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Investigations on the directive effects of a single *meso*-substituent via nitration of 5,12,13,17,18-pentasubstituted porphyrins: syntheses of conjugated β-nitroporphyrins

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Abstract—Vilsmeier formylation of 5-substituted 1,9-diunsubstituted dipyrromethanes afforded 1,9-diformyldipyrromethanes in good yields. Their MacDonald condensation with tetra-β-alkyldipyrromethanes produced 5,12,13,17,18-pentasubstituted porphyrins. A *meso*-electron-donating group, presumably acting by destabilizing the porphyrin a_{2u} ground state, directs the nitrations to the *meso*-carbons. β-Nitration takes place on porphyrins bearing a *meso*-electron-withdrawing group. Unhindered β-nitro groups are shown to exert stronger electronic effects relative to *meso*-nitro groups by conjugating effectively with the porphyrin macrocycle.

1. Introduction

Electrophilic, nucleophilic, and radical reactions on porphyrins bearing vacant *meso*- and β-positions occur preferentially at the methine bridges.[1,2] Exceptions leading to β-functionalizations result from the core-complexation of electropositive metals such as nickel(II) or palladium(II),[3] steric impediments (e.g. upon bromination, formylation, mercuration)[4] or changes in the physical state of the initial products (e.g. upon sulfonation).[5] Nitration reactions are particularly insensitive to peripheral crowding and prevail at the *meso*-positions (for example nitrations of unsubstituted porphyrin,[1c] 5,15-diarylporphyrin,[2b,c] deuteroporphyrin[6] and octaethylporphyrin[7]). Nitrations of the zinc(II) or magnesium(II) *meso*-tetraphenylporphyrins (TPPs) take place at the crowded *meso*-positions,[8a] but use of bulkier *meso*-substituents such as 2,6-dichlorophenyl inhibits such *ipso*-attacks.[9]

Complexation with electronegative metals (Cu(II), Ni(II), Pd(II)) ensure β-nitrations and afford 2-nitro-tetraphenylporphyrins in good yields.[8] However, electronegative metals do not always promote β-functionalizations of tetra-*meso*-substituted porphyrins. Indeed, reactions of nickel(II) or copper(II) 5,10,15,20-tetrapropylporphyrin with N_2O_4 resulted in electrophilic dealkylative nitration (affording 5-nitro-10,15,20-tripropylporphyrin) or ring-opening of the porphyrin macrocycle.[10]

From these previous studies, we can assume that *meso*-substituents have an important electronic influence upon the outcome of the nitration reaction. Effects of a single *meso*-substituent on the reactivity of the porphyrin system were investigated using 5-phenyl-12,13,17,18-tetraethylporphyrin.[11] As expected, bromination of this porphyrin took place under strong steric regulation at an unhindered β-position. Nitration reactions, which are little influenced by steric crowding, are better suited to investigate the directive effect (if any) of a single *meso*-substituent on the reactivity of pentasubstituted porphyrins. Herein, we report the synthesis and N_2O_4 nitrations of a series of zinc(II) and nickel(II) complexes of 5,12,13,17,18-pentasubstituted porphyrins. Conditions to obtain porphyrins bearing β-nitro substituents free of flanking *meso*- and/or β-substituents and concomitantly displaying strongly perturbed optical spectra are discussed. Prior to this work a few *meso*-unsubstituted-β-nitroporphyrins[12] and a 2,3-dinitroporphyrazine[13] have been prepared, but the strong π-acceptor nitro groups were sterically prevented from conjugation with the porphyrin ring.

2. Results and discussion

β-Nitration of the porphyrin periphery has been recognized to advantageously alter the chemical reactivities at the various pyrrolic positions.[14] β-Nitroporphyrins have been used in various nucleophilic addition[15] and substitution reactions,[16] and have been investigated for their nonlinear optical,[17] catalytic[18] and photophysical properties.[19,20] We prepared a first coplanar β-nitroporphyrin **1** by nitration of the nickel(II) complex of a *meso*-free hexa-β-alkylporphyrin,[10] and (erroneously) assumed that the predominant

Keywords: nitroporphyrin; porphyrin; regioselective nitration; Vilsmeier formylation.

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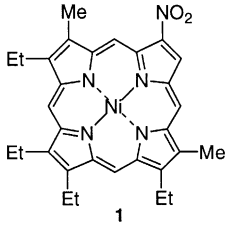
electronic effect leading to *meso*-nitration could be overridden by a careful balance of steric effects. As a result, 5-substituted-12,13,17,18-tetraalkylporphyrins were targeted as they offer similar structural features (two sterically unhindered β-unsubstituted positions), but could be readily prepared from *meso*-substituted β-free dipyrromethanes. β-Free dipyrromethanes are useful synthetic porphyrin intermediates,[21] which have also been oxidized to dipyrromethenes,[22] mono- and di-acylated with pyridyl thioester,[23] and brominated.[24] Two examples of Vilsmeier reactions were reported to afford 1,9-diformyl-5-(aryl)-dipyrromethanes.[25,26] These can also be obtained in three steps via the cyanovinyl protection of 2-formylpyrrole.[27] Herein, we extend the Vilsmeier reaction to a series of β-unsubstituted-5-(alkyl)-dipyrromethanes.



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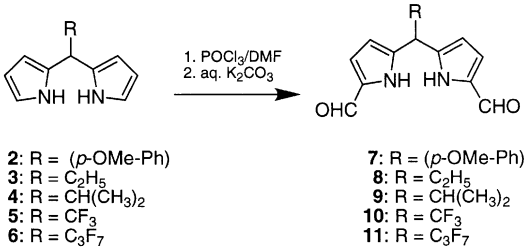

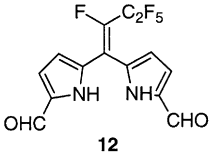

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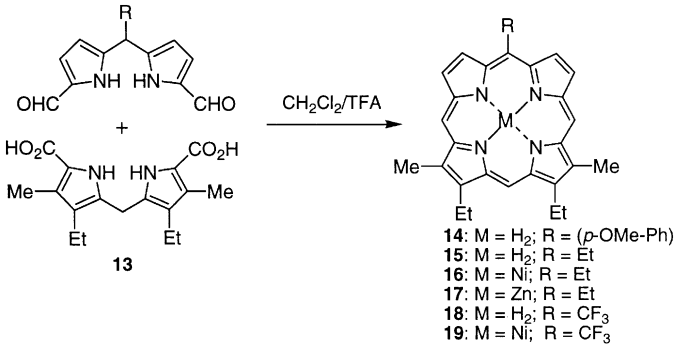
2.1. Synthesis of 5,12,13,17,18-pentasubstituted porphyrins

Condensation of *p*-anisaldehyde, propionaldehyde and isobutyraldehyde with excess pyrrole[28] in the presence of trifluoroacetic acid (TFA) gave moderate yields of 5-substituted dipyrromethanes **2**–**4**. Treatment of 2 equiv. of pyrrole with trifluoroacetaldehyde or heptafluorobutyraldehyde (as their hydrate or hemiacetal) afforded perfluoroalkyldipyrromethanes **5** and **6**.[29] Reaction of dipyrromethanes **2**–**5** with excess $POCl_3$/DMF in dichloromethane followed by hydrolysis with saturated aqueous K_2CO_3 produced bench-stable 1,9-diformyldipyrromethanes **7**–**10**. *meso*-Heptafluoropropyldipyrromethane **6**, when reacted with $POCl_3$/DMF, gave traces of diformyldipyrromethane **11**. Instead, upon hydrolysis, a base-catalyzed elimination of HF yielded 1,1-bis(5-formylpyrrol-2-yl)ethene **12**. In dichloromethane, bis(pyrrolyl)ethene **12** exists in the methylidene form (as shown) rather than as the conjugated dipyrromethene tautomer.[30] Addition of TFA turned the yellow solution to red, as expected for dipyrromethene salts.

Two β-tetraethyl-5-phenylporphyrins have been obtained by acid-catalyzed condensation of two 1,19-di-unsubstituted-a,c-biladienes with benzaldehyde followed by oxidation with DDQ.[11] We followed a modified MacDonald (2+2) pathway and reacted 1,9-diformyldipyrromethanes **7**, **8** and **10** with 3,7-diethyl-2,8-dimethyldipyrromethane-1,9-dicarboxylic acid **13**[31] in CH_2Cl_2 in the presence of TFA; this afforded, after oxidation with DDQ and chromatographic purifications, penta-substituted porphyrins **14**, **15** and **18** in 17–32% yield. Of note is that 1,9-diformyl-2,3,7,8-tetraethyldipyrromethane failed to condense with **2** to give a tetraethylporphyrin analogue of **14**.[25] 1,1-Bis(5-formylpyrrol-2-yl)ethene **12** was reacted with 2,3,7,8-tetraethyldipyrromethane in the presence of TFA to give porphyrin **20** after DDQ oxidation and migration of the exocyclic double bond.



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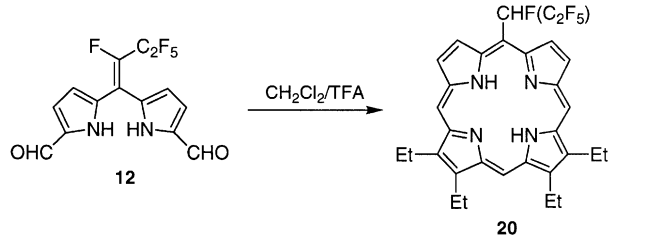


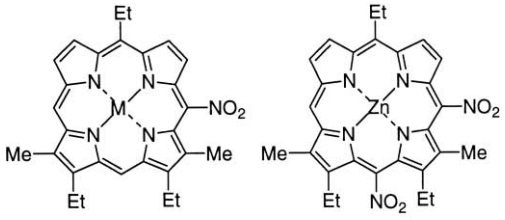
12 20

2.2. Nitrations of metalated 5,12,13,17,18-pentasubstituted porphyrins

Many studies have focused attention on the nitration of porphyrins; various reagents such as N_2O_4,[8a,10] $AgNO_2/I_2$[16a] or $Cu(NO_3)_2/AcOH/Ac_2O$,[8b,c] have been used. The nature of the nitrating species ($NO_2^{\cdot}$ or NO_2^+) and the nitration mechanisms are ambiguous and could involve radical combination of the porphyrin π-cation radical with $NO_2^{\cdot}$,[8a] NO_2^+ electrophilic substitution[10] and/or charge-transfer process (likely between NO_2^+ and low redox potential porphyrin derivatives).[32] Reaction of the zinc complex **17** with $AgNO_2/I_2$ in CH_3CN/CH_2Cl_2 yielded simultaneously the brown-red 10-nitro-**21** and 10,15-dinitro-**22** products along with some starting material. Upon HNO_3 nitration of 5-nitroporphyrin in H_2SO_4, a 5,10-dinitro-product was also obtained and its formation was rationalized by considering the relative stabilities of the two potential σ-complexes leading to the nitration (5,10 vs 5,15) products.[2c] The 5,10-disubstituted products are favored as no resonance structure with a positive charge on the *meso*-carbon bearing the 5-nitro group can be written upon nitronium attack at the 10-position. When the nickel(II) complex **16** was nitrated with $AgNO_2/I_2$, N_2O_4 or $Cu(NO_3)_2$, the *meso*-nitroporphyrin

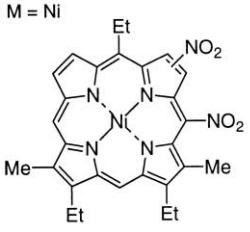
23 was obtained in moderate yield. In contrast to the zinc complex, further nitration took place at unsubstituted β-positions giving rise to a regioisomeric mixture of green dinitroporphyrins **24** (characterized by mass spectrometry and ^{1}H NMR spectroscopy). Bulkier β-substituents [as in nickel(II) 5,12,18-triisopropyl-13,17-dimethylporphyrin, not shown] did not prevent *meso*-nitrations.

Strong electron-withdrawing *meso*-groups are known to preferentially stabilize the a_{2u} porphyrin orbitals (which has large amplitude at the *meso*-positions) relative to the highest occupied a_{1u} orbitals (with a large amplitude on the α and β-carbons).[19] Therefore, to favor β- over *meso*-nitration, we turned our attention to 5-perfluoroalkyl-porphyrins hoping to perturb the porphyrin electronic distribution by altering the macrocycle frontier orbitals. Indeed, N_2O_4 nitration of nickel(II) 5-trifluoromethyl-12,18-dimethyl-13,17-diethylporphyrin **19** [or the nickel(II) complex of **20**, not shown] gave rise simultaneously to three mono-nitroporphyrins (**25**–**27**) as shown by thin layer chromatography (TLC). Some *meso*-nitration occurred and the red *meso*-nitroporphyrin **27** was obtained in 38% yield. Two green β-nitro derivatives were isolated in a combined yield of 53%. The preferential formation of the crowded β-nitroporphyrin **25** relative to the truly β-coplanar-nitroporphyrin **26** may result from the relative ability of their likely charged intermediates to accommodate a positive charge. $AgNO_2/I_2$ nitration of zinc(II) 5-trifluoromethyl-12,18-dimethyl-13,17-diethylporphyrin gave a regioisomeric mixture of mono-*meso*-nitroporphyrin (not shown), showing that a *meso*-electron-withdrawing group did not upset the strong *meso*-directive effect of an electropositive metal.



21: M = Zn
23: M = Ni

22



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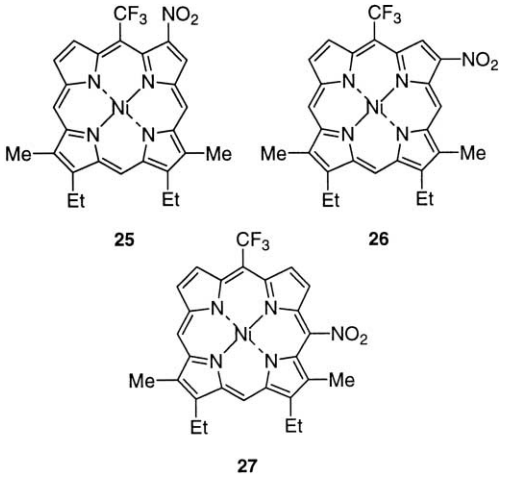
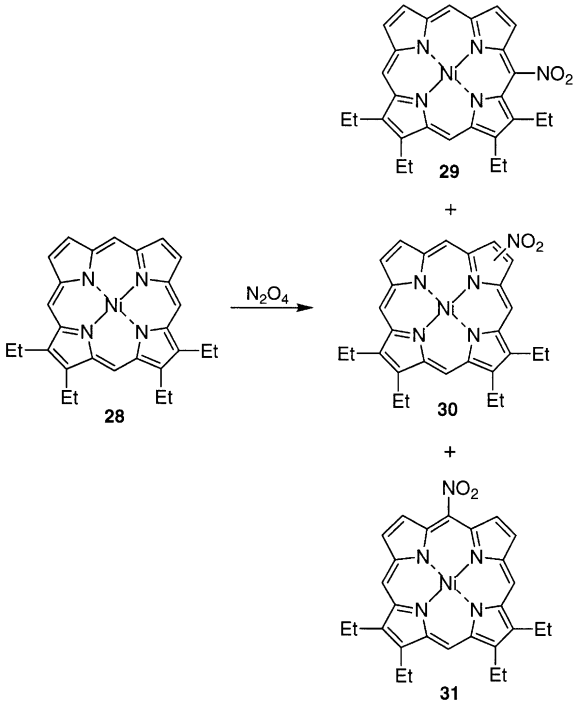
N_2O_4 nitration of nickel(II) 2,3,7,8-tetraethylporphyrin **28** produced four nitroporphyrins: the red *meso*-nitroporphyrin **29**, two non-separable green β-nitroporphyrins **30**, and the brown *meso*-nitroporphyrin **31** in a roughly 2:4:1 ratio (respectively). The formation of these two β-nitro derivatives (despite the presence of an unhindered *meso*-position) suggests that the four β ethyl groups alone do not induce a large electronic perturbation and presumably preserve the a_{1u} ground state of the unsubstituted porphyrin.[33]



25 **26**

27



29 + **28** → N_2O_4 → **30** + **31**

The ^{1}H NMR spectra of coplanar β-nitroporphyrins reflect the magnetic anisotropy and resonance effect of the nitro group. A coplanar β-nitro group places the adjacent β- and *meso*-protons in a region of strong negative shielding (porphyrin **26**, β-H at δ 9.75 and *meso*-H at 9.92), whereas the shielding of the other *meso*-protons (δ 9.10–9.15) stems from a reduced aromatic ring current. The absorption spectra were more sensitive to the nitration site and reflect the orientation of the nitro group relative to the macrocycle (for Figure, see ref. 10). *meso*-Nitration only slightly red-shifted the optical spectra relative to the starting porphyrins. β-Nitration resulted in an intense Q-band absorption, the signature of an effective intramolecular charge transfer.[34] The absorption spectrum of β-nitroporphyrin **26** also displayed split Soret bands at 370 and 421 nm. Theoretical calculations on β-nitroporphyrins have shown that a coplanar nitro group would result in such splitting of the Soret band.[20] Two β-nitrovinyl porphyrins prepared by direct nitrosation of protoporphyrin IX displayed similar

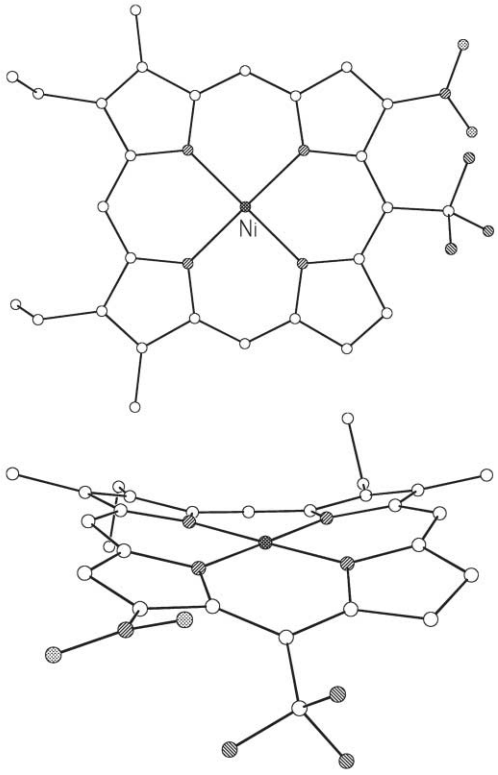


Figure 1. The molecular structure of **25**; (top) top view, (bottom) side view. Hydrogens have been omitted for clarity.

split Soret bands, while their IR spectra suggested the presence of a conjugated nitro-group.[35]

In the infrared spectra spectra of *meso*-nitroporphyrins such as **27**, peaks at 1362 cm^{-1} were attributed to the symmetric stretching mode of NO_2. In the IR spectrum of **26** the occurrence of the symmetric mode at lower frenquencies (1331 cm^{-1}) is in accord with structures containing a coplanar aromatic nitro group.[36] For β-nitroporphyrin **25**, this peak was found at an intermediate frequency (1349 cm^{-1}) and supports some conjugation of the nitro group with the π-system.

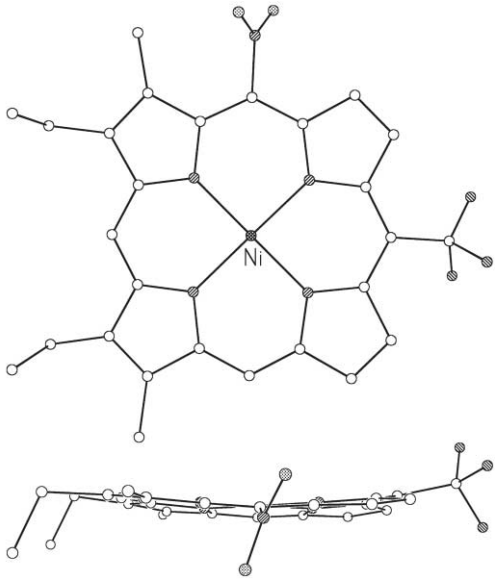


Figure 2. The molecular structure of **27**; (top) top view, (bottom) side view. Hydrogens have been omitted for clarity.

The molecular structures of **25** and **27**, as determined by X-ray crystallography, are shown in Figs. 1 and 2, respectively. Selected geometrical features for all reported *meso* and β substituted mono- and di-nitroporphyrin crystal structures are given in Table 1. The macrocycle of **25** exhibited a non-planar ruffled distortion, a nitro-to-PMP (porphyrin mean plane) dihedral angle of 21.5°, and an average Ni–N bond length of 1.933[5] Å. Steric strain between the nitro and trifluoromethyl groups along with the tendency of Ni(II) ions to contract porphyrin 4N cores were causative factors for the non-planar distortion. The macrocycle of **27** was only slightly non-planar with a predominantly ruffled distortion, a nitro-to-PMP dihedral angle of 69.5° (within the range observed for *meso*-nitroporphyrins, Table 1), and an average Ni–N bond length of 1.962[5] Å.

The structure of **25**, along with those of 2-nitro-TPP[39] (nitro-to-PMP dihedral angle=48.1°), and 2,13-dinitro-TPP[40] (nitro-to-PMP dihedral angles=42.7° and 45.1°) represent the only published crystal structure determinations of β-nitroporphyrins. While taking into account steric restrictions to nitro rotation (imposed by adjacent *meso* substituents) it is clear from these data that the β-nitro groups tend towards coplanarity with their porphyrin macrocycles. In contrast, *meso*-nitroporphyrins exhibit nitro-to-PMP dihedral angles that approximate perpendicularity (Table 1). Once structural investigations into porphyrins with unhindered β-nitro groups (such as **26** or **30**) are obtained we will have better physical evidence pertaining to the geometry and electronic interactions involved in these systems.

3. Conclusions

meso-Substituted 1,9-diformyldipyrromethanes were prepared in good yields by Vilsmeier formylation of α,β-di-unsubstituted dipyrromethanes. Their MacDonald condensation with tetraalkyldipyrromethane afforded 5,12,13,17,18-pentasubstituted porphyrins. β-Nitration of these porphyrins can compete with *meso*-nitration depending upon an appropriate choice of metal (nickel) and *meso*-substituent (electron-withdrawing groups). The steric effects were found to be negligible. The effect of a *meso*-electron-donating group was more pronounced, and resulted in exclusive *meso*-nitrations presumably by destabilizing the porphyrin a_{2u} ground state (which has large amplitude at the *meso*-positions). Alternatively, a single *meso*-perfluoroalkyl group did not sufficiently stabilize the a_{2u} porphyrin orbitals to induce exclusive β-nitration. While most substituents exert stronger electronic effects at the *meso*-positions than at the β-positions, unhindered β-nitro groups are an exception as they are sterically allowed to lie in the plane of the porphyrin and can conjugate effectively with the macrocycle, thus resulting in strongly perturbed electronic spectra.

Table 1. Selected geometrical features for all reported *meso* and β substituted mono- and di-nitro porphyrin crystal structures

Compound	CSD refcode[41]	MDPMP[a] (Å)	Nitro/PMP[b] dihedral angle (°)
(**25**), Ni(II) 13,17-diethyl-12,18-dimethyl-3-nitro-5-trifluoromethyl *P*[c]	–	0.250	21.5
(**27**), Ni(II) 13,17-diethyl-12,18-dimethyl-10-nitro-5-trifluoromethyl *P*[c]	–	0.096	69.5
5-Nitro-10,20-diphenyl *P*[c,d,2b]	NESHOI	0.134	62.4
2-Nitro-TPP[d,e,39]	NOZKUI	0.088	48.1
[Fe(III)Cl] 5-nitro-OEP[f,42]	TOYSAB	0.093	84.0
5-nitro-OEP[d,f,43]	WAVLOU	0.029	86.0
[Zn(II)] 5-nitro-OEP[f,43]	WAVMAH	0.028	87.6
[Zn(II)-pyridine] 5-nitro-OEP[f,43]	WAVLUA	0.041	87.7
[Zn(II)-MeOH] 5-nitro-OEP[f,43]	WAVMEL	0.025	89.4
2,13-dinitro-TPP[d,e,40]	HAVFUF	0.284	42.7, 45.1

[a] MDPMP=The mean deviation of the 24 macrocyclic atoms from their least-squares plane.
[b] PMP=Porphyrin mean plane, calculated as the 24 atom macrocyclic least-squares plane.
[c] *P*=porphyrin.
[d] In free base form.
[e] TPP=5,10,15,20-tetraphenylporphyrin.
[f] OEP=2,3,7,8,12,13,17,18-octaethylporphyrin.

4. Experimental

4.1. General

Mps were measured on a Thomas/Bristoline microscopic hot stage apparatus and were uncorrected. Silica gel 60 (70–230 and 230–400 mesh) was used for column chromatography. Preparative thin layer chromatography was carried out on 20×20 cm glass plates coated with Merck G 254 silica gel (1–2 mm thick). Analytical thin layer chromatography (TLC) was performed using Macherey–Nagel Polygram SIL G/UV_{254} (precoated silca gel sheets, 0.2 mm thick). ^{1}H NMR spectra were obtained in deuteriochloroform solution at 300 MHz using a General Electric QE300 spectrometer; chemical shifts are expressed in ppm relative to chloroform (7.26 ppm). Elemental analyses were performed at the Midwest Microlab., Inc., Indianapolis, IN. Electronic absorption spectra were measured in dichloromethane solution using a Hitachi U-2000 spectrophotometer. Mass spectra were obtained at the Mass Spectrometry Facility, University of California, San Francisco, CA, and at the Facility for Advanced Instrumentation, University of California, Davis, CA (LDI-TOF). N_2O_4 gas was prepared by reacting concentrated HNO_3 with zinc metal.[15e] 5-(*p*-Methoxyphenyl)dipyrromethane, 5-(trifluoromethyl)dipyrromethane, 5-(heptafluoromethyl)dipyrromethane **6**, and 2,8-dimethyl-3,7-diethyldipyrromethane-1,9-dicarboxylic acid **13** were prepared according to the literature (vide infra).

4.1.1. 5-Ethyldipyrromethane 3. A mixture of pyrrole (69.4 mL, 1 mol) and propionaldehyde (2.9 mL, 0.04 mol) in a round bottomed flask was degassed with argon for 5 min. Trifluoroacetic acid (0.58 mL, 7.5 mmol) was added and the solution was stirred for 5 min at room temperature under argon. The reaction mixture was quenched with 0.1 M NaOH. Ethyl acetate was added and the organic phase was washed with water, dried and evaporated under vacuum to afford a brownish oil. Excess pyrrole was removed by vacuum distillation at room temperature and the residue was chromatographed on silica gel (eluting with CH_2Cl_2) to yield the product as off white crystals (3.85 g, 55%). It was recrystallized from CH_2Cl_2/petroleum ether, mp 47–48°C. ^{1}H NMR δ 0.93 (t, J=7.6 Hz, 3H), 1.97 (m, 2H), 3.86 (t, J=7.6 Hz, 1H), 6.09 (s, 2H), 6.16 (m, 2H), 6.60 (s, 2H), 7.66 (br s, 2H); Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08; Found: C, 76.02; H, 8.20; N, 15.96. MS: *m/e* 174.1 (92), 157.1 (60), 145.1 (–Et, 100).

4.1.2. 5-Isopropyldipyrromethane 4. Pyrrole (69.4 mL, 1 mol) and 2-methylpropionaldehyde (2.88 g, 0.04 mol) were reacted by the procedure described for **3** (silica gel column eluted with CH_2Cl_2). Recrystallization from CH_2Cl_2/petroleum ether afforded **4** as white crystals (4.36 g, 58%), mp 83–84°C. ^{1}H NMR δ 0.95 (d, J=6.4 Hz, 6H), 2.30 (m, 1H), 3.78 (d, J=6.4 Hz, 1H), 6.07 (m, 2H), 6.16 (m, 2H), 6.62 (m, 2H), 7.79 (br s, 2H); Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.56; H, 8.57; N, 14.88; Found: C, 76.32; H, 8.46; N, 14.63. MS: *m/e* 188.2.

4.1.3. 1,9-Diformyl-5-(*p*-methoxyphenyl)-dipyrromethane 7. $POCl_3$ (5 mL, 0.054 mmol) was added dropwise to a 250 mL three necked round bottomed flask charged with DMF (15 mL) at 0°C under an inert atmosphere. The mixture was stirred for 30 min before adding 5-(*p*-methoxyphenyl)dipyrromethane **2** (2.2 g, 8.72 mmol) dissolved in CH_2Cl_2 (150 mL). The ice bath was removed and the mixture was refluxed for 2 h. The reaction mixture was poured into water, followed by slow addition of K_2CO_3 until a pH >11 was reached. After 1 h, additional K_2CO_3 was added and the mixture was left stirring overnight. The organic phase was separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were washed several times with water and evaporated to dryness. The residue was recrystallized from CH_2Cl_2/hexane to yield 2.19 g of white–beige powder (86%), mp 197–199°C; ^{1}H NMR δ 3.79 (s, 3H), 5.51 (s, 1H, CH), 6.06 (m, 2H), 6.86 (m, 2H), 6.87 (d, 2H), 7.20 (d, 2H), 9.20 (s, 2H), 10.37 (br s, 2H); Anal. Calcd For $C_{18}H_{16}N_2O_2$: C, 68.91; H, 5.44; N, 9.45. Found: C, 69.17; H, 5.27; N, 9.13. MS: *m/e* 308.12 (M^+, 100).

4.1.4. 5-Ethyl-1,9-diformyldipyrromethane 8. Vilsmeier reagent was prepared by adding $POCl_3$ (4 mL, 0.043 mol) dropwise to dimethylformamide (26.6 mL) at 0°C under argon. 5-Ethyldipyrromethane **3** (3.13 g, 0.018 mol) was dissolved in CH_2Cl_2 (60 mL) and the solution was cooled to 0°C. To this solution was added dropwise the Vilsmeier

reagent (2.4 equiv.) and the mixture was stirred at 0°C for 2 h under argon. Saturated aq. Na_2CO_3 solution (200 mL) was added carefully and solid Na_2CO_3 was added until the solution was basic (pH around 12). After 1 h, additional Na_2CO_3 was added and the mixture was left stirring overnight at room temperature. The solution was extracted with CH_2Cl_2 and the extracts were washed with brine. Evaporation of the solvent gave a brown oil which was chromatographed on silica gel eluting with ethyl acetate/cyclohexane (2:3) to yield the product as an off white powder. It was recrystallized from hexane/CH_2Cl_2 (2.73 g, 66%), mp 128–129°C. ^{1}H NMR δ 0.95 (t, J=7.2 Hz, 3H), 2.19 (m, 2H), 4.11 (t, J=7.2 Hz, 1H), 6.21 (m, 2H), 6.94 (m, 2H), 9.43 (s, 2H), 11.38 (br s, 2H). Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17; Found: C, 67.60; H, 6.03; N, 11.95. MS: *m/e* 230.2 (100, M^+).

4.1.5. 1,9-Diformyl-5-isopropyldipyrromethane 9. 5-Isopropyldipyrromethane **4** (3.38 g, 0.018 mol) was reacted with the Vilsmeier reagent using the procedure described for **8** [silica gel column eluted with ethyl acetate/cyclohexane (1:1)]. Recrystallization from hexane/CH_2Cl_2 gave **9** (2.72 g, 62%) as off white crystals, mp 182–183°C. ^{1}H NMR δ 0.96 (d, J=6.3 Hz, 6H), 2.62 (m, 1H), 3.77 (d, J=6.4 Hz, 1H), 6.26 (m, 2H), 6.92 (m, 2H), 9.48 (s, 2H), 11.62 (br s, 2H). Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47; Found: C, 68.37; H, 6.02; N, 11.28. MS: *m/e* 244.2 (M^+, 100).

4.1.6. 1,9-Diformyl-5-trifluoromethyldipyrromethane 10. 5-Trifluoromethyldipyrromethane **5**[29] (2.57 g, 0.012 mol) was reacted with the Vilsmeier reagent using the procedure described for **8**. The reaction mixture was heated under reflux for 1 h. The silica gel column was eluted with ethyl acetate/cyclohexane (1:1). Recrystallization from hexane/CH_2Cl_2 gave **10** (2.60 g, 79%) as off white crystals, mp 174–175°C. ^{1}H NMR δ 5.11 (q, J=9.0 Hz, 1H), 6.43 (m, 2H), 6.99 (m, 2H), 9.52 (s, 2H), 11.15 (br s, 2H). Anal. Calcd for $C_{12}H_9F_3N_2O_2$: C, 53.34; H, 3.36; N, 10.37; Found: C, 53.08; H, 3.29; N, 10.13. MS: *m/e* 270.2 (M^+, 100).

4.1.7. 1,1-Di(5-formylpyrrol-2-yl)-2-fluoro-2-(pentafluoroethyl)ethene 12. 5-Heptafluoropropyldipyrromethane **6**[29] (6.28 g, 0.02 mol) was reacted with the Vilsmeier reagent by using the procedure described for **8**. The reaction mixture was heated under reflux for 1 h. The silica gel column was eluted with ethyl acetate/cyclohexane (1:1). Recrystallization from hexane/CH_2Cl_2 gave **12** (5.71 g, 82%) as off white crystals, mp 159–160°C. ^{1}H NMR δ 6.58 (m, 1H), 6.75 (m, 1H), 6.92 (m, 1H), 7.04 (m, 1H), 9.14 (s, 1H), 9.21 (s, 1H), 10.41 (br s, 1H), 11.06 (br s, 1H). Anal. Calcd for $C_{14}H_8F_6N_2O_2 \cdot 0.5H_2O$: C, 46.81; H, 2.52; N, 7.79; Found: C, 47.27; H, 2.29; N, 7.75. MS: *m/e* 350.0 (100, M^+).

4.1.8. 13,17-Diethyl-5-(*p*-methoxyphenyl)-12,18-dimethylporphyrin 14. To a light-shielded suspension of **7** (1.0 g, 3.2 mmol) and 3,7-diethyl-2,8-dimethyldipyrromethane-1,9-dicarboxylic acid[13] (1.10 g, 1 equiv) in degassed CH_2Cl_2 (250 mL) was added 8 mL of TFA. The reaction mixture was further degassed with argon for 5 min and stirred for 16 h. Chloranil (790 mg, 3.2 mmol) was added all at once and the mixture was stirred for 4 h. The reaction mixture was reduced under vacuum to 10 mL and filtered successively through a short silica gel plug and an alumina (Grade III) plug (eluting with CH_2Cl_2). After evaporation of the solvent, the residue was recrystallized from CH_2Cl_2/MeOH to yield 540 mg of purple powder (32%), mp >300°C. UV–Vis: λ_{max} 402 nm (ϵ 226000), 498 (14500), 529 (3500), 567 (5000). ^{1}H NMR δ −3.40 (s, 2H), 1.81 (t, 6H), 3.58 (s, 6H), 4.10 (q, 4H), 4.12 (s, 3H), 7.33 (d, J=7.8 Hz, 2H), 8.18 (d, J=7.8 Hz, 2H), 9.05 (d, J=3.6 Hz, 2H), 9.30 (d, J=3.6 Hz, 2H), 10.0 (s, 1H), 10.15 (s, 2H). Anal. Calcd for $C_{33}H_{32}N_4O$: C, 79.17; H, 6.44; N, 11.19; Found: C, 79.06; H, 6.54; N, 11.05. MS: *m/e* 501.1 (MH^+, 100).

4.1.9. 5,13,17-Triethyl-12,18-dimethylporphyrin 15. 3,7-Diethyl-2,8-dimethyldipyromethane-1,9-dicarboxylic acid **13** (796 mg, 2.5 mmol) was stirred in 5 mL of TFA for 5 min at room temperature under argon. The mixture was diluted with water and extracted twice with CH_2Cl_2; the combined organic layers were washed with saturated $NaHCO_3$, dried over anhydrous Na_2SO_4, and the volume of CH_2Cl_2 was reduced to 250 mL. 5-Ethyl-1,9-diformyldipyromethane **8** (575 mg, 2.5 mmol) was added and the solution was purged with argon for 5 min. TFA (0.05 mL) was then added and the mixture was stirred at room temperature for 16 h under argon before addition of chloranil (613 mg, 2.5 mmol) and stirring for another 4 h at room temperature. The reaction mixture was passed through an alumina (Grade III) plug, eluting with CH_2Cl_2. Evaporation of the solvent gave a residue which was chromatographed on a silica gel column eluting with CH_2Cl_2 to give 230 mg (22%) of the product as red crystals after recrystallization from methanol/CH_2Cl_2, mp 252–253°C. UV–Vis: λ_{max} 395 nm (ϵ 225000), 497 (14500), 529 (3100), 568 (5300), 620 (1500). ^{1}H NMR δ −3.10 (br s, 2H), 1.87 (t, J=7.6 Hz, 6H), 2.20 (t, J=7.6 Hz, 3H), 3.59 (s, 6H), 4.04 (q, J=7.6 Hz, 4H), 5.09 (q, J=7.6 Hz, 2H), 9.36 (d, J=4.6 Hz, 2H), 9.60 (d, J=4.6 Hz, 2H), 9.88 (s, 1H), 10.05 (s, 2H). Anal. Calcd for $C_{28}H_{30}N_4$: C, 79.59; H, 7.16; N, 13.26; Found: C, 79.20; H, 7.16; N, 13.24. MS: *m/e* 422.3 (MH^+, 100).

4.1.10. Nickel(II) 5,13,17-triethyl-12,18-dimethylporphyrin 16. 5,13,17-Triethyl-12,18-dimethylporphyrin **15** (105 mg, 0.25 mmol) and nickel acetylacetonate (257 mg, 4 equiv.) were refluxed in toluene for 16 h. Toluene was evaporated and the residue was purified on a silica gel column eluting with CH_2Cl_2/cyclohexane (1:1) to give 112 mg (93%) of the title compound, mp 210–211°C. UV–Vis: λ_{max} 393 nm (ϵ 270000), 513 (10500), 547 (12000). ^{1}H NMR δ 1.77 (t, J=7.8 Hz, 6H), 2.12 (t, J=7.7 Hz, 3H), 3.38 (s, 6H), 3.82 (q, J=7.8 Hz, 4H), 4.74 (q, J=7.7 Hz, 2H), 9.11 (d, J=4.6 Hz, 2H), 9.44 (d, J=4.6 Hz, 2H), 9.54 (s, 1H), 9.62 (s, 2H). Anal. Calcd for $C_{28}H_{28}N_4Ni \cdot 2H_2O$: C, 65.27; H, 6.26; N, 10.87; Found: C, 65.88; H, 5.77; N, 10.57. MS: *m/e* 478.3 (M^+, 100).

4.1.11. Zinc(II) 5,13,17-triethyl-12,18-dimethylporphyrin 17. 5,13,17-Triethyl-12,18-dimethylporphyrin **15** (106 mg, 0.25 mol) and zinc acetate (220 mg, 4 equiv.) were refluxed in $CHCl_3$/Methanol (1:1) for 1 h. The solvents were evaporated and the residue was purified on a silica gel column eluting with CH_2Cl_2/cyclohexane (1:1) to give 105 mg (87%) of the title product, mp 295–296°C. UV–Vis: λ_{max}

401 nm (ϵ 300000), 530 (15000), 568 (5500). ^{1}H NMR δ 1.82 (t, J=7.6 Hz, 6H), 2.18 (t, J=7.6 Hz, 3H), 3.51 (s, 6H), 3.96 (q, J=7.6 Hz, 4H), 5.06 (q, J=7.6 Hz, 2H), 9.26 (br s, 2H), 9.58 (br s, 2H), 9.71 (s, 1H), 9.86 (s, 2H). Anal. Calcd for $C_{28}H_{28}N_4Zn{\cdot}0.5CH_3OH$: C, 68.20; H, 6.02; N, 11.16; Found: C, 68.50; H, 6.36; N, 10.58. MS: *m/e* 484.16 (M^+, 100).

4.1.12. 13,17-Diethyl-12,18-dimethyl-5-trifluoromethylporphyrin 18. 3,7-Diethyl-2,8-dimethyldipyromethane-1,9-dicarboxylic acid **13** (1.27 g, 4.0 mmol) and 5-trifluoromethyl-1,9-diformyldipyrromethane **10** (1.08 g, 4.0 mmol) were reacted by the procedure described for **15** (silica gel column eluted with CH_2Cl_2). Recrystallization from methanol/CH_2Cl_2 yielded 318 mg (17%) of the title compound, mp 310–311°C. UV–Vis: λ_{max} 393 nm (ϵ 163000), 498 (10500), 534 (10500), 569 (5500), 621 (7500). ^{1}H NMR δ −4.05 (br s, 1H), −3.60 (br s, 1H), 1.80 (t, J=7.6 Hz, 6H), 3.52 (s, 6H), 4.00 (q, J=7.6 Hz, 4H), 9.41 (d, J=4.8 Hz, 2H), 9.74 (m, 2H), 9.96 (s, 1H), 10.12 (s, 2H). Anal. Calcd for $C_{27}H_{25}F_3N_4$: C, 70.12; H, 5.45; N, 12.11; Found: C, 69.88; H, 5.44; N, 12.10. MS: *m/e* 462.4 (M^+, 100).

4.1.13. Nickel(II) 13,17-diethyl-12,18-dimethyl-5-trifluoromethylporphyrin 19. 13,17-Diethyl-12,18-dimethyl-5-trifluoromethylporphyrin **18** (231 mg, 0.5 mmol) and nickel acetylacetonate (257 mg, 1 mmol) were refluxed in toluene (20 mL) for 16 h. The toluene was evaporated under vacuum and the residue was purified on a silica gel column eluting with CH_2Cl_2/cyclohexane (1:2) to give 228 mg (88%) of the product, mp 229–230°C. UV–Vis: λ_{max} 391 nm (ϵ 165000), 526 (10000), 565 (19500). ^{1}H NMR δ 1.72 (t, J=7.6 Hz, 6H), 3.25 (s, 6H), 3.73 (q, J=7.6 Hz, 4H), 8.98 (d, J=4.8 Hz, 2H), 9.35 (s, 1H), 9.36 (s, 2H), 9.47 (m, 2H). Anal. Calcd for $C_{27}H_{23}F_3N_4Ni$: C, 62.46; H, 4.47; N, 10.79; Found: C, 62.16; H, 4.51; N, 10.69. MS: *m/e* 518.1 (M^+, 100).

4.1.14. 12,13,17,18-Tetraethyl-5-(3,3,3,2,2,1-hexafluoropropyl)-porphyrin 20. 2,3,7,8-Tetraethyldipyromethane-1,9-dicarboxylic acid (1.04 g, 3.0 mmol) and 1,1-dipyrroethene **12** (1.05 g, 3.0 mmol) were reacted following the procedure described for **5** [silica gel column eluted with CH_2Cl_2/cyclohexane (1:1)]. Recrystallization from methanol/CH_2Cl_2 gave 480 mg (28%) of the product, mp 228–229°C. UV–Vis: λ_{max} 396 nm (ϵ 168000), 498 (11000), 533 (7500), 568 (5200), 620 (4500). ^{1}H NMR δ −3.99 (br s, 1H), -3.40 (br s, 1H), 1.92 (m, 12H), 4.07 (m, 8H), 8.56 (m, 1H), 9.48 (d, J=4.8 Hz, 2H), 9.64 (br s, 2H), 10.07 (s, 1H), 10.21 (s, 2H). Anal. Calcd [Ni(II) complex] $C_{31}H_{28}F_6N_4Ni$: C, 59.17; H, 4.49; N, 8.90; Found: C, 59.05; H, 4.55; N, 8.79. MS: *m/e* 572.2 (MH^+, 100).

4.2. General procedure for N_2O_4 nitration of nickel(II) porphyrins

A solution of nickel(II) porphyrin (e.g. 100 mg) in dichloromethane (40 mL) was stirred vigorously. A N_2O_4 solution in petroleum ether was added dropwise.[15e] Close reaction monitoring by TLC (SiO_2, CH_2Cl_2/cyclohexane 2:3) is crucial to avoid over-nitration. After evaporation of the solvents under vacuum, the residue was purified by chromatography on preparative silica gel plates.

4.2.1. General procedure for $AgNO_2/I_2$ nitration of nickel (II) or zinc(II) porphyrins. To a solution of the zinc(II) or nickel(II) porphyrin (e.g. 0.1 mmol) in a mixture of CH_2Cl_2 (10 mL) and CH_3CN (4 mL) at 0°C and protected from light, was added $AgNO_2$ (21 mg, 0.13 mmol) in CH_3CN (4 mL) followed by I_2 (16.5 mg, 0.067 mmol) in CH_2Cl_2 (4 mL). The reaction mixture was stirred under argon for 2 h at 0°C and then filtered. The solvents were evaporated under vacuum and the residue was purified by chromatography on preparative silica gel plates.

4.2.2. Zinc(II) 5,13,17-triethyl-12,18-dimethyl-10-nitroporphyrin 21. $AgNO_2/I_2$ nitration of **17** (48.5 mg, 0.1 mmol) gave porphyrins **21** and **22** [running slower on TLC (silica, CH_2Cl_2/cyclohexane 1:1)]. The more polar compound (brown red) was identified as **22** (recrystallized from methanol/CH_2Cl_2, 13 mg, 25%). The less polar compound (brown red) was identified as **21** (recrystallized from methanol/CH_2Cl_2, 28 mg, 53%), mp >300°C. UV–Vis: λ_{max} 403 nm (ϵ 220000), 535 (14000), 569 (7000). ^{1}H NMR δ 1.76 (m, 6H), 2.08 (t, J=7.6 Hz, 3H), 3.23 (s, 3H), 3.45 (s, 3H), 3.94 (m, 4H), 4.98 (q, J=7.6 Hz, 2H), 9.13 (d, J=4.6 Hz, 1H), 9.20 (d, J=4.6 Hz, 1H), 9.48 (d, J=4.6 Hz, 1H), 9.58 (d, J=4.6 Hz, 1H), 9.83 (s, 1H), 9.88 (s, 1H). Anal. Calcd for $C_{28}H_{27}N_5O_2Zn{\cdot}0.5H_2O$: C, 62.29; H, 5.23; N, 12.97; Found: C, 62.19; H, 5.24; N, 12.64. MS: *m/e* 529.2 (M^+, 100).

4.2.3. Zinc(II) 5,13,17-triethyl-12,18-dimethyl-10,15-dinitroporphyrin 22. Obtained in 25% yield (13 mg). Mp: decomposed without melting. UV–Vis: λ_{max} 407 nm (ϵ 141000), 540 (11000), 594 (4500). ^{1}H NMR δ 1.33 (t, J=7.6 Hz, 3H), 1.67 (t, J=7.6 Hz, 3H), 1.83 (t, J=7.6 Hz, 3H), 3.31 (s, 3H), 3.40 (s, 3H), 3.61 (q, J=7.6 Hz, 2H), 3.79 (q, J=7.6 Hz, 2H), 3.89 (q, J=7.6 Hz, 2H), 7.66 (d, J=4.6 Hz, 1H), 7.86 (d, J=4.6 Hz, 1H), 8.52 (s, 1H), 8.87 (d, J=4.6 Hz, 1H), 8.94 (d, J=4.6 Hz, 1H). Anal. Calcd for $C_{28}H_{26}N_6O_4Zn{\cdot}3H_2O$: C, 53.38; H, 5.12; N, 13.34; Found: C, 53.79; H, 4.55; N, 12.54. MS: *m/e* 574.2 (M^+, 100).

4.2.4. Nickel(II) 5,13,17-triethyl-12,18-dimethyl-10-nitroporphyrin 23. $AgNO_2/I_2$ nitration of **16** (47.8 mg, 0.1 mmol) gave porphyrin **23** [running slower on TLC (silica, CH_2Cl_2/cyclohexane 1:1)]. Recrystallized from methanol/CH_2Cl_2 (25 mg, 48%). A more polar compound (green) was found to be a regioisomeric mixture of β-nitro-10-nitroporphyrins **24** (12.4 mg, 22%). **23**: mp >300°C. UV–Vis: λ_{max} 395 nm (ϵ 140000), 519 (10000), 553 (11000). ^{1}H NMR δ 1.68 (m, 6H), 1.97 (t, J=7.6 Hz, 3H), 3.15 (s, 3H), 3.24 (s, 3H), 3.68 (q, J=7.6 Hz, 2H), 3.75 (q, J=7.6 Hz, 2H), 4.48 (q, J=7.6 Hz, 2H), 8.86 (d, J=4.8 Hz, 1H), 9.01 (d, J=4.8 Hz, 1H), 9.17 (d, J=4.8 Hz, 1H), 9.28 (d, J=4.8 Hz, 1H), 9.30 (s, 1H), 9.32 (s, 1H). Anal. Calcd for $C_{28}H_{27}N_5O_2Ni{\cdot}0.5H_2O$: C, 63.07; H, 5.29; N, 13.13; Found: C, 63.34; H, 5.20; N, 13.19. MS: *m/e* 523.4 (100, M^+) IR: 1529 (ν_{as}-NO_2), 1361 (ν_s-NO_2).

4.2.5. Nickel(II) 13,17-diethyl-12,18-dimethyl-3-nitro-5-trifluoromethylporphyrin 25. N_2O_4 nitration of **19** (45 mg, 0.085 mmol) gave three nitroporphyrins **25**–**27**

[all running slower on TLC (silica, CH_2Cl_2/cyclohexane 1:1). Separation was carried out on preparative silica plates eluting with CH_2Cl_2/cyclohexane (1:1)]. The least polar compound (red) was identified as **27** (recrystallized from CH_2Cl_2/methanol, 13.8 mg, 28%). The next compound (green) was identified as **26** (recrystallized from CH_2Cl_2/methanol, 7.5 mg, 15%). The most polar and major compound (green) was identified as **25** (recrystallized from CH_2Cl_2/methanol, 18.6 mg, 38%), mp >300°C (decomp.). UV–Vis: λ_{max} 410 nm (ϵ 84000), 601 (15500). ^{1}H NMR δ 1.68 (m, 6H), 3.26 (s, 3H), 3.29 (s, 3H), 3.75 (m, 4H), 8.99 (d, J=4.8 Hz, 1H), 9.28 (s, 1H), 9.35 (s, 1H), 9.37 (s, 1H), 9.39 (m, 1H), 9.42 (s, 1H). Anal. Calcd for $C_{27}H_{22}F_3N_5O_2Ni\cdot1.5H_2O$: C, 54.85; H, 4.26; N, 11.85; Found: C, 54.88; H, 4.09; N, 11.40. MS: *m/e* 563.1. IR: 1349 (ν_s-NO_2).

4.2.6. Nickel(II) 13,17-diethyl-12,18-dimethyl-2-nitro-5-trifluoromethylporphyrin 26. Mp: decomposed without melting. UV–Vis: λ_{max} 370 nm (ϵ 31000), 421 (61500), 609 (16000). ^{1}H NMR δ 1.65 (m, 6H), 3.23 (s, 3H), 3.26 (s, 3H), 3.71 (m, 4H), 8.74 (d, J=4.8 Hz, 1H), 8.97 (s, 1H), 9.10 (s, 1H), 9.15 (m, 1H), 9.75 (m, 1H), 9.92 (s, 1H). Anal. Calcd for $C_{27}H_{22}F_3N_5O_2Ni\cdot H_2O$: C, 55.70; H, 4.16; N, 12.03; Found: C, 55.89; H, 4.04; N, 11.52. MS: *m/e* 563.1. IR: 1331 (ν_s-NO_2).

4.2.7. Nickel(II) 13,17-diethyl-12,18-dimethyl-10-nitro-5-trifluoromethylporphyrin 27. Mp>300°C (decomp). UV–Vis: λ_{max} 395 nm (ϵ 70000), 521 (5000), 567 (9500). ^{1}H NMR δ 1.74 (m, 6H), 3.15 (s, 3H), 3.25 (s, 3H), 3.75 (m, 4H), 8.99 (d, J=4.8 Hz, 1H), 9.07 (d, J=4.8 Hz, 1H), 9.37 (s, 1H), 9.38 (m, 1H), 9.42 (s, 1H), 9.45 (m, 1H). Anal. Calcd for $C_{27}H_{22}F_3N_5O_2Ni\cdot0.5H_2O$: C, 56.58; H, 4.04; N, 12.22; Found: C, 56.75; H, 3.93; N, 12.07. MS: *m/e* 563.1. IR: 1362 (ν_s-NO_2).

4.2.8. Nickel(II) 2,3,7,8-tetraethylporphyrin 28. Condensation of 1,9-diformyldipyrromethane[37] with 2,3,7,8-tetraethyldipyrromethane-1,9-dicarboxylic acid followed by DDQ oxidation afforded 2,3,7,8-tetraethylporphyrin in 25% yield.[11] 2,3,7,8-Tetraethylporphyrin (63.3 mg, 0.15 mmol) and nickel acetylacetonate (64 mg, 0.25 mmol) were refluxed in toluene (10 mL) for 16 h. The toluene was evaporated under vacuum and the residue was purified on a silica gel column eluting with CH_2Cl_2/petroleum ether (2:3) to give 66 mg (92%) of the product, mp: 183–184°C. UV–Vis: λ_{max} 385 nm (ϵ 190000) 507 (10500), 541 (21000). ^{1}H NMR δ 1.84 (m, 12H), 3.96 (m, 8H), 9.26 (m, 4H), 9.85 (s, 1H), 9.90 (s, 2H), 9.97 (s, 1H). MS: *m/e* 479.2 (M^+, 100).

4.2.9. Nickel(II) 2,3,7,8-tetraethyl-10-nitroporphyrin 29. N_2O_4 nitration of **28** (40 mg, 0.08 mmol) gave three nitroporphyrins **29**–**31** running slower on TLC (SiO_2, CH_2Cl_2/cyclohexane 2:3). The most polar compounds (green) were identified as **30** (recrystallized from CH_2Cl_2/MeOH, 15 mg, 37% yield). The second band (brown) and the third band (red) were identified as **31** and **29**, respectively. Separation was carried out on preparative silica gel plates eluting with CH_2Cl_2/cyclohexane 2:3. Mp: 145–150°C. UV–Vis: λ_{max} 387 nm (ϵ 110000), 514 (7000), 549 (11500). ^{1}H NMR: δ 1.61 (t, J=7.5 Hz, 3H), 1.85 (m, 9H), 3.63 (q, J=7.5 Hz, 2H), 3.90 (m, 6H), 9.16 (m, β-H, 4H), 9.71 (s, 1H), 9.76 (s, 1H), 9.81 (s, 1H). MS: *m/e* 522.15 (M^+, 100). Amount of final products was insufficient for elemental analyses. The substituent regiochemistry of porphyrin **29** was further confirmed by X-ray crystallography.[38]

4.2.10. Regioisomeric mixture of nickel(II) 2,3,7,8-tetraethyl-12-nitroporphyrin and 2,3,7,8-tetraethyl-13-nitroporphyrin 30. UV–Vis: λ_{max} (rel. int.) 364 nm (0.74), 423 (1.0), 591 (0.32). Anal. Calcd for $C_{28}H_{27}N_5NiO_2\cdot0.25H_2O$: C, 63.60; H, 5.24; N, 13.24; Found: C, 63.53; H, 5.32; N, 13.06. MS: *m/e* 522.31 (M^+, 100). IR: 1462 (ν_{as}-NO_2), 1342, 1333 (sh) (ν_s-NO_2).

4.2.11. Nickel(II) 2,3,7,8-tetraethyl-15-nitroporphyrin 31. Mp: 225–230°C. UV–Vis: λ_{max} 390 nm (ϵ 69500), 559 (8500). ^{1}H NMR δ 1.74 (m, 12H), 3.83 (m, 8H), 9.15 (d, J=4.8 Hz, 2H), 9.29 (d, J=4.8 Hz, 2H), 9.63 (s, 1H), 9.71 (s, 2H). MS: *m/e* 522.35 (M^+, 100). Amount of final product was insufficient for elemental analyses. The substituent regiochemistry of porphyrin **31** was further confirmed by X-ray crystallography.[38]

4.3. Crystal structure data for 25 and 27

Crystals were grown by slow evaporation of a $CDCl_3$ solution of **25** and by solvent diffusion from CH_2Cl_2/MeOH for **27** [regioisomers with $C_{27}H_{22}F_3N_5NiO_2$, FW=564.21]. For **25**, the purple prismatic crystal (0.08×0.33×0.54 mm) had a triclinic unit cell, space group $P\bar{1}$, with cell dimensions a=9.2690(4), b=11.1634(4), c=13.1328(5) Å, α=109.274(1)°, β=96.803(1)°, γ=107.804(1)°, V=1184.35(13) Å^3, and Z=2. For **27**, the red parallelepiped crystal (0.04×0.16×0.40 mm) had a triclinic unit cell, space group $P\bar{1}$, with cell dimensions a=9.4498(3), b=11.6596(4), c=12.1112(4) Å, α=104.8400(10)°, β=106.0690(10)°, γ=107.5700(10)°, V=1135.32(6) Å^3, and Z=2. Data were collected on a Bruker SMART 1000 diffractometer with a sealed tube source [λ (MoKα)=0.71073 Å] at 90(2) K. A 2θ cutoff of 60° was applied to both datasets to afford 12287 and 15330 total reflections (when two values are given they refer to **25** and **27**, respectively) of which 6787 and 6567 were unique and of those 5839 and 5490 were observed ($I>2\sigma$) [R_{int}=0.0314, 0.0247; T_{min}=0.65, 0.71; T_{max}=0.93, 0.96; μ=0.880, 0.918 mm^{-1}]. An empirical absorption correction was applied to the datasets (SADABS 2.0, Sheldrick 2000). The structures were solved by direct methods and refined (based on F^2 using all data) by full matrix least-squares methods with 347 and 365 parameters (Bruker SHELXS-97, SHELXL-97). All hydrogen atom positions were refined with a riding model. Final R factors were $R1$=0.042, 0.044 (observed data) and w$R2$=0.125, 0.110 (all data).

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