



Digest paper

Recent advances in mixed β -pyrrole substituted *meso*-tetraphenylporphyrins



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ABSTRACT

The modulation of physicochemical properties of the porphyrin macrocycle could find applications in nonlinear optics, dye-sensitized solar cells, photodynamic therapy etc. The synthesis of such porphyrins is challenging and gaining considerable importance. By appending appropriate substituents at the β -pyrrole or *meso*-carbon positions of the macrocycle could modulate the frontier orbitals of the porphyrin π -system. The present review discusses the reported synthetic routes employed for various mixed β -pyrrole substituted *meso*-tetraphenylporphyrins. Further, earlier work over the past 15 years on the influence of mixed β -substituent pattern in the electronic spectral, electrochemical redox and stereochemistry of the porphyrin macrocycle will be briefly discussed in this review article including their future prospects.

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Contents

Introduction	5150
Syntheses of mixed β -substituted TPPs	5151
Mixed β -tri and β -penta substituted TPPs	5151
Unsymmetrically mixed β -hepta and β -octa-substituted TPPs	5151
Symmetrically and unsymmetrically mixed β -octasubstituted TPPs	5151
Electronic absorption spectral properties	5151
Electrochemical redox properties	5156
Structural chemistry of mixed β -substituted porphyrins	5158
Normal-coordinate structural decomposition analysis	5165
Conclusion	5166
Acknowledgment	5166
References and notes	5166

Introduction

Synthetic porphyrins are of remarkable interest owing to their usefulness as model compounds of biological tetrapyrrole pigments.^{1–3} Of the synthetic porphyrin analogues, 5,10,15,20-tetraphenylporphyrin, H₂TPP (Fig. 1) and its derivatives have been widely used for its ease of preparation, large π -conjugation and

facile functionalization at both the *meso*-phenyl and β -pyrrole positions. Moreover, it can incorporate a variety of metal ions with variable oxidation states and diverse coordination geometry.³ From the past few decades there has been a shift in the derivatization of porphyrins with suitable substituents at both the *meso*-carbons and/or β -pyrrole positions for their use in potential material applications.^{4–6} The synthetic strategies with varying yields for the variety of *meso*-tetraarylporphyrins have been reported by various groups.^{7,8} Earlier methods involve the reaction

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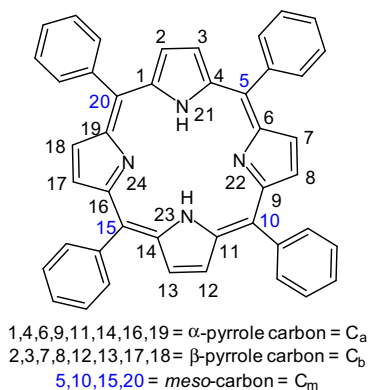


Figure 1. Molecular structure of H_2TPP and its IUPAC numbering scheme of the porphyrin ring.

of β -substituted pyrroles with aldehydes under appropriate experimental conditions to produce some mixed β -substituted porphyrins.^{7,8} Other synthetic routes for mixed *meso*-substituted porphyrins have been published in the literature.⁸ The TPPs with similar β -octasubstituents revealed unusual physicochemical properties.³ The porphyrins with similar substituents such as β -octafluoro-TPP,^{9a,b} and β -octachloro-TPP,^{9c} β -octabromo-*meso*-tetrakis(2',6'-chlorophenyl)porphinato iron(III) chloride^{9d} have been reported in the literature. The mixed β -substituted systems generally offer unique changes in physicochemical properties when compared to *meso*-substituted porphyrins. The modulation of such properties of the porphyrin ring is vital in some material applications.¹ For example, introducing appropriate substituents (electron donor and acceptor) at the peripheral positions of the macrocycle induce 'push-pull' effect on the porphyrin π -system and they find applications in nonlinear optics.^{10–12} Further, β -substituents/extended π -conjugation can shift the electronic absorption bands to the near infrared region and such systems may find use in photodynamic therapy^{13,14} and dye-sensitized solar cells.^{15–17}

In this digest article, an account on the role of mixed β -pyrrole substituents (here after referred as mixed β -substituents) of TPPs on some tunable physicochemical properties will be discussed briefly. Modulation of the properties of the porphyrin ring can be induced by appending appropriate substituents which are in direct conjugation with the porphyrin π -system. This article discusses the reported syntheses of different types of mixed β -substituted TPPs followed by their optical absorption spectral and electrochemical redox properties. Furthermore, the some crystal structures of the free base porphyrins and their metal complexes have been reviewed.

Syntheses of mixed β -substituted TPPs

Mixed β -tri and β -penta substituted TPPs

These mixed substituted porphyrins and their metal complexes have been reported by few research groups and they were synthesized using various strategies.^{18–28} The synthetic routes for the unsymmetrically mixed β -tri and β -penta-substituted TPPs (Scheme 1) were reported by employing Cu(II) and Ni(II)-porphyrins as versatile precursors because of their greater stability relative to free base porphyrins under strong acidic/oxidative reaction conditions. In some of these schemes, the bromination, metallation and demetallation reactions are often used because of their utility in the synthesis of other derivatives. Mixed β -trisubstituted porphyrins were synthesized using

β -mono-formyl¹⁸ or β -mono-nitro¹⁹ H_2TPP to generate regioselectively brominated $H_2TPP(R)Br_2$ ($R = NO_2$ or CHO). The $H_2TPP(NO_2)(CN)_2$ and other Suzuki or Stille cross-coupled products, $H_2TPP(R)X_2$ ($X = Ph, PE$ and 2'-thienyl) were isolated in very good yields (Scheme 1a).^{18,19} Kadish group²⁰ reported the synthesis of the β -penta substituted TPP series (Scheme 1b) by formylation or nitration of $NiTPP(Ph)_4$ followed by demetallation to generate their $H_2TPP(X)(Ph)_4$ ($X = CHO$ and NO_2). The more electron rich $H_2TPP(CH_2OH)(Ph)_4$ was obtained by the reduction of $H_2TPP(CHO)(Ph)_4$ with $NaBH_4$.

Unsymmetrically mixed β -hepta and β -octa-substituted TPPs

The tri-mixed β -hepta substituted porphyrin was generated by bromination of $NiTPP(NO_2)(Ph)_4$ with liq. Br_2/py yielded $NiTPP(NO_2)(Ph)_4Br_2$ ²⁰ (Scheme 2i) and its acid demetallation produced very good yields of the $H_2TPP(NO_2)(Ph)_4Br_2$. It was further cyanated to generate $NiTPP(NO_2)(Ph)_4(CN)_2$ in 44% yield. Bhyrappa and Bhavana²¹ reported the bromination of $CuTPP(NO_2)$ followed by acid demetallation resulted in $H_2TPP(NO_2)Br_n$ ($n = 6$ and 7) and unexpected H_2TPPBr_8 in moderate yields (Scheme 2ii).²¹ $CuTPP(NO_2)Br_6$ was also prepared using NBS induced bromination of $CuTPP(NO_2)$ by Kumar and Sankar.^{19b} Further, $NiTPP(NO_2)Cl_7$ was isolated by the chlorination of $NiTPP(NO_2)$ with NCS in refluxing 1,1,2,2-tetrachloroethane (TCE) and the desired $H_2TPP(NO_2)Cl_7$ was isolated along with small amounts of $NiTPPCl_8$.²² The Suzuki and Stille cross-coupling reaction of $H_2TPP(NO_2)Br_6$ produced another class of $H_2TPP(NO_2)X_6$ ($X = Ph, PE$ and 2'-thienyl) porphyrins in moderate-to-high yields.^{19b}

Symmetrically and unsymmetrically mixed β -octasubstituted TPPs

In 2006, Bhyrappa et al., reported the synthesis of two series of antipodal symmetrically mixed β -substituted TPPs, $H_2TPP(R)_4X_4$.²³ These derivatives were prepared using H_2TPPBr_4 as the precursor (Scheme 3).²⁴ The first step involves preparation of $H_2TPP(R)_4$ ($R = CH_3$ and Ph) derivatives in high yields by Suzuki cross-coupling reactions.²³ The halogenation of $NiTPP(R)_4$ with N -halosuccinimide produces corresponding $NiTPP(R)_4(X)_4$ ($X = Br$ and Cl) in very good yields. Further, $H_2TPP(R)_4(CN)_4$ derivatives were prepared by the cyanation of $NiTPP(R)_4Br_4$ followed by acid demetallation reaction. In these cyanation reactions, small amounts of $NiTPP(R)_4(CN)_3$ were also reported (15–20%). Other Stille cross-coupled products, $H_2TPP(R)_4X_4$ ($X = PE$ and 2'-thienyl) were prepared by facile reaction of $H_2TPP(R)_4Br_4$ with $(n-Bu)_3Sn(X)$ using $Pd(O)$ catalyst.^{25a}

In 2015, another class of unsymmetrically mixed β -octasubstituted $H_2TPP(Ph)_3X_5$ ($X = H, Cl, Br$ and CH_3) were reported using H_2TPPBr_3 ²⁶ as the precursor (Scheme 4).^{27a} The antipodal β -trifluoromethyl-TPP has also been reported in the literature.^{27b} Suzuki cross-coupling reaction of H_2TPPBr_3 generates $H_2TPP(Ph)_3$ in high yields. Its Ni(II)-complex, $NiTPP(Ph)_3$ on facile halogenation produced moderate-to-high yields of $NiTPP(Ph)_3X_5$ ($X = Br$ and Cl).^{27a} Suzuki cross-coupling reaction of $H_2TPP(Ph)_3Br_3$ generates desired $H_2TPP(Ph)_3(CH_3)_5$ in 41% yield. The more electron-deficient, $NiTPP(Ph)_3(CN)_5$ was also prepared by cyanation of its $NiTPP(Ph)_3Br_3$.²⁸ Some divalent metal complexes of these mixed substituted TPPs reported in Schemes 1–4 have been reported in the literature.^{19–28}

Electronic absorption spectral properties

The electronic absorption properties of substituted porphyrins have been examined by various groups.²⁹ Gouterman's^{29a}

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