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PAPER

Unexpected hydroxylamine-induced ring-closure reactions of *meso*-tetraphenylsecochlorin bisaldehyde†

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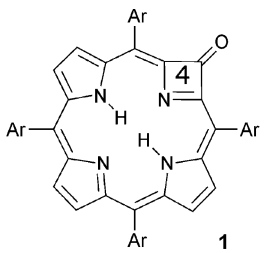
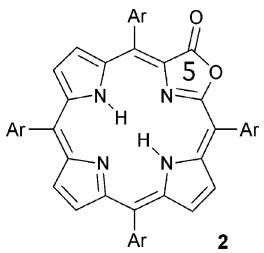
Reaction of *meso*-tetraphenylsecochlorin bisaldehyde with hydroxylamine results in the formation of the known *meso*-tetraphenyl-2-nitroporphyrin and the novel *meso*-tetraphenylimidazolophorphyrin. The products are the result of two diverging pathways of the presumed intermediate monooxime monoaldehyde that are unusual and surprising, but fully rationalized. The structures of both products were confirmed by spectroscopic techniques and single crystal X-ray diffractometry. This reaction represents the first reaction in which a pyrrole in a porphyrin was formally replaced by an imidazole moiety. The optical properties of the free base and metalloimidazoloporphyrin under neutral and acidic conditions are discussed. Further, an alternative synthesis of the imidazoloporphyrin Ni(II) based on *meso*-tetraphenyl-1-formyl-chlorophin is presented.

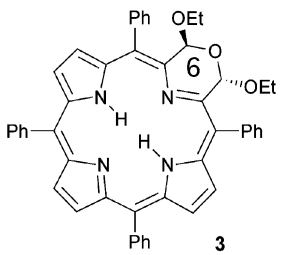
Introduction

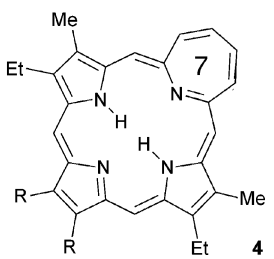
The development of synthetic methodologies toward the synthesis of chlorins and related oligopyrrolic macrocycles constitutes a major aspect of current porphyrin research.[1] This is because of the often attractive optical properties of these macrocycles with respect to their use as UV-vis or fluorescent labels in biological systems, their phototoxicity, or their promise in artificial light-harvesting systems. Two principal approaches toward the synthesis of chlorins and their analogues, such as porphyrinoids containing a non-pyrrolic building block, can be pursued: total synthesis,[2] or the β,β′-manipulation of a preformed porphyrin.[1,3] We, and others,[4–7] pursued the latter approach and developed methods toward the formal replacement of one (or two) pyrrolic units of *meso*-tetraaryl- or β-octaalkylporphyrins by a non-pyrrolic building block, generating pyrrole-modified porphyrins that are frequently chlorin-like.[8–17]

Thus, pyrrole-modified porphyrins containing four- (azete)[7,13,16] (**1**), five- (oxazole)[4,10,18–20] (**2**) and six-membered (morpholine (**3**),[8,10,11] pyridinone,[5,14] and pyrazine[9]) heterocycles have become known. We like to paraphrase our three-step approach as the 'breaking and mending of porphyrins' (Scheme 1). In Step A, one (or two) β,β′-double bond(s) of a porphyrin are activated, generally by conversion to the corresponding 2,3-dihydroxychlorin.[8,14,15,21]









This is followed by Step B, a diol cleavage reaction to the corresponding secochlorin (the 'breaking' of the porphyrin).[13,20,22,23] The secochlorin bisaldehyde is subsequently reacted under conditions that lead to the formation of, for instance, a non-pyrrolic building block (Step C). This 'mending' stage of the synthesis may involve more than one functional group transformation.[8–12,14,20]

We recently reported a mild synthesis of the long-time elusive free base secochlorin bisaldehyde **5** by oxidative cleavage of the corresponding diolchlorin under basic conditions (Scheme 2).[20] Secochlorin **5** (and its Ni(II) complex **5Ni**)[13,22] showed in all the reactions tested to date the typical reactivity of an aromatic aldehyde. We therefore surmised that the reaction of hydroxylamine with bisaldehyde **5** would form oxime **I** that is poised to undergo an intramolecular ring-closure to form the hemiacetal **II** and subsequently lactone **III** upon spontaneous oxidation.

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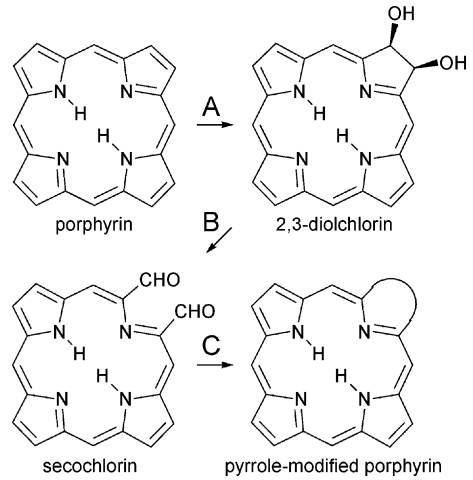
† Electronic supplementary information (ESI) available: ^{1}H, ^{13}C NMR and UV-vis/fluorescence spectra of all novel compounds obtained, select 2D NMR spectra, and experimental details to the crystal structure determination of **6** and **7**, including the cif file. CCDC reference numbers 798353 and 798354. See DOI: 10.1039/c0ob00920b/



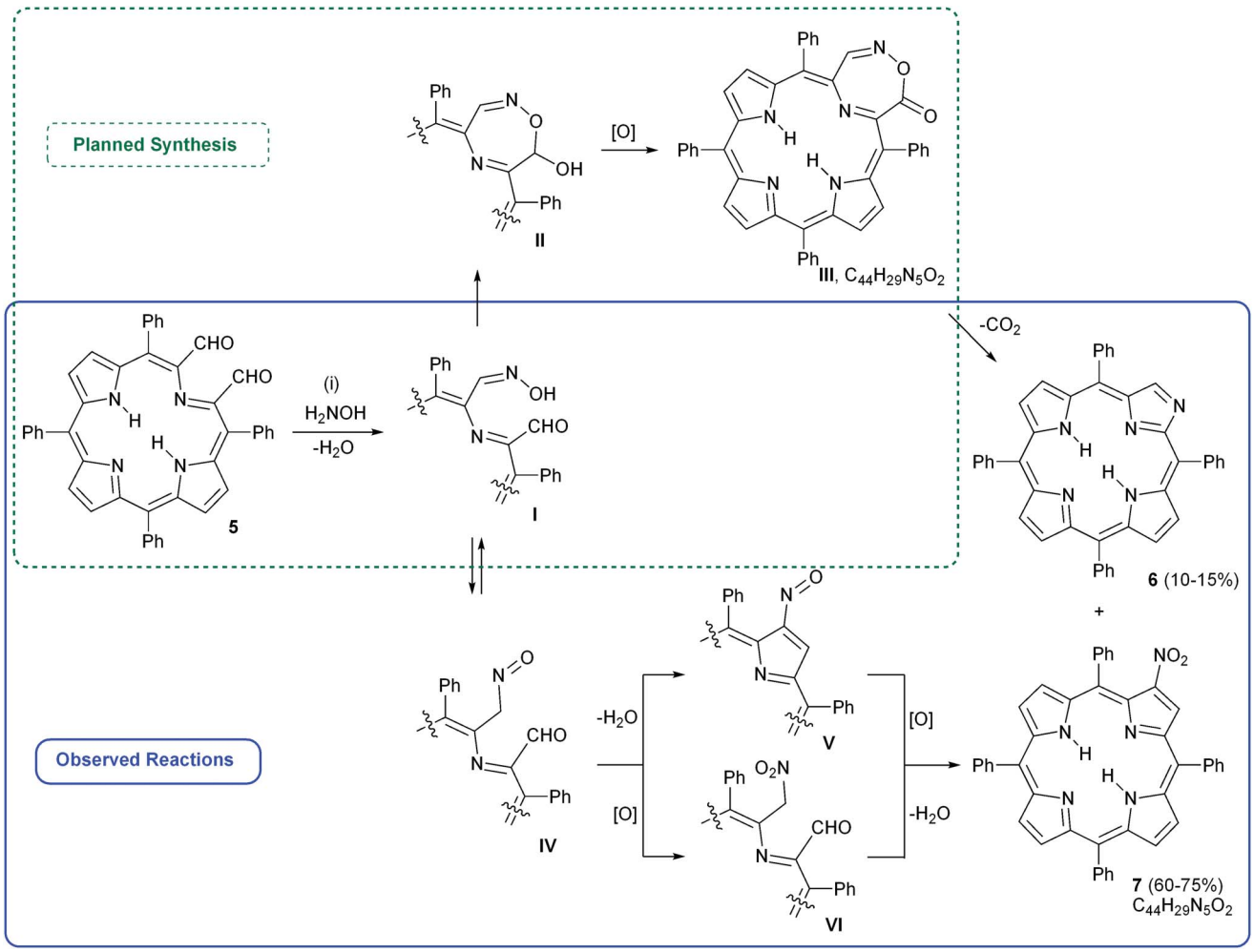
Scheme 1 The 'breaking and mending' principle of conversion of a porphyrin in three steps to a pyrrole-modified porphyrin.

Precedent reactions suggest that hemiacetals of type **II** are readily susceptible to oxidation.[20,23] As a result, the formal replacement of a pyrrole by a seven-membered oxadiazepinone ring would have been accomplished. Since only one other porphyrinoid containing a seven-membered carbacycle, tropiporphyrin **4**, synthesized using total synthesis by the group of Lash, is known,[24] we were intrigued by the idea of synthesizing a porphyrinoid containing a seven-membered heterocycle using the 'breaking and mending' approach. We report here the results of those experiments.

Results and discussion

Reaction of secochlorin bisaldehyde 5 with hydroxylamine

Reaction of medium-polarity (R_f 0.61, silica-CH_2Cl_2), brownish **5** with a 30-fold stoichiometric excess of hydroxylamine hydrochloride ($H_2NOH{\cdot}HCl$) in refluxing pyridine generates, over the course of 1 h under aerobic conditions, one major non-polar (R_f 0.73, silica-CH_2Cl_2), brownish (62% isolated yield) and one minor polar (R_f 0.25, silica-CH_2Cl_2), purple product (15% isolated yield). No reaction was observed under anaerobic conditions. As determined by HR-MS (ESI+, 100% CH_3CN), the major product possessed the composition $C_{44}H_{30}N_4O_2$ (for MH+, expected: 660.2400; found: 660.2337), fitting the expected oxadiazepinone derivative **III**. The ^1H NMR ($CDCl_3$) of this product showed the presence of a porphyrinoid with no axial symmetry (*e.g.*, six d assigned to



Scheme 2 Planned and observed reactions. Reaction conditions: (i) 30 eq $NH_2OH{\cdot}HCl$, pyridine, Δ, 1 h. All compounds in Roman numerals were not directly observed.

the β-protons), and a seemingly diagnostic low-field peak (s at 9.06 ppm) we assigned to the imine proton (see ESI†).

The UV-vis spectrum of the compound is a red-shifted distorted porphyrin-like spectrum (Fig. 1). At first glance, this may strike one as incongruent with structure **III** but the spectrum of porpholactone **2**, for instance, provides a precedent.[4,10] The presence of the single sp^2-β-carbon in **2** causes a porphyrin-like—and not a chlorin-like—spectrum. In contrast, oxazolochlorins carrying an sp^3-carbon at this position are chlorin-like.[19,20,23,25] In transference, the sp^2-imine carbon in **III** may very well be responsible for its porphyrin-like spectrum.

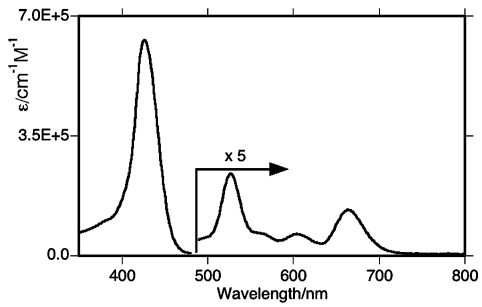


Fig. 1 UV-vis spectrum (CH_2Cl_2) of the presumed species **III**, the major, non-polar reaction product from the reaction of **5** with hydroxylamine.

Using standard methodologies,[26] metal insertion of Ni(II), Pd(II), and Pt(II) into the major product proceeded smoothly, providing the corresponding complexes with the expected compositions, spectral data, and metalloporphyrin-like optical properties (see ESI†).

Irrespective of the supporting evidence for the assignment of the major product as the desired oxadiazepinone **III**, a number of findings ran counter to this: at 156 ppm the most deshielded peak in the ^{13}C NMR spectrum of the product did not quite fit the expectation of a carbonyl/lactone carbon shift (see ESI†), but since the lactone carbonyl is also shifted in porpholactones (167 ppm for **2**),[10] this finding in itself was not alarming. The FT-IR spectrum of the major product (neat, ATR) did not indicate the presence of a carbonyl group (see ESI†). Moreover, the collision-induced tandem MS of the major product did not show any of the expected fragmentation patterns and, instead, showed a prominent fragmentation suggestive of the loss of NO_2. Lastly, a convincing chemical finding directly contradicted the oxadiazepinone structure: reaction of the low polarity compound with $NaBH_4$ quantitatively formed *meso*-tetraphenylporphyrin (TPP)!

Identification of the low polarity compound

A crystal structure analysis of the major, non-polar product provided a conclusive resolution of the conflicting evidence (Fig. 2). It proved to be the known 2-nitro-tetraphenylporphyrin **7**![27–29] Incidentally, this product possesses the same composition ($C_{44}H_{30}N_4O_2$) as the targeted oxadiazepinonoporphyrin; the β-hydrogen adjacent to the nitro group is significantly low-field shifted and it does, naturally, not contain a carbonyl group. Moreover, its $NaBH_4$ reduction to generate the corresponding porphyrin is a known reaction.[30]

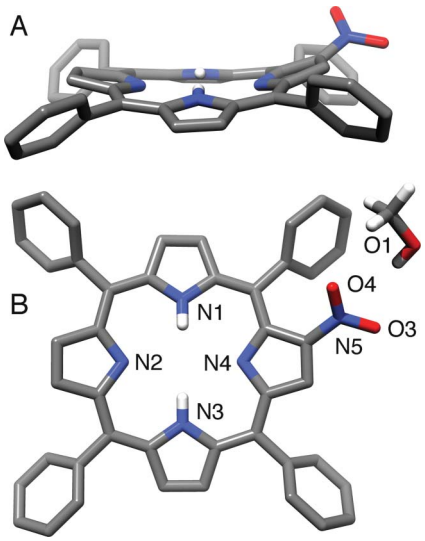


Fig. 2 X-ray structure of low polarity product 2-nitroporphyrin **7**. A: side view; B: top view. All hydrogens attached to sp^2-carbons removed for clarity. For details, see ESI.†

Since nitroporphyrin **7** is known, including its crystal structure (even though the CH_3OH solvate of **7** crystallized here was not known),[31] we will not describe this compound (or its known Ni(II) and novel Pd(II) and Pt(II) complexes formed by metal insertion into the free base) in any detail (see ESI†). Instead, we will focus on its mode of formation.

The finding of a 2-nitroporphyrin **7** as the major product from the reaction of secochlorin bisaldehyde **5** and hydroxylamine might appear incongruous at first. However, a sequence of straight forward reactions rationalize its formation (Scheme 2). Formation of oxime **I** is followed by an oxime-to-nitrone (**IV**) tautomeric exchange, a known tautomer equilibrium.[32] Either this nitrone oxidizes spontaneously to the corresponding nitro compound **VI**, which then undergoes an intramolecular Henry reaction to form **7**, or the nitrone is basic enough to undergo an intramolecular Henry-type condensation to form nitrone porphyrin **V**, followed by oxidation to the final product **7**.[33] Whatever the exact mechanism might be, the reaction is surprisingly efficient and clean, likely reflecting the large thermodynamic stability of the final product. Provided that 2-nitroporphyrins are readily made by direct nitration of porphyrins using a range of methods,[27,28] this new method for the formation of nitroporphyrins does not constitute a competitive synthetic pathway.

Identification of the high polarity compound

The identification of the high polarity reaction product held another surprise. Its UV-vis spectrum in neutral solution is porphyrin-like but exhibits a very unusual optical shift in acidic conditions (for a detailed description of the UV-vis spectrum of this compound, *vide infra*). Its ^1H NMR spectrum reflects a porphyrin without axial symmetry (*e.g.*, six signals for six non-equivalent β-protons), containing one unusual s at 10.2 ppm (see ESI†). Its composition, as measured by HR-MS (ESI+, 100% CH_3CN) indicated the composition $C_{43}H_{28}N_5$ for MH+, *i.e.*, the formal replacement of one CH group in **6** by a nitrogen. This provided a tantalizing hint that this

product might be imidazoloporphyrin **6**. Indeed, this structural assignment could be confirmed by single crystal crystallography (Fig. 3).

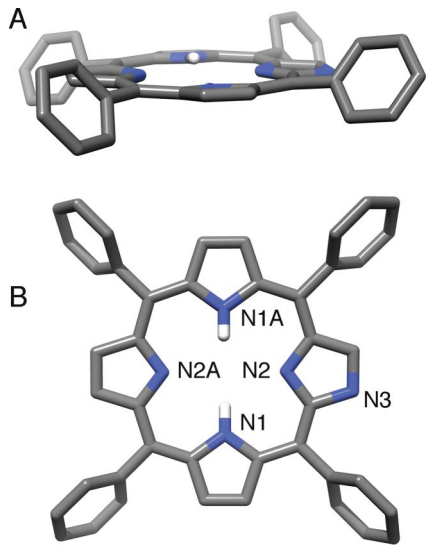
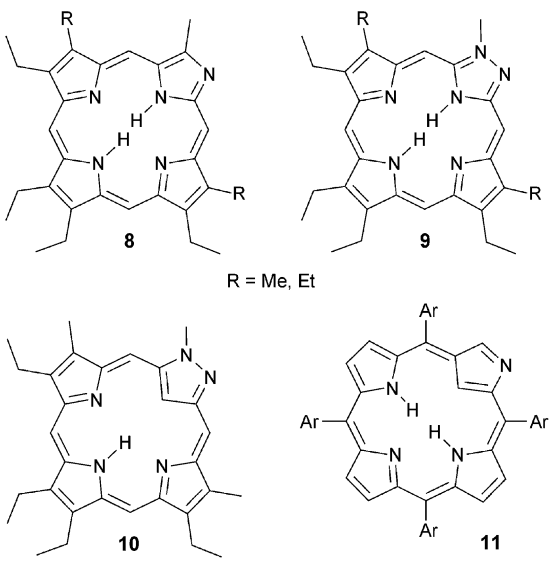


Fig. 3 X-Ray structure of high-polarity product imidazoloporphyrin **6**. A: top view; B: side view. All hydrogens attached to sp^2-carbons removed for clarity. For details, see ESI†.

The crystal structure of **6** is isostructural to the solvent-free triclinic polymorph of TPP,[34] highlighting how the packing of these molecules is only determined by the overall shape of the molecule and the *meso*-substituents. An equivalent observation was made for the crystal structure of *N*-confused TPP **11**.[35] The second nitrogen atom of the imidazole moiety was found to be nearly randomly distributed between all eight possible positions, with an occupation between 6.1(3) and 17.1(3)% per site. Nonetheless, the data obtained did allow for a reliable determination of the distribution of N atoms *vs.* CH groups, thus unambiguously confirming the compound as imidazoloporphyrin **6** by diffractometry (for details, see ESI†).



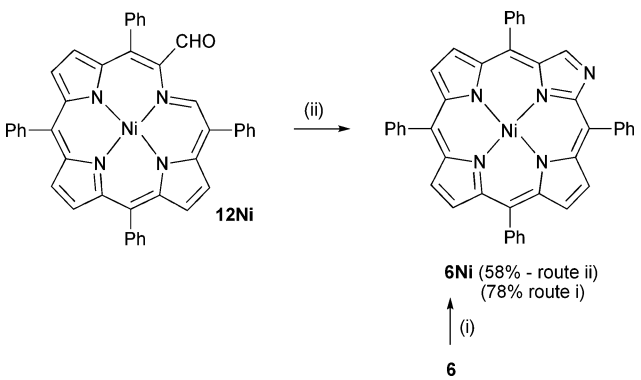
Imidazoloporphyrin **6** is one of the few examples of β-azaporphyrins and β-azacarbaporphyrins. Examples include the imidazoloporphyrin **8**,[36] the triazoloporphyrin **9**,[37] and the pyrazole derivative **10**.[38,39] All the β-alkylderivatives were prepared along 3 + 1-type total syntheses. Among the *meso*-arylporphyrinoids, *N*-confused porphyrin **11** might be the closest relative to imidazoloporphyrin **6**. In essence **11** is the carbaporphyrin analogue to **6**.

We interpret the occurrence of imidazoloporphyrin **6** as indirect proof that the target compound, diazepinone **III** is formed by the reaction of bisaldehyde **5** with hydroxylamine after all (Scheme 2). This is because the formation of **6** can be rationalized by the extrusion of CO_2 from **III**. Neither the thermally induced loss of CO_2 from (electron-rich) aromatic compounds nor the decarboxylation of porphyrinoids at this position (*cf.* the formation of porpholactone **2** by MnO_4^--induced oxidation of the corresponding 2,3-diolchlorin)[10] is surprising.

Interestingly, reaction of the Ni(II) complex of secochlorin bisaldehyde **5** with hydroxylamine under the conditions described above generates exclusively the Ni(II) complex of the 2-nitroporphyrin **7**, and not a trace of the Ni(II) imidazoloporphyrin **6Ni**.

Ni(II) complex of imidazoloporphyrin 6, and alternative synthesis of 6Ni

Insertion of Ni(II) into free base imidazoloporphyrin **6** proceeds smoothly under standard conditions,[26] producing the complex **6Ni** (Scheme 3). It possesses all the expected spectroscopic properties. Its optical properties are delineated below.



Scheme 3 *Reaction Conditions*: (i) 10 eq $Ni(OAc)_2 \cdot 4H_2O$, pyridine, Δ, 24 h. (ii) 45 eq $NH_2OH \cdot HCl$, pyridine, Δ, 1 h.

An alternative synthesis for **6Ni** is available by reaction of **12Ni** with hydroxylamine under the conditions described above for **5**/**5Ni**, and generates the Ni-complex of imidazoloporphyrin **6Ni** in moderate yields (Scheme 3). [*meso*-Tetraphenyl-1-formylchlorophinato]Ni(II) (**12Ni**) is available either by means of deformylation of secochlorin bisaldehyde **5Ni**, or by Vilsmeier–Haak formylation of the corresponding chlorophin.[13,16,22] Evidently, the intermediate oxime loses water to ring-close in an oxidative fashion. It thus represents yet another novel, step-wise and rational way of incorporating a nitrogen into the porphyrin framework. The difficulty in preparing **12Ni** in larger quantities, however, renders this synthesis of interest only to academics.[13,16,22]

This reaction raises the question whether the reaction mechanism of the reaction of **5** with hydroxylamine as described in Scheme 2 proceeds *via* the seven-membered intermediates shown, or if a spontaneous (thermal) deformylation of monooxime **I** takes place. We cannot be sure but tend to discount the latter option as we never observed any other spontaneous deformylations of the secochlorin bisaldehydes, even after prolonged heating in a range of solvents (including benzonitrile, b.p. 188–191 °C).

Optical properties of imidazoloporphyrins 6 and 6Ni

The UV-vis spectrum of **6** in neutral medium is a typical etio-type porphyrin spectrum and very similar, albeit 3–5 nm bathochromically shifted, compared to that of the spectrum of TPP (Fig. 4).[40] Likewise, the fluorescence spectrum of **6** (Fig. 5) and the UV-vis spectrum of its Ni(II) complex, **6Ni**, (Fig. 6) are in shape and position very similar to those of TPP and its Ni(II) complex, TPPNi.

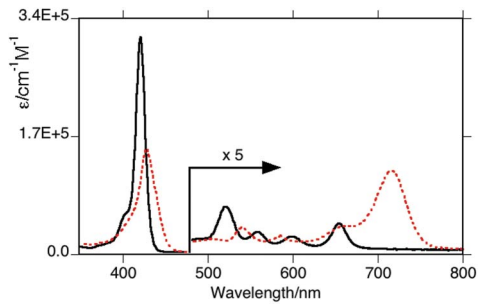


Fig. 4 UV-vis spectrum of imidazoloporphyrin **6** in CH_2Cl_2 (solid trace) and CH_2Cl_2 + 2% TFA (dotted trace).

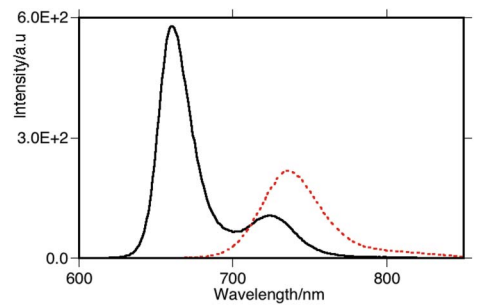


Fig. 5 Fluorescence spectrum of imidazoloporphyrin **6** in CH_2Cl_2 (solid trace) and CH_2Cl_2 + 2% TFA (dotted trace).

In contrast, optical spectra vastly different from those of TPP and TPPNi were recorded under acidic conditions. Protonation of free base **6** resulted in a dramatic bathochromic shift of the UV-vis and fluorescence spectra (Fig. 4 and 5), whereas only minor red-shifts are observed for TPP.[18] Also, for protonated **6**, four side bands were still discernible, whereas protonated TPP shows only two side bands. We interpret the differences by protonation of the nitrogen in the porphyrinic β-position as well as at the inner nitrogen(s). The shift of the Soret band upon protonation might indicate the distortion of the porphyrin from planarity upon protonation of the inner nitrogens whereas the number of side bands and their red-shift might be an indication of the

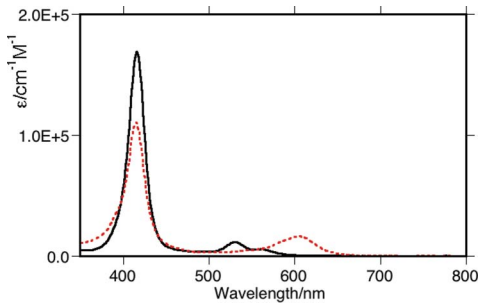


Fig. 6 UV-vis spectrum of imidazoloporphyrin **6Ni** in CH_2Cl_2 (solid trace) and CH_2Cl_2 + 2% TFA (dotted trace).

protonation of the periphery (and the low overall symmetry of the chromophore).[41] The fluorescene yield of TPP is greatly diminished upon protonation. However, **6** still shows strong fluorescence under acidic conditions, and the spectrum reflects the red-shifted absorption spectrum. Whether one or two (or none) of the inner nitrogens are protonated and what the respective relative basicities of the inner and outer nitrogen(s) are is a matter of current study.

TPPNi is inert toward inner nitrogen protonation (at the conditions of 2% TFA in CH_2Cl_2). Imidazolo-analogue **6Ni**, however, can be protonated at the outer nitrogen. This causes a large red-shift of the metallochlorin-like spectrum (Fig. 6) but because protonation at this position most likely does not change the conformation of the chromophore, it does not shift the position of the Soret band (though it reduces its extinction coefficient by about a third).

Conclusions

In conclusion, the reaction of secochlorin **5** with hydroxylamine provides as the major product the known 2-nitroporphyrin **7** and as a minor product the novel imidazoloporphyrin **6**, the latter likely by way of an intermediate oxadiazepinochlorin. Both products reflect the large driving force in porphyrinoids to form a planar macrocycle incorporating four (planar) five-membered heterocycles. The two syntheses of imidazoloporphyrin **6** presented show, for the first time, how a β-CH group in *meso*-tetraphenylporphyrin can be replaced in a step-wise and rational approach by an imine-type nitrogen. We thus again demonstrated the potential of the 'porphyrin breaking and mending' strategy for the preparation of novel pyrrole-modified porphyrinoids.

We are currently engaged in finding more efficient pathways for the synthesis of **6**, and the study of the acid/base, chemical, and coordination properties of this unique pyrrole-modified TPP derivative.

Experimental

Materials and instruments

All solvents and reagents (Aldrich, Acros) were used as received. *meso*-Tetraphenylsecochlorinato bisaldehyde **5** was freshly prepared by oxidative cleavage ($NaIO_4$/silica) of *meso*-tetraphenyl-2,3-dihydroxychlorin as described before, and used immediately.[20]

[*meso*-Tetraphenyl-1-formyl-chlorophinato]Ni(II) (**12Ni**) was prepared by partial deformylation of the corresponding bisaldehyde or, alternatively, by Vilsmeier–Haak formylation of [*meso*-tetraphenylchlorophinato]Ni.[13,16,22] Analytical (aluminium backed, silica gel 60, 250 μm thickness), preparative (20 × 20 cm, glass backed, silica gel 60, 500 or 1000 μm thickness) TLC plates, and the flash column silica gel (standard grade, 60 Å, 32–63 μm) used were provided by Sorbent Technologies, Atlanta, GA. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX400 or a Varian 500 MHz 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 Cary 50, and the fluorescence spectra on a Cary Eclipse spectrophotometer, both Varian Inc. IR spectra were acquired on a JASCO FT-IR-410 using an ATR (ZnSe) unit.

meso-Tetraphenyl-2-aza-porphyrin 6 and *meso*-tetraphenyl-2-nitro-porphyrin 7 by reaction of *meso*-tetraphenyl-secochlorin-2,3-bisaldehyde 5 with hydroxylamine

In a round-bottom flask equipped with a magnetic stir bar, crude bisaldehyde **5** (61 mg, 9.42×10^{-2} mmol; from the reaction of 61 mg *meso*-tetraphenyl-2,3-dihydroxychlorin) was dissolved in pyridine (20 mL). $NH_2OH{\cdot}HCl$ (196 mg, 2.82 mmol, ~30 eq) was added and the mixture was heated to reflux for 1 h. Once the starting material was consumed (reaction control by UV-vis and TLC), the reaction mixture was evaporated to dryness by rotary evaporation. The dry residue was taken up in CH_2Cl_2 and filtered through a plug of silica gel in a glass frit (M), the filtrate washed with water (2 × 10 mL), dried over anhyd. Na_2SO_4, and evaporated to dryness by rotary evaporation. The resulting mixture was separated on a preparative TLC plate (silica, CH_2Cl_2-pet ether 1 : 1). Isolated yields of **7** were 62% (38 mg), and of **6** 15% (8.5 mg). **6**: R_f (silica-CH_2Cl_2) 0.25; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.2 (s, 1H), 9.10 (d, ^3J = 4.0 Hz, 1H), 9.06 (d, ^3J = 4.0 Hz, 1H), 8.95–8.92 (m, 2H), 8.74 (s, 2H), 8.29–8.26 (m, 4H), 8.22–8.20 (m, 4H), 7.83–7.75 (m, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0, 161.3, 156.8, 156.4, 148.2, 141.9, 141.8, 141.1, 140.2, 139.9, 139.7, 139.5, 138.2; 135.3, 135.25, 135.2, 134.8, 134.7, 129.5, 128.8, 128.7, 128.5, 128.4, 128.15, 128.1, 127.9, 127.3, 127.2, 127.0, 120.9, 120.7, 120.5, 120.4 ppm; UV-vis ($CHCl_2$ + drop Et_3N): λ_{max} (log ε) 420 (5.49), 520 (4.14), 559 (3.83), 600 (3.72), 654 (3.95) nm; UV-vis ($CHCl_2$ + 2% TFA) λ_{max} (log ε) 427 (5.18), 541 (3.90), 586 (3.76), 658 (3.92), 717 (4.39) nm; MS (ESI$^+$, 100% CH_3CN) *m*/*z* calcd for $C_{43}H_{30}N_5$ (for M·H$^+$) 616.2501, found 616.2585. **7**: R_f (silica-CH_2Cl_2) = 0.73; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (s, 1H), 9.02 (d, ^3J = 5.2 Hz, 1H), 8.95 (d, ^3J = 4.8 Hz, 1H), 8.92–8.90 (m, 2H), 8.74–8.71 (m, 2H), 8.26 (d, ^3J = 8 Hz, 2H), 8.23–8.17 (m, 6H), 7.83–7.70 (m, 12H), –2.60 (s, 2H, exchangeable with D_2O) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 156.4, 153.1, 146.0, 142.5, 141.6, 141.4 141.1, 140.4, 140.2, 139.4, 138.0, 135.06, 135.04, 134.7, 134.6, 131.9, 129.9, 129.5, 128.9, 128.6, 128.4, 128.3, 128.0, 127.1, 126.99, 126.94, 126.90, 123.0, 120.8, 120.6, 120.1 ppm; UV-vis ($CHCl_2$) λ_{max} (log ε) 427 (5.80), 527 (4.68), 5.64 (4.12), 604 (4.11), 664 (4.43) nm; MS (ESI$^+$, 100% CH_3CN) *m*/*z* calcd for $C_{44}H_{30}N_5O_2$ 660.2400 ([M·H]$^+$), found 660.2337. The data, included here for comparison, are commensurate with those reported before.[27,29]

[*meso*-Tetraphenyl-2-aza-porphyrinato]Ni(II) (6Ni) from reaction of [*meso*-tetraphenyl-1-formyl-chlorophinato]Ni(II) (12Ni) with hydroxylamine (Route A)

Monoaldehyde **12Ni** (4.5 mg, 6.95×10^{-6} mol) was dissolved in pyridine (5.0 mL) in a round-bottom flask equipped with a magnetic stir bar. H_2N-OH·HCl (22.0 mg, 3.17×10^{-4} mol) was added and the mixture was heated to reflux for 14 h. Once the starting material was consumed (reaction control by TLC), the reaction mixture was evaporated to dryness by rotary evaporation, taken up in CH_2Cl_2 and filtered through a plug of silica gel in a glass frit (M). The filtrate was washed with water (2 × 10 mL), dried over anhydrous sodium sulfate, and evaporated to dryness by rotary evaporation. The resulting solid was separated on a preparative TLC plate (6 × 20 cm glass-backed, 500 μm silica, CH_2Cl_2/25% petroleum ether 30–60). Isolated yield of **6Ni** was 56% yield (2.6 mg).

[*meso*-Tetraphenyl-2-aza-porphyrinato]Ni(II) (6Ni) by insertion of Ni(II) into free base 6 (Route B)

Free base imidazoleporphyrin **6H$_2$** (7.0 mg, 1.14×10^{-5} mol) was added to a solution of pyridine (10 mL) and $Ni(CH_3CO_2)_2{\cdot}4H_2O$ (32 mg, 1.4×10^{-4} mol, ~11 eq) in a round-bottom flask equipped with a magnetic stir bar and the mixture was heated to reflux for 24 h. When the starting material was consumed (reaction control by UV-vis and TLC), the mixture was allowed to cool, the solvent was removed in *vacuo* and triturated in a minimal amount of CH_2Cl_2. The resulting mixture was separated on a preparative TLC plate (CH_2Cl_2/25% petroleum ether 30–60). Isolated yield of **6Ni** was 78% (5.9 mg). **6Ni**: R_f (silica-CH_2Cl_2) 0.45; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.1 (s, 1H), 8.83 (two overlapping d, ^3J = 4.0 Hz, 2H), 8.72–8.70 (m, 4H), 8.09 (dd, ^3J = 8.0, 1.0 Hz, 2H), 8.06 (dd, ^3J = 8.0, 1.0 Hz, 2H), 8.02–7.98 (m, 4H), 7.75–7.64 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 151.0, 146.1, 145. 1, 144.9, 144.7, 144.2, 143.4, 140.8, 140.0, 139.2, 136.5, 134.5, 134.3, 134.0, 133.9, 133.3, 133.2, 132.9, 132.4, 132.3, 128.5, 128.2, 128.1, 127.9, 127.4, 127.3, 127.2, 120.5, 120.0, 119.4, 119.3 ppm; UV-vis (CH_2Cl_2 + drop Et_3N) λ_{max} (log ε) 416 (5.23), 531 (4.06), 562 (3.75) nm; UV-vis (CH_2Cl_2 + 2% TFA) λ_{max} (log ε) 415 (5.04), 605 (4.22); MS (ESI$^+$, cone voltage = 30 V, 100% CH_3CN); HR-MS (ESI$^+$, 100% CH_3CN) *m*/*z* calcd for $C_{43}H_{28}N_5Ni$ 672.1698, found 672.1598.

[*meso*-Tetraphenyl-2-nitroporphyrinato]Ni(II) 7Ni by reaction of 5Ni with hydroxylamine

Prepared as described for the free base reaction using bisaldehyde **5Ni**. The resulting mixture was separated on a preparative TLC plate (silica, CH_2Cl_2-pet ether 2 : 3) and **7Ni** was isolated in 38% yield (12.9 mg). Spectroscopic data for **7Ni** are identical to those reported before (see also ESI†).[42]

Crystal structure determinations

Single crystals of **6** (CH_2Cl_2/MeOH) and **7** (CH_2Cl_2/MeOH) were grown by vapour phase diffusion of a non-solvent into dilute solutions of the compounds using the solvent combinations indicated in parentheses (solvent/non-solvent). The crystals were mounted in inert oil on a glass fibre or Mitegen micromesh mount

Table 1 Crystal data[a]

Compound	**6**	**7·CH$_3$OH**
Formula	$C_{43}H_{29}N_5$	$C_{45}H_{33}N_5O_3$
M/g mol^{-1}	615.71	691.76
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$(#2)	$C2/c$
a, b, c/Å	6.334 (2), 10.352 (3), 12.149 (4)	38.963 (16), 9.070 (4), 25.863 (11)
α, β, γ (°)	94.288 (5), 99.895 (5), 101.107 (5)	90.00, 130.953 (5), 90.00
V/Å^3	765.2 (4)	6902 (5)
T/K	100(2)	100(2)
Z	1	8
Reflections measured	7609	16363
Unique (R_{int})	3744 (0.059)	7040 (0.089)
Data/restraints/parameters	3744/0/223	7040/0/480
Goodness-of-fit on F^2	1.092	0.961
$R(F)$ [$I > 2\sigma(I)$]	0.062	0.086
$R(F)$ [all data]	1.223	0.1951
w$R(F_2)$ [$I > 2\sigma(I)$]	0.1457	0.2202
w$R(F_2)$ [all data]	0.1625	0.2784

[a] For details, see ESI.

and transferred to the cold gas stream of the diffractometer. Crystal data are listed in Table 1. For additional information, see ESI†.

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