Polyhedron 87 (2015) 170–180

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Unsymmetrically mixed β-octasubstituted *meso*-tetraphenylporphyrins: Structural and electrochemical redox properties

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ARTICLE INFO

Article history:
Received 28 August 2014
Accepted 24 October 2014
Available online 13 November 2014

Keywords:
Substituted porphyrins
Metalloporphyrins
Crystal structures
Redox potentials
NSD analysis

ABSTRACT

A new family of unsymmetrically mixed β-octasubstituted porphyrins, $H_2TPP(Ph)_3X_5$ (X = H, Cl, Br and CH_3), and their metal complexes were synthesized. These porphyrins feature red-shifted electronic absorption bands, depending on the nature of the 'X' group and following the trend: H < CH_3 < Cl < Br. The crystal structures of the $NiTPP(Ph)_3X_5$ complexes reveal an enhanced distortion of the macrocycle, as evidenced from root-mean square (r.m.s.) values, and it varies with the size of X (H, 0.407(2) Å; CH_3, 0.700(2) Å). Similarly, the structure of $CuTPP(Ph)_3(CH_3)_5$ showed an enhanced distortion (r.m.s. = 0.599(4) Å) of the macrocycle. Normal-coordinate structure decomposition analysis of the crystal structures revealed mainly saddling (40–78%) and ruffling (15–51%) deformations. The electrochemical properties of these derivatives generally exhibited an anodic shift of the redox potentials and the HOMO–LUMO gap determined from the redox data correlates reasonably well with the longest wavelength absorption spectral data.

1. Introduction

Synthetic porphyrin analogs with varying functional groups at the peripheral positions are of remarkable interest due to their use as models for tetrapyrrole pigments in nature. Many reports have also appeared on the exploration of the physicochemical properties of these substituted porphyrins. Furthermore, these porphyrins find use in some potential material applications [1,2]. *Meso*-tetrarylporphyrins, TArP, are of continued interest owing to their facile synthesis, diverse coordination chemistry and having many peripheral positions available for functionalization. Introduction of β-pyrrole substituents significantly alters the physicochemical properties of the macrocycle since they can undergo direct conjugation with the porphyrin π-system. Moreover, an increase in the number of peripheral substituents induces an enhanced steric repulsion between the substituents, leading to a non-planar conformation of the porphyrin ring. Such distorted structures serve as model compounds for the non-planar conformations of heme in heme proteins [3].

Notably, perhalogenated metalloporphyrins have been used as models of cytochrome P_{450} due to their enhanced robustness towards oxidative degradation in the presence of strong oxygen donors [4–8]. The electrochemical redox properties of halogenated porphyrins feature an interesting trend in their redox behavior [9]. An increase in the number of halogens at the pyrrolic positions of *meso*-tetraphenylporphyrin, H_2TPP, produces an anodic shift in oxidation for up to four bromine atoms, which then gradually decreases with a further increase in the number of bromine atoms [10,11]. Previous studies on symmetrically mixed β-octasubstituted TPPs and their metal complexes showed unique physicochemical properties [12]. A wide variety of substituted porphyrins have been synthesized and their structural properties have been examined [13]. The introduction of substituents of different sizes and shapes at the pyrrolic positions generally produces variable degrees of distortion of the porphyrin ring [3a,12]. β-Brominated H_2TPP derivatives are useful precursors in the preparation of other synthetically difficult or inaccessible porphyrin derivatives *via* cross-coupling reactions and they exhibit interesting properties [14]. Moreover, the many reported structures of these symmetrically substituted porphyrins mainly reveal a saddle-shaped distortion of the macrocycle. In addition, the non-planar conformation of the porphyrin ring induces facile metal insertion reactions [15]. The synthesis and properties of unsymmetrically mixed β-pyrrole substituted porphyrins have been largely unexamined [16]. A variety of unsymmetrical *meso*-substituted porphyrins are known in the literature [17]. Notably, some functionalised porphyrins and metalloporphyrins have been employed in potential non-linear optical applications [18]. Unsymmetrical

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http://dx.doi.org/10.1016/j.poly.2014.10.033
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substitution of electron-donor and electron-withdrawing groups at the *β*-pyrrolic positions of the porphyrin are anticipated to alter the non-linear optical properties.

To examine the role of unsymmetrical substituents at the *β*-pyrrolic positions of TPP on the electronic absorption, electrochemical redox and stereochemical properties of the macrocycle, a new class of substituted porphyrins and their metal complexes were synthesised and they feature significant differences in their properties relative to TPP bearing similar *β*-pyrrole substituents (Fig. 1).

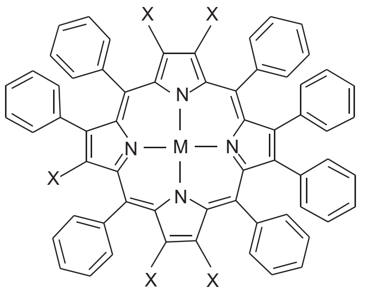
2. Experimental

2.1. Materials

5,10,15,20-Tetraphenylporphyrin, H_2TPP, was prepared using a literature method [19]. All the solvents purchased from Rankem (India) were of high purity and distilled prior to use [20]. N-bromosuccinimide (NBS) was recrystallized from hot water and dried at 343 K for 12 h under vacuum (8.0 mbar) before use. N-chlorosuccinimide (NCS) obtained from Sigma–Aldrich (India) was recrystallized from benzene and dried at 333 K under vacuum (8.0 mbar) for 10 h. Calcium hydride, pyrrole, $CDCl_3$, CD_2Cl_2, DMSO-d_6, superbase (2,8,9-triisobutyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane), phenylboronic acid, methylboronic acid and tetrakis(triphenylphosphine)palladium(0) were purchased from Sigma–Aldrich (India) and used as received. The metal salts $Cu(OAc)_2{\cdot}H_2O$, $Zn(OAc)_2{\cdot}2H_2O$, $Ni(OAc)_2{\cdot}4H_2O$ and anhydrous Na_2SO_4 were procured from Sigma–Aldrich (India) and used without further purification. Silica gel (100–200 mesh) for column chromatography was purchased from Rankem (India) and used as such. Tetrabutylammonium hexafluorophosphate, $TBAPF_6$ was purchased from Fluka (Switzerland) was used as received. Dry distilled CH_2Cl_2, employed for electrochemical measurements, was procured from Rankem (India) and distilled twice from CaH_2 before use. Precoated thin-layer silica gel chromatography and aluminium plates were purchased from E. Merck (Germany) and used as received.

2.2. Instrumentation and methods

Electronic absorption spectra of the free base porphyrins and their metal complexes were measured on a computer interfaced JASCO V-550 model UV–Vis spectrophotometer using a pair of quartz cells of 10 mm path length in analytical reagent grade CH_2Cl_2 at 298 K. ^1H and ^{13}C NMR spectra of the porphyrins were recorded on Bruker Avance 400 and 500 MHz FT-NMR spectrometers in $CDCl_3$, DMSO-d_6 and CD_2Cl_2, using tetramethylsilane as an internal reference. The mass spectra of the free base porphyrins were carried out on an electrospray ionization (ESI) mass spectrometer, micromass Q-TOF micro™ model, using a CH_2Cl_2 solution of the porphyrin containing 5% formic acid. The metal complexes were analyzed by matrix assisted laser desorption time-of-flight (MALDI-TOF) spectra on a Voyager DE-PRO model mass spectrometer using α-cyano-4-hydroxycinnamic acid as the matrix under positive ion mode conditions. Elemental analysis of the samples was performed on a Perkin Elmer CHNO/S analyzer model 2400 series. Single crystal X-ray diffraction data were collected at 173(1) K on a Bruker Apex-II CCD diffractometer equipped with a liquid nitrogen cryostat.



$M(TPP(Ph)_3X_5)$
M = 2H, Ni(II), Cu(II), Zn(II)
X = H, Br, Cl and CH_3

Fig. 1. Chemical structures of unsymmetrically mixed *β*-octasubstituted *meso*-tetraphenylporphyrins.

Crystals of the Ni(II)-porphyrin, $NiTPP(Ph)_3$ and $NiTPP(Ph)_3(CH_3)_5$ complexes were grown by slow vapor diffusion of hexane and methanol separately into saturated solutions of the respective porphyrins in toluene. Crystals of $CuTPP(Ph)_3(CH_3)_5$ were obtained by vapor diffusion of hexane into a concentrated porphyrin solution in 1,2-dichloroethane over a period of 5 days. The SIR92 (WINGX) program [21] was used to solve the structure by direct methods. The structures were refined on F^2 by the full matrix least squares technique using SHELXL-97 software (Sheldrick, 1997) [22]. ORTEPs of the structures were drawn using ORTEP-3 [23] program and intermolecular short contacts in these structures were calculated by the PLATON program [24].

2.3. Synthesis of 2,3,5,10,12,15,20-heptaphenylporphyrin, $H_2TPP(Ph)_3$, and its metal (M = Ni(II), Cu(II) and Zn(II)) complexes

$H_2TPP(Ph)_3$ was prepared using H_2TPPBr_3 as the precursor by the literature method [25]. The $MTPP(Ph)_3$ (M = Ni(II), Cu(II) and Zn(II)) complexes were synthesized using reported procedures [26]. All the synthesised porphyrins were characterised using electronic absorption, ^1H NMR and mass spectroscopic methods. ***$H_2TPP(Ph)_3$***: $R_f = 0.64$ ($CHCl_3$/hexane, 4:1). ^1H NMR, $CDCl_3$, δ_H (ppm): 8.69 (s, 1H, *β*-pyrrole-H), 8.66 (d, $J = 4.8$ Hz, 1H, *β*-pyrrole-H), 8.51 (d, $J = 4.8$ Hz, 2H, *β*-pyrrole-H), 8.41 (d, $J = 4.8$ Hz, 1H, *β*-pyrrole-H), 8.25 (m, 2H, *meso*-*o*-Ph-H), 7.94 (d, $J = 6.8$ Hz, 2H, *meso*-*o*-Ph-H), 7.82 (d, $J = 7.2$ Hz, 4H, *meso*-*o*-Ph-H), 7.73 (m, 3H, *meso*-*m* and *p*-Ph-H), 7.36 (m, 2H, *meso*-*m*-Ph-H), 7.20 (m, 12H, *meso* and *β*-pyrrole-Ph-H), 6.94 (d, $J = 7.2$ Hz, 4H, *β*-pyrrole-*o*-Ph-H), 6.87 (m, 6H, *β*-pyrrole-*m* and *p*-Ph-H), −2.23 (s, 2H, NH). ^{13}C NMR, $CDCl_3$, δ (ppm): 142.4, 141.4, 141.5, 140.4, 136.3, 135.5, 135.3, 134.8, 131.8, 130.4, 127.8, 127.5, 127.5, 127.3, 126.9, 126.7, 126.3, 126.0, 126.0, 125.6; 121.2, 121.1, 119.8. HR-ESI MS calcd. for $C_{62}H_{42}N_4$ $[M+H]^+$: 843.3487 (found: 843.3486). Elemental *Anal.* Calc. for $C_{62}H_{42}N_4$: C, 88.33; H, 5.02; N, 6.65. Found: C, 87.97; H, 4.82; N, 6.73%. ***$NiTPP(Ph)_3$***: $R_f = 0.59$ ($CHCl_3$/hexane, 3:7). ^1H NMR, $CDCl_3$, δ_H (ppm): 8.62 (s, 1H, *β*-pyrrole-H), 8.56 (d, $J = 5.2$ Hz, 1H, *β*-pyrrole-H), 8.31 (d, $J = 4.8$ Hz, 1H, *β*-pyrrole-H), 8.25 (m, 2H, *β*-pyrrole-H), 7.99 (m, 2H, *meso*-*o*-Ph-H), 7.63 (m, 6H, *meso*-*o*-Ph-H), 7.50 (d, $J = 7.2$ Hz, 2H, *meso*-*m*-Ph-H), 7.42 (d, $J = 7.2$ Hz, 2H, *meso*-*m*-Ph-H), 7.12 (m, 13H, *meso* and *β*-pyrrole-Ph-H), 6.85 (m, 10H, *β*-pyrrole-Ph-H). MALDI-TOF MS calcd. for $NiC_{62}H_{40}N_4$: 898.2606 (found: 897.81). ***$CuTPP(Ph)_3$***: $R_f = 0.62$ ($CHCl_3$/hexane, 1:4). MALDI-TOF MS Calc. for $CuC_{62}H_{40}N_4$: 903.254 (found: 902.9). ***$ZnTPP(Ph)_3$***: $R_f = 0.48$ ($CHCl_3$/hexane, 3:2). ^1H NMR, $CDCl_3$, δ_H (ppm): 8.82 (m, 2H, *β*-pyrrole-H), 8.67 (d, $J = 4.8$ Hz, 1H, *β*-pyrrole-H), 8.63 (d, $J = 4.4$ Hz, 1H, *β*-pyrrole-H), 8.54 (d, $J = 4.8$ Hz, 1H, *β*-pyrrole-H), 8.22 (m, 2H, *meso*-*o*-Ph-H), 7.88 (m, 2H, *meso*-*o*-Ph-H), 7.77 (m, 4H, *meso*-*o*-Ph-H), 7.71 (m, 3H, *meso*-*m* and *p*-Ph-H), 7.36 (m, 2H, *meso*-*m*-Ph-H), 7.18 (m, 12H, *meso* and *β*-pyrrole-Ph-H), 6.98 (m, 4H, *β*-pyrrole-*o*-Ph-H), 6.87 (m, 6H, *β*-pyrrole-*m* and *p*-Ph-H). MALDI-TOF MS calcd. for $ZnC_{62}H_{40}N_4$: 904.254 (found: 905.50).