

A new general method for selective β -polynitration of porphyrins; preparation and redox properties of Zn-porphyrins bearing one through to eight β -nitro substituents and X-ray structure of the first Zn β -pernitro porphyrin†

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Selective β -polynitration of Zn-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin, Zn(TDCPP), is achieved by controlled titration with the $\text{HNO}_3\text{-CF}_3\text{SO}_3\text{H-(CF}_3\text{SO}_2)_2\text{O}$ system, and affords a full series of Zn porphyrins bearing one through to eight β -nitro groups in high yield and exhibiting a wide range of reduction potentials (from -920 to $+155$ mV vs. SCE); an X-ray structure of the first reported β -pernitroated Zn porphyrin Zn(TDCPN₈P)(EtOH)₂·2EtOH confirms the synthetic methodology.

Iron and manganese meso-tetraaryl porphyrins bearing electron-withdrawing β -substituents have been shown to be efficient catalysts for cytochrome P450-mimetic oxygenations of hydrocarbons.¹ In an effort to obtain metalloporphyrins with significantly altered redox potentials and unusual reactivities, we have attempted to synthesize metalloporphyrins bearing as many electron-withdrawing β -nitro substituents as possible.² Nitration of TDCPPH₂³ with red fuming HNO_3 led us to mixtures of β -pentanitro- and β -hexanitro-TDCPPH₂.^{2a} More recently, we reported that a more powerful nitrating agent, consisting of a mixture of HNO_3 and $(\text{CH}_3\text{CO})_2\text{O}$ in the presence of K10 montmorillonite, reacted with Zn(TDCPP) to afford the corresponding β -heptanitroporphyrin, Zn(TDCPN₇P), in 50% yield.^{2b} However all the nitrating systems that we have used so far suffered from two main drawbacks, (i) they did not permeate the porphyrin to the β -octanitro level, and (ii) they did not act as general nitrating agents to produce all the desired β -polynitroporphyrins, Zn(TDCPN_xP) ($x = 1\text{--}8$), as the number of nitrating equivalents was increased. Indeed, selective formation of any one

TDCPN_xP porphyrin required a different nitrating system² for each value of x .

We have now developed a nitrating system based on HNO_3 and the superacid $\text{CF}_3\text{SO}_3\text{H}$ in the presence of $(\text{CF}_3\text{SO}_2)_2\text{O}$ that acts as a general nitrating agent for the selective synthesis of the full TDCPN_xP series. We describe here the successful use of this nitrating procedure to prepare all eight members of the Zn(TDCPN_xP) series in high yield, present the first X-ray structure of a β -pernitroporphyrin, Zn(TDCPN₈P), prepared by this method, and report the strikingly wide range of redox potentials now accessible *via* the eight members of the Zn(TDCPN_xP) series.

Titration of Zn(TDCPP) with 1, 2, 3, 4 or 6 equiv. of red fuming HNO_3 and $\text{CF}_3\text{SO}_3\text{H}$ (1:1)⁴ selectively led to Zn(TDCPN_xP) with $x = 1, 2, 3, 4$ or 6, respectively with yields between 50 and 70% (Table 1). However, the use of 5 equiv. of $\text{HNO}_3\text{-CF}_3\text{SO}_3\text{H}$ led to a complex mixture of Zn(TDCPN_xP) with $x = 4, 5$ and 6. Moreover, low yields of Zn(TDCPN₈P) were obtained (*ca.* 25%, Table 1) when using the same system.

A slightly modified system consisting of red fuming HNO_3 in the presence of < 1 equiv. of $\text{CF}_3\text{SO}_3\text{H}$ and $(\text{CF}_3\text{SO}_2)_2\text{O}$, in order to limit side reactions [demetallation and destruction of Zn(TDCPP)], allowed us to prepare each compound of the Zn(TDCPN_xP) series in much higher yields. Thus, titration of Zn(TDCPP) with increasing amounts of the $\text{HNO}_3\text{-CF}_3\text{SO}_3\text{H-(CF}_3\text{SO}_2)_2\text{O}$ (1:0.12:0.06) mixture selectively led to each compound of the Zn(TDCPN_xP) series ($x = 1\text{--}7$) with yields between 78 and 95%. Formation of the desired porphyrin was followed by thin-layer chromatography and addition of the nitrating agent was stopped after complete formation of the target product. The pernitroated Zn(TDCPN₈P) was selectively obtained with a satisfactory 50% yield by the same method under the conditions described in Table 1. The full range of β -nitro products obtained with this system contrasts sharply with

† Electronic supplementary information (ESI) available: ORTEP plots for 1, bond distances and displacements from the plane of the porphyrin core. See <http://www.rsc.org/suppdata/cc/b0/b004160m/>

Table 1 Synthesis and reduction potentials of Zn(TDCPN_xP)

Synthesis method	x							
	1	2	3	4	5	6	7	8
	Yield (%)							
$\text{HNO}_3\text{-CF}_3\text{SO}_3\text{H}$ (1:1) ^a	60	62	67	63	— ^b	60	53	25
$\text{HNO}_3\text{-CF}_3\text{SO}_3\text{H-(CF}_3\text{SO}_2)_2\text{O}$ (1:0.12:0.06) ^c	78	90	86	93	80	95	90	50
$E_{1/2}$ (first reduction)/mV vs. SCE ^d	-920	-750	-595	-470	-300	-150	0	+155

^a Yields of Zn(TDCPN_xP) after addition of x equiv. of red fuming HNO_3 and $\text{CF}_3\text{SO}_3\text{H}$ (1:1) to 5.2×10^{-5} M Zn(TDCPP) in CH_2Cl_2 at 20 °C and 0.5, 1, 2, 4, 5, 24, 48 and 72 h reaction time for $x = 1$ to 8, respectively. For $x = 7$ and 8, 10 and 40 equiv. of nitrating agent were added, respectively. ^b Only case in which Zn(TDCPN_xP) was not largely predominant. ^c Yields of Zn(TDCPN_xP) after titration of Zn(TDCPP) with the $\text{HNO}_3\text{-CF}_3\text{SO}_3\text{H-(CF}_3\text{SO}_2)_2\text{O}$ mixture. For $1 \leq x \leq 5$, reactions at 20 °C in CH_2Cl_2 for 24 h after addition of 1.1, 3.5, 6.5, 9 and 11 equiv. of HNO_3 , respectively. For $x = 6, 7$ and 8, reactions at 30 °C in MeNO_2 for 1, 2 and 5 days and after addition of 18, 150 and 380 equiv. of HNO_3 , respectively. ^d $E_{1/2}$ for the first one-electron reduction of Zn(TDCPN_xP), 10^{-3} M in CH_2Cl_2 containing 0.1 M NBu_4PF_6 ; $E_{1/2}$ for Zn(TDCPP) = -1285 mV.^{2b}

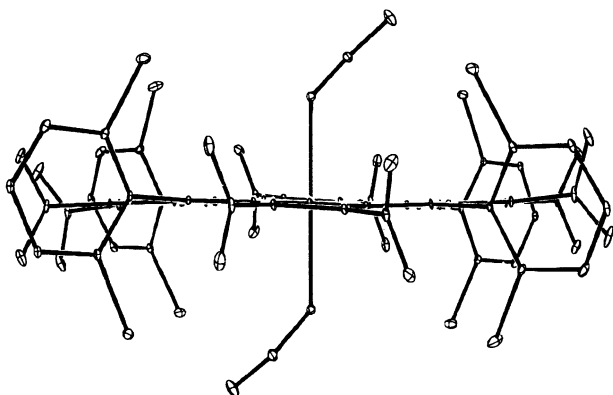


Fig. 1 Edge-on-view of Zn(TDCPN₈P)(EtOH)₂ **1**. Thermal ellipsoids have been reduced to 1% to illustrate the planarity of the porphyrin skeleton and the orientations of the substituents.

the classical nitrating HNO₃–H₂SO₄ system which was found to be efficient only for the preparation of the first four members of the Zn(TDCPN_xP) series (yield ca. 80%).

All the Zn(TDCPN_xP) compounds ($x = 1-8$) were completely characterized by elemental analysis and UV–VIS, ¹H NMR spectroscopy and mass spectrometry. Additional details of the syntheses and full characterizations will be presented elsewhere. It is of note that Zn(TDCPNP), Zn(TDCPN₇P) and Zn(TDCPN₈P) are single pure compounds while the other members of the Zn(TDCPN_xP) series are mixtures of regioisomers with different relative positions of the β-nitro substituents.

The molecular structure of the first β-pernitrated porphyrin to be reported, Zn(TDCPN₈P)(EtOH)₂ **1**, was confirmed by an X-ray crystallographic study of **1**·2EtOH obtained by crystallization from CH₂Cl₂–EtOH.⁵ As shown in Fig. 1, the Zn is axially coordinated by two molecules of EtOH with Zn–O distances of 2.272(10) Å and average Zn–N distances to the pyrrole nitrogens of 2.075(8) Å. The Zn–O and Zn–N distances are, respectively, the shortest and longest bond distances reported to date for hexacoordinated Zn porphyrins with oxygen donor axial ligands.⁶ The tight axial bonds and the expanded porphyrin core are readily attributable to the multiple electron-withdrawing groups of **1**. In spite of the 12 peripheral substituents, which generally result in severe skeletal distortions,⁷ the macrocycle of **1** is essentially planar with an average deviation from the 24-atom porphyrin plane of only 0.035 Å, and maximum displacements of only 0.08 and 0.07 Å at any one β or meso carbon, respectively. Macrocycle planarity is achieved by orienting all the peripheral substituents nearly orthogonal to the porphyrin plane: the two crystallographically independent phenyl rings align at 80 and 90° to the porphyrin plane whereas the four independent nitro groups subtend angles of 76, 82, 87, 77° to the same plane.

As established by cyclic voltammetry, all eight Zn(TDCPN_xP) undergo a reversible one-electron reduction leading to the formation of π-anion radicals. Formation of such radicals⁸ is confirmed by controlled-potential electrolysis of Zn(TDCPN₈P) at 0 V vs. SCE in CH₂Cl₂ which yields a species that exhibits new absorption bands centered at 900 nm and a singlet EPR spectrum centered at $g = 2.00$.⁹ Table 1 compares the reduction potentials of each ZnP/ZnP[–] couple for all eight nitro derivatives. The potentials increase in a linear manner, the introduction of each additional β nitro group causing a shift of ca. +150 mV. Thus, the incorporation of eight β-nitro groups in Zn(TDCPP) leads to a strikingly large positive shift of ca. 1.4 V

of the reduction potential and thus readily explains why the π-anion radical of Zn(TDCPN₈P) forms under such mild reducing conditions, even in the presence of O₂.

In conclusion, we have developed a new general method for selective β-polynitration of Zn(TDCPP) in high yield based on controlled titration of the starting porphyrin with HNO₃–CF₃SO₃H–(CF₃SO₂)₂O. The method leads to a complete series of porphyrins bearing 1–8 β-nitro groups with a wide span of reduction potentials that range from –920 to +155 mV. Similar results were obtained with Ni(TDCPP) and methods for selective demetallation of the Zn and Ni polynitroporphyrins have been recently developed. Use of metallo-β-polynitroporphyrins in catalysis, and application of the nitration method to other polyaromatic molecules are under investigation.

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