



# Mixed $\beta$ -pyrrole substituted *meso*-tetraphenylporphyrins and their metal complexes: Synthesis, structures and electrochemical redox properties



P. Bhyrappa\*, U.K. Sarangi, B. Varghese

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, Tamil Nadu, India

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## ABSTRACT

Synthesis of two new classes of mixed  $\beta$ -pyrrole substituted tetraphenylporphyrins,  $H_2TPP(Ph)_4(R)_4$  ( $R = 2$ -thienyl and phenylethynyl, PE) and  $H_2TPP(CH_3)_4(R)_4$  ( $R = 2$ -thienyl and PE) and their metal complexes have been reported. These porphyrins showed dramatic red-shift in electronic absorption bands relative to their corresponding  $MTTPP(R)_4$  derivatives. Crystal structures of  $H_2TPP(R)_4(2$ -thienyl) $_4$  ( $R = Ph$  and  $CH_3$ ) and  $MTTPP(CH_3)_4(PE)_4$  ( $M = Zn(II)$  and  $Cu(II)$ ) derivatives are highly nonplanar as evidenced from the mean displacement of  $\beta$ -pyrrole carbon ( $\Delta C_b$ ) in the range  $\pm(0.33$ – $1.07)$  Å. Normal-coordinate structural decomposition analysis of the 24-atom core in these crystal structures revealed largely *saddle* (73–93%) combined with different degree of *ruffled*, *domed* and *wave* distortions. Electrochemical redox properties of these porphyrins exhibited interesting trend in redox potentials relative to their corresponding  $H_2TPP(R)_4$ s. The tunable trend in redox potentials and electronic absorption bands of mixed substituted porphyrins suggests the role of nonplanarity of macrocycle and electronic effects of the substituents.

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## 1. Introduction

Over the past three decades, interdisciplinary studies performed with porphyrins and metalloporphyrins to exemplify the applications in various fields: as biomimetic models for tetrapyrrole pigments of nature [1–5], catalysts [6–11], opto-electronics [12–17] and sensors [18–20] and others [1]. The position, nature and number of the substituents at the periphery of the macrocycle often dictate the use of such porphyrins or metalloporphyrins in specific applications. In general, the *meso*-tetraarylporphyrins,  $T(Ar)_4Ps$  are useful precursors in the preparation of variety of other substituted porphyrins because of their ease of synthesis and many available positions for functionalization at the periphery of the macrocycle [21]. Among the porphyrins,  $\beta$ -pyrrole substituted tetraarylporphyrins exhibited dramatic changes in physicochemical properties when compared to unsubstituted porphyrins. The electronic properties of the porphyrins can be altered by appending suitable substituents at the *meso*- or  $\beta$ -pyrrole carbons and/or at both the positions. Electron-donating [22–33] or electron withdrawing [34–46] groups at the  $\beta$ -pyrrole positions of porphyrin ring lead to unique physicochemical properties.

An increase in steric crowding produces dramatic changes in stereochemistry of the macrocycle and this varies with the shape, size and number of substituents in the periphery of the porphyrin ring [47–50]. These nonplanar porphyrins or metalloporphyrins have been used as model compounds to study the distortions of metalloporphyrinoids in biology. As reported previously, the introduction of halogens at the  $\beta$ -pyrrole and *meso*-phenyl positions of the tetraphenylporphyrin, TPP enhances the robust nature of the porphyrin ring in presence of strong oxygen donors and it was ascribed to the stabilization of the highest occupied  $\pi$ -molecular orbitals, HOMOs relative to the lowest unoccupied  $\pi$ -molecular orbitals, LUMOs [38,51].

The introduction of similar  $\beta$ -octa-functionalised TPPs with varying size, shape and nature of the substituents produces unique physicochemical properties [22]. However, the mixed  $\beta$ -pyrrole substituents at the antipodal positions of the TPP induce tunable optical absorption and electrochemical redox properties [48]. Furthermore, the previous work has shown that the mixed antipodal  $\beta$ -octa-substitution (CN/Cl/Br versus phenyl) of TPP produced increase in nonplanar distortion with an increase in size of the substituents [50]. Synthesis and exploration of various porphyrins with different types of mixed substituents at the antipodal  $\beta$ -pyrrole positions could provide better control on the physicochemical properties of the macrocycle and such systems have been largely

\* Corresponding author. Tel.: +91 44 2257 4222.

E-mail address: [byra@iitm.ac.in](mailto:byra@iitm.ac.in) (P. Bhyrappa).

unexamined. This article reports the synthesis of two new families of mixed  $\beta$ -substituted porphyrins, 2,3,12,13-tetramethyl-7,8,17,18-tetra(2-thienyl/PE)-5,10,15,20-tetraphenylporphyrin,  $H_2TPP(CH_3)_4(2\text{-thienyl/PE})_4$  and 2,3,5,10,12,13,15,20-octaphenyl-7,8,17,18-tetra(2-thienyl/PE)porphyrin,  $H_2TPP(Ph)_4(2\text{-thienyl/PE})_4$  and their metal (Co(II), Cu(II), and Zn(II)) complexes (Fig. 1) and explored their physicochemical properties.

## 2. Experimental

### 2.1. Materials and instrumentation

5,10,15,20-Tetraphenylporphyrin,  $H_2TPP$  [52], 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin,  $H_2TPPBr_4$  [53], 2,3,5,10,12,13,15,20-octaphenylporphyrin,  $H_2TPP(Ph)_4$ , 2,3,12,13-tetrabromo-5,7,8,10,15,17,18,20-octaphenylporphyrin,  $H_2TPP(Ph)_4Br_4$  [48], 2,3,12,13-tetramethyl-5,10,15,20-tetraphenylporphyrin,  $H_2TPP(CH_3)_4$  [48] and 2,3,12,13-tetrabromo-7,8,17,18-tetramethyl-5,10,15,20-tetraphenylporphyrin,  $H_2TPP(CH_3)_4Br_4$  were synthesized using the literature methods [48].

All the solvents were of analytical grade purchased from SRL (India) or Rankem (India) and purified before use [54]. *N*-Bromosuccinimide, NBS purchased from Rankem (India) were recrystallized from hot water and dried at 60 °C under vacuum (2.0 mbar) for 12 h prior to use. Benzaldehyde, propionic acid, sulfuric acid, anhydrous potassium carbonate, calcium hydride and sodium were purchased from SRL (India) were used as received. Pyrrole,  $CDCl_3$ , super base (2,8,9-triisobutyl-2,5,8,9-tetraaza-1-phospha-bicyclo[3.3.3]-undecane), phenylboronic acid, methylboronic acid, tetrakis(triphenylphosphine)palladium(0), tributyl(phenylethynyl)tin, tributyl(2-thienyl)tin were purchased from Sigma–Aldrich (India) and used as received. Copper(II) acetate monohydrate, zinc(II) acetate dihydrate, cobalt(II) acetate tetrahydrate and anhydrous sodium acetate were purchased from SRL (India) and used without further purification. Silica gel (100–200 mesh) for column chromatography was purchased from Rankem (India) and used as such. Pre-coated thin-layer silica gel chromatography and aluminium plates were purchased from E. Merck (Germany) and used as received.

Electronic absorption spectra of porphyrins and their metal complexes were performed on a computer interfaced JASCO V-550 model UV–Vis spectrophotometer using a pair of quartz cells

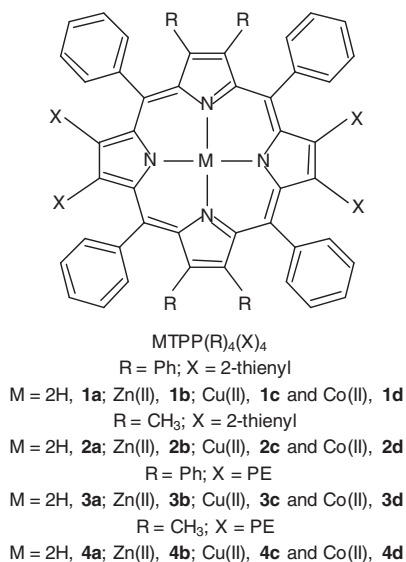


Fig. 1. Chemical structures of mixed  $\beta$ -pyrrole substituted MTPPs.

of 10 mm path length in  $CH_2Cl_2$  at 298 K.  $^1H$  NMR spectra of porphyrins were recorded on a Bruker Avance 400 MHz FT-NMR spectrometer in  $CDCl_3$ . Mass spectral measurements of samples were carried out using electrospray ionization (ESI) mass spectrometer model Micromass Q-TOF Micro using 10% formic acid in methanol as solvent medium. In some cases, a matrix assisted laser desorption time-of-flight (MALDI-TOF) spectrum on a voyager DE-PRO model mass spectrometer was used by employing  $\alpha$ -cyano-4-hydroxycinnamic acid as the matrix. Elemental analysis of the samples was performed on a Perkin Elmer CHNO/S analyzer model 2400 series. Cyclic voltammetric measurements on the porphyrin samples were performed using an Autolab Potentiostat–Galvanostat equipped with a PGSTAT-12 differential electrometer amplifier. The electrochemical cell consists of a three-electrode cell assembly: a platinum button as a working electrode, Ag/AgCl as a reference electrode and platinum wire as the counter electrode. The concentration of all the porphyrins employed were 0.5–1.0 mM, and 0.1 M tetrabutylammonium hexafluorophosphate, TBAPF<sub>6</sub> was used as the supporting electrolyte. It was recrystallized from absolute ethanol twice and dried in a vacuum desiccator before use. Porphyrin solutions were purged and maintained under high purity argon gas before measurements. All electrochemical measurements were carried out in  $CH_2Cl_2$  triply distilled from  $CaH_2$  and stored over 4 Å molecular sieves. Single crystal X-ray diffraction data collection was performed at 173 K on a Bruker Apex-II CCD diffractometer equipped with a liquid nitrogen cryostat.

#### 2.1.1. Crystal structures

Crystals of  $\mathbf{1a} \cdot (C_6H_{12}) \cdot (C_2H_4Cl_2)$  were grown by the slow vapor diffusion of cyclohexane to the saturated solution of porphyrin in 1,2-dichloroethane, DCE over a period of five days. Similarly, crystals of  $\mathbf{2a} \cdot (C_2H_4Cl_2)_2$  were grown by slow diffusion of methanol to a saturated solution of porphyrin in DCE. Solvated metalloporphyrin complexes,  $\mathbf{4b}$  and  $\mathbf{4c}$  crystals were grown by slow diffusion of vapors of methanol to a saturated solution of porphyrin in DCE over a period of week. SIR92 (WINGX) [55] program was used to solve the structure by direct methods. The structure refinement was performed on  $F^2$  using SHELXL97 software [56]. Structure was refined using full matrix least squares technique. The structure  $\mathbf{1a}$  showed disordered lattice solvate, cyclohexane and disordered one of the 2-thienyl groups on the porphyrin. In case of structure  $\mathbf{2a}$ , each lattice DCE solvates exhibited two disordered positions and rotational disorder of one of the 2-thienyl group of the porphyrin. Structure,  $\mathbf{4b}$  shows two positions for the disordered carbon of the coordinated  $CH_3OH$ . The structure  $\mathbf{4c}$  exhibited two disordered positions for one of the lattice DCE solvate. In these structures, the disordered lattice solvates or the 2-thienyl groups were refined using few or more of the SUMP, SIMU, DFIX, EADP and ISOR constraints/restraints. The ORTEP diagrams were generated using ORTEP3 [57] and intermolecular interactions were calculated using PLATON program [58]. The asymmetric unit of the structure,  $\mathbf{4b} \cdot (CH_3OH) \cdot (C_2H_4Cl_2)_{0.5}$  has unaccounted residual electron density of  $2.48 e \text{ \AA}^{-3}$  at a distance of 2.734 Å from the coordinated methanol oxygen and 2.139 Å from the Cl1 of the  $(C_2H_4Cl_2)_{0.5}$ .

#### 2.1.2. Synthesis of mixed $\beta$ -pyrrole substituted meso-tetraphenylporphyrins, $MTPP(R)_4(X)_4$ derivatives

$H_2TPP(R)_4Br_4$  ( $R = CH_3$  and Ph) were prepared using reported procedure [48] and subjected to Stille cross coupling reaction by Pd(0) as catalyst using the modified literature method [59]. Metal [Zn(II), Cu(II) and Co(II)] complexes of the free base porphyrins were prepared by conventional procedures [41].

**Synthesis of  $H_2TPP(Ph)_4(2\text{-thienyl})_4$ ,  $\mathbf{1a}$ :** A two-necked, stoppered round bottomed Schlenk flask (250 ml) containing 1,4-dioxane freshly distilled from  $CaH_2$  followed by metallic sodium (100 ml), was charged with  $H_2TPP(Ph)_4Br_4$  (0.195 g, 0.158 mmol) and

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