.5, 145.8, 144.6, 140.3, 138.4, 137.6, 135.1, 133.6, 132.6, 132.5, 132.3, 127.2, 126.2, 126.0, 125.9, 125.6, 124.7, 122.2, 120.1, 114.6, 113.2, 105.0, 36.7, 35.1 ppm; UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 413 (5.10), 506 (3.93), 538 (3.87), 636 (3.61), 701 (4.44) nm; HR-MS (DART$^+$, orifice voltage = 20 V, 100% $CH_3CN$, TOF) $m/z$ calcd for $C_{47}H_{28}F_{12}N_5O$ 906.2102 ($[M{\cdot}H]^+$), found 906.2097.

### *meso*-Tetrakisphenyl-2-aza-3-chloroporphyrin (15a)

*meso*-Tetrakisphenyl-2-aza-3-oxo-porphyrin **10a** (10 mg, 1.58 × $10^{-5}$ mol) was dissolved in dry toluene (10 mL) and magnetically stirred. To this was added phosphoryl chloride ($POCl_3$; 100 μL, ~50 equiv.) and the mixture was heated to reflux for 3–5 h. When the starting material was consumed (reaction monitored by UV-visible and TLC), the reaction mixture was quenched by the addition of triethylamine (~0.1 mL), allowed to cool to room temperature and was evaporated to dryness by rotary evaporation. The residue was taken up in $CH_2Cl_2$, washed with water (2 × 10 mL), and dried over anhydrous $Na_2SO_4$. The product was purified by preparative TLC ($CH_2Cl_2$/20% petroleum ether 30–60) to furnish **15a** in 97% (10.0 mg) as a purple solid: $R_f$ (silica–$CH_2Cl_2$) = 0.55; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 9.05 (d, $^3J$ = 4.9 Hz, 1H), 8.92 (d, 5.1 Hz, 1H), 8.86 (s, 2H) 8.72 (s, 2H), 8.25 (dd, $^3J$ = 7.8 Hz, 2H), 8.21–8.17 (m, 4H), 8.05 (dd, $^3J$ = 6.7, 1.4 Hz, 2H) 7.81–7.74 (m, 12H) −2.51 (s, 1H, exchangeable with $D_2O$) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 159.5, 157.3, 157.1, 156.7, 141.8, 141.7, 141.6, 140.9, 140.2, 139.8, 139.7, 139.4, 135.7, 135.4, 135.3, 134.8, 134.7, 133.7, 130.1, 129.5, 128.8, 128.4, 128.3, 127.9, 127.6, 127.2, 127.1, 121.4, 120.8, 119.9, 119.8 ppm; UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (log $\varepsilon$) 423 (5.68), 522 (4.30), 560 (3.74), 599 (3.78), 655 (4.06) nm, UV-vis ($CH_2Cl_2$ + 10% TFA) $\lambda_{max}$ (log $\varepsilon$) 448 (5.46), 679 (4.58) nm; HR-MS (ESI$^+$, cone voltage = 30 V, 100% $CH_3CN$, TOF) $m/z$ calcd for $C_{43}H_{29}ClN_5$ 650.2111 ($[M{\cdot}H]^+$), found 650.2118.

### *meso*-Tetrakisphenyl-2-azaporphyrin (5a)

*meso*-Tetrakisphenyl-2-aza-3-chloroporphyrin **15a** (10 mg, 1.54 × $10^{-5}$ mol) was dissolved in dry toluene (7 mL) and magnetically stirred. To this was added zinc dust (45 mg) and 2 N aq. $H_2SO_4$ (3 mL) and the mixture was heated to reflux for 5 h. The reaction mixture was added to an aq. sat'd. $Na_2CO_3$ solution (caution: gas evolution, foam formation) until all acid was neutralized. The products were extracted with $CH_2Cl_2$. The organic phase was dried over anhyd. $Na_2SO_4$ and after evaporation under reduced pressure, the residue was separated on a preparative TLC plate (silica–$CH_2Cl_2$/1% MeOH) to furnish **5a** in 10% and **10a** in 72% yields. The spectroscopic and analytical properties of this product were identical to those reported previously.[16]

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