The Hyperporphyrin Concept: A Contemporary Perspective

Carl C. Wamser* and Abhik Ghosh*

ABSTRACT: The Gouterman four-orbital model conceptualizes porphyrin UV−visible spectra as dominated by four frontier molecular orbitals—two nearly degenerate HOMOs and two exactly degenerate LUMOs under D_{4h} symmetry. These are well separated from all the other molecular orbitals, and normal spectra involve transitions among these MOs. Unusual spectra occur when additional orbitals appear in this energy range, typically as a consequence of the central coordinated atom. For example, metals with empty d orbitals in a suitable energy range may lead to charge transfer from porphyrin (ligand) to metal, that is, so-called LMCT transitions. Metals with filled p or d orbitals may lead to charge transfer from metal to porphyrin, MLCT transitions. These cases lead to additional peaks and/or significant redshifts in the spectra and were classified as hyperporphyrins by Gouterman. Cases in which spectra are blueshifted were classified as hypsoporphyrins; they are common for relatively electronegative late transition metal porphyrins. Many of the same principles apply to porphyrin analogues, especially corroles. In this Perspective, we focus on two newer classes of hyperporphyrins: one reflecting substituent effects in protonated or deprotonated free-base tetraphenylporphyrins and the other reflecting “noninnocent” interactions between central metal ions and corroles. Hyperporphyrin effects on spectra can be dramatic, yet they can be generated by relatively simple changes and subtle structural variations, such as acid−base reactions or the selection of a central metal ion. These concepts suggest strategies for engineering porphyrin or porphyrinoid dyes for specific applications, especially those requiring far-red or near-infrared absorption or emission.

KEYWORDS: hyperporphyrin, hypsoporphyrin, hypercorrole, hypsocorrole, Gouterman four-orbital model

1. INTRODUCTION

Porphyrins and their analogues exhibit a wide range of properties that underlie a myriad of biological roles and an ever-expanding number of applications in chemistry, medicine, and the technological sphere. These have been documented in numerous review articles and the ongoing book series *Handbook of Porphyrin Science*, now running to 45 volumes with 217 chapters, as well as in numerous review articles (one of the most notable being a special issue of *Chemical Reviews* on expanded, contracted, and isomeric porphyrins). A distinctive hallmark of porphyrin-type macrocycles is their rich array of optical properties. Furthermore, simple substituent-mediated tuning of optical and electronic properties allows for facile application in chemical catalysis, photocatalysis, medicine, and increasingly, materials science and technology. This Perspective aims to summarize and further elucidate the mechanisms underlying the tunability of the optical and electronic properties of porphyrins, specifically the generation and characterization of hyperporphyrins.

Martin Gouterman, who passed away recently, is widely regarded as the father of modern porphyrin spectroscopy and introduced the term hyperporphyrin. He is arguably best remembered for his eponymous four-orbital model, which was developed in the early 1960s on the basis of extended Hückel calculations. The calculations on the porphyrin π system identified two HOMOs and two LUMOs energetically well separated from all other π molecular orbitals: the two HOMOs are nearly degenerate (a_{1u} and a_{2u} under D_{4h} symmetry), and the two LUMOs are exactly degenerate (e_g under D_{4h}). Configuration interaction was taken into account, and the characteristic porphyrin Q and B (Soret) bands were accurately assigned to transitions among these four molecular orbitals (Figure 1). Simple perturbation theory arguments then explained why blood (i.e., hemoglobin) is red and grass (i.e., chlorophyll) is green.
“1) p-Type hyperporphyrins are found with main group metals in lower oxidation states, that is, Sn(II), Pb(II), As(III), Sb(III), and Bi(III). The extra bands are fairly well established as due to charge transfer (CT) transitions $\alpha_{2u} (np, \pi) \rightarrow \epsilon_g(\pi^*)$ (ring).

“2) d-Type hyperporphyrins are found with transition metals in configurations $d^m$, $1 < m < 6$, that have holes in the $\epsilon_g(d_{2g})$ orbitals and relatively stable lower oxidation states. The extra bands, with somewhat less certainty, are attributed to CT transitions $\alpha_{2u} (\pi), \alpha_{2u} (\pi) \rightarrow \epsilon_g(d_{2g})$ (metal).”

In general, the unique features of metalloporphyrin hyper spectra reflect the presence of additional orbitals in the vicinity of the four porphyrin frontier orbitals. If a central metal (or element) possesses filled valence p orbitals of appropriate symmetry, a metal-to-ligand charge transfer (MLCT) transition is typically observed. However, if the metal harbors empty d orbitals of appropriate symmetry, a ligand-to-metal charge transfer (LMCT) transition is often observed. In both cases, the new transition will necessarily be of lower energy (redshifted) compared with what is predicted by the four-orbital model. The observation and interpretation of hyper spectra led to the correct identification of a number of key heme protein intermediates, especially for thiolate-ligated heme proteins such as chloroperoxidase and cytochrome P450.

The present Perspective is not intended to be a comprehensive survey of hyperporphyrins. Instead, after presenting a short introduction to p- and d-type hyperporphyrins, we will focus on two avenues of research on hyperporphyrin systems that we have pursued in recent years in our own laboratories. The first of these, originating largely from the Wamser laboratory, centers around protonated free-base meso-tetraarylporphyrins, for which the redshifted spectral features are thought to reflect aryl-to-porphyrin, i.e., ligand-to-ligand, charge transfer (LLCT) transitions. The second line of work, originating largely from the Ghosh laboratory, focuses on certain meso-triarylcorrole derivatives, in which similar aryl-to-corrole LLCT transitions account for strong substituent effects on the position of the Soret maxima.

2. CLASSICAL p- AND d-TYPE HYPERPORPHYRINS

As mentioned above, p-type hyperporphyrin systems typically involve lower-valent p-block element centers with a lone pair. Classic p-type hyperporphyrins include trivalent Group 13 (Al, Sb, and Bi) and divalent Group 14 (Ge, Sn, and Pb) porphyrins. Although the first examples were synthesized almost a century ago, some of the classic synthetic work was reported by Johann Buchler, who provided samples to Gouterman for detailed spectroscopic studies. The unsung hero of the field was Phil Sayer, who was a doctoral student of Gouterman and Rex Robinson, subsequently a postdoctoral associate in Gouterman’s laboratory, and a meticulous physical chemist. Sayer’s experimental work—during the 1970s until his untimely death in 1985, while still a member of Gouterman’s laboratory—still forms much of what we know of p-type hyperporphyrin spectra.

Figure 2 depicts the classic p-type hyperporphyrin spectra of divalent Ge and Sn tetraphenylporphyrin (TPP) derivatives. These are characterized by a split, or shouldered, Soret band and a lowest-energy Q band that extends well into the red or near-infrared. As mentioned, the extra features in these spectra are thought to involve excitations from one or more MOs with p-element lone pair character into the porphyrin...
LUMOs. Detailed, modern quantum chemical studies of these spectra, however, are yet to be reported. Interestingly, trivalent antimony corroles may provide a fascinating example of a p-type “hypercorrole” spectrum; oxidation to an SbO corrole results in a spectral blueshift, that is, a so-called “normal” corrole spectrum (Figure 3).

A contemporary account of p-type hyperporphyrins would be incomplete without some mention of the remarkable axial ligand reactivity of germanium(II) porphyrins. Vaid et al. found that the addition of axial ligands to these complexes results in dramatic electronic-structural and spectral changes, reflecting an intramolecular redox process that effects a two-electron oxidation of the Ge and a two-electron reduction of the porphyrin to isophlorin. Subsequently, the authors reported a similar Si isophlorin system, while Brothers et al. reported an analogous diboron isophlorin. It should be noted that these systems require a careful distinction between valence and oxidation state (the latter being indicated with Roman numerals in Chart 1).

The archetypal examples of hyperporphyrins—specifically d-type hyperporphyrins—involve middle transition metal deriv-
atives with d electron counts less than six, such as Cr(III), Mn(III), and Fe(III) porphyrins. In contrast, d electron counts of six or higher often lead to hypsoporphyrins. Archetypal examples of the latter include Co(III), Co(II), Ni(II), Pd(II), Pt(II), and Cu(II); simple porphyrin derivatives of these metal ions typically exhibit blueshifted Soret and Q bands relative to their Mg and Zn analogues. Gouterman considered the hyper/hypso distinction to be significant because, unlike d-type hyperporphyrins, many (but not all) hypsoporphyrins exhibit characteristic emission properties. For example, Pd(II), Pt(II), and Ir(III) porphyrin derivatives are typically strongly phosphorescent. Corrole analogues of hypsoporphyrins include many 5d metallocorroles such as d^2 Os(VI)N corroles, d^6 Ir(III) and Pt(IV) corroles, and d^8 Au(III) corroles, which exhibit both hypsochromically shifted Soret and Q bands as well as near-IR phosphorescence at room temperature.

Iron porphyrins exemplify some of the most instructive and important examples of hyperporphyrins. We hasten to add, however, that most six-coordinate hemes as well as their Ru(II) and Os(II) analogues exhibit hypso spectra. A classic example of an iron(II) porphyrin with a hyper spectrum is provided by CO-ligated cytochrome P450. Besides a moderately redshifted Soret band at 446 nm, the enzyme was also found to exhibit a strong near-UV band at 363 nm. Interestingly, such a spectrum could also be generated by passing CO into a solution of ferroprotoheme IX and a thiolate (but not a thiol). In a polarized single-crystal UV−vis study, Hanson et al. (Gouterman’s group) established that both bands represented the full concentration of the enzyme (i.e., a single species) and also had the same polarization (Figure 4). The logical conclusion was made that a near-UV excitation of E_u symmetry was mixing heavily with a classic Soret transition to steal the latter’s intensity and push it to the red. Subsequent extended Hückel calculations clearly implicated the axial thiolate in determining the Soret and post-Soret absorption profile of P450, with a substantial amount of sulfur character mixing in with the porphyrin a_2u HOMO.

Iron porphyrins exemplify some of the most instructive and important examples of hyperporphyrins. We hasten to add, however, that most six-coordinate hemes as well as their Ru(II) and Os(II) analogues exhibit hypso spectra. A classic example of an iron(II) porphyrin with a hyper spectrum is provided by CO-ligated cytochrome P450. Besides a moderately redshifted Soret band at 446 nm, the enzyme was also found to exhibit a strong near-UV band at 363 nm. Interestingly, such a spectrum could also be generated by passing CO into a solution of ferroprotoheme IX and a thiolate (but not a thiol). In a polarized single-crystal UV−vis study, Hanson et al. (Gouterman’s group) established that both bands represented the full concentration of the enzyme (i.e., a single species) and also had the same polarization (Figure 4). The logical conclusion was made that a near-UV excitation of E_u symmetry was mixing heavily with a classic Soret transition to steal the latter’s intensity and push it to the red. Subsequent extended Hückel calculations clearly implicated the axial thiolate in determining the Soret and post-Soret absorption profile of P450, with a substantial amount of sulfur character mixing in with the porphyrin a_2u HOMO.

Iron porphyrins exemplify some of the most instructive and important examples of hyperporphyrins. We hasten to add, however, that most six-coordinate hemes as well as their Ru(II) and Os(II) analogues exhibit hypso spectra. A classic example of an iron(II) porphyrin with a hyper spectrum is provided by CO-ligated cytochrome P450. Besides a moderately redshifted Soret band at 446 nm, the enzyme was also found to exhibit a strong near-UV band at 363 nm. Interestingly, such a spectrum could also be generated by passing CO into a solution of ferroprotoheme IX and a thiolate (but not a thiol). In a polarized single-crystal UV−vis study, Hanson et al. (Gouterman’s group) established that both bands represented the full concentration of the enzyme (i.e., a single species) and also had the same polarization (Figure 4). The logical conclusion was made that a near-UV excitation of E_u symmetry was mixing heavily with a classic Soret transition to steal the latter’s intensity and push it to the red. Subsequent extended Hückel calculations clearly implicated the axial thiolate in determining the Soret and post-Soret absorption profile of P450, with a substantial amount of sulfur character mixing in with the porphyrin a_2u HOMO.
The extra 363 nm Soret feature qualifies P450 as a hyperporphyrin, and Hanson and co-workers correctly noted an analogy with p-type hyperporphyrins, which also exhibit split Soret bands. Perhaps most notably, these studies established the heme–thiolate core of cytochrome P450.40 Much more recently, it has become clear that {FeNO}6− heme–thiolate complexes isoelectronic to cytochrome P450 also exhibit qualitatively similar split Soret features (Figure 5).27

Higher-valent heme protein intermediates also exhibit hyperporphyrin spectra, as illustrated by the following examples. Figure 6 presents crystal absorption spectra of three different states of the heme–thiolate protein chloroperoxidase (from the fungus Caldarimomyces fumago),28 which catalyzes hydrogen-peroxide-mediated halogenation reactions. The spectra depicted are those for the Fe(III)–thiolate resting state, the ferric hydroperoxide state (Compound 0), and a ferric superoxide or oxyneme state (Compound III).

Figure 7 depicts the electronic absorption spectra of Compound I and Compound II, which are high-valent Fe(IV) states of the P450 enzyme CYP119.29–32 Both states exhibit distinctive split Soret bands and weak absorptions in the red/near-infrared, as expected for hyperporphyrin spectra. It should be noted that the S = 1/2 Compound I state is thought to involve an Fe(IV) center and an antiferromagnetically coupled radical that is delocalized over both the porphyrin and the thiolate axial ligand. The S = 1 Compound II state for this enzyme is believed to involve an Fe3+OH rather than Fe4+O center, which reflects the enhanced basicity of the latter group as a result of the thiolate ligand. Figure 8 depicts the UV–vis spectrum of the Compound II intermediate of catalase (HPC-II), a tyrosine-ligated heme enzyme from Helicobacter pylori.33 Unsurprisingly, the spectrum of this Fe3+OH species is qualitatively very similar to that of CPO-II (Figure 7b).

Importantly, the above spectra, and heme protein spectra in general, remain largely unassigned via modern quantum chemical calculations.

3. PROTONATED meso-TETRAARYLPORPHYRINS AS HYPERPORPHYRINS

Although Gouterman initially described only certain metalloporphyrins (and some metalloid derivatives) as hyperporphyrins, he and his co-workers later also included certain free-base derivatives as hyperporphyrins.34 A classic example involves the diprotonation of free-base 5,10,15,20-tetrakis(4-aminophenyl)porphyrin, H2[TAPP]. The diprotonated or "diacid" form, \( \text{H}_2\text{[TAPP]} \), exhibits significant bathochromic shifts of both the Q and B bands, as well as an extreme increase in intensity of the far-red Q band (Figure 9).35,36 In these cases, the charge-transfer effects obviously cannot be described as MLCT or LMCT but are entirely within the organic ligand; these will be called LLCT transitions.

Electronic communication between meso-aryl groups and the porphyrin ring is constrained by their relative spatial orientation. In simple free-base and metal-complexed TPP derivatives, steric interactions between the pyrrole \( \beta \)-hydrogens and the aryl ortho-hydrogens lead to significant twisting of the aryl groups out of the main porphyrin plane.27 Thus, aryl substituents typically exert only a modest influence on the electronic character of the porphyrin ring. In general, substituents exert comparable effects on the first oxidation and first reduction potentials, which leads to relatively constant electrochemical HOMO–LUMO gaps (defined as the algebraic difference between the oxidation and reduction potentials) and parallel Hammett plots.38–40 For a wide range of substituents, the absorption spectra of neutral tetra(\( p \)-X-phenyl)porphyrins (TXPPs) are also relatively consistent.41 With strongly electron-donating substituents (such as alkoxy and amino), however, there is a sharp break in the Hammett plots for oxidation potentials42 as well as a bathochromic shift of the Q bands,41,42 which can be interpreted as a gradual impingement of aryl-based MOs into the energy range of the porphyrin’s four Gouterman-type frontier MOs.

Table 1 presents highlights of substituent effect data on the free-base porphyrins as well as for the diprotonated forms in which strong hyperporphyrin effects appear.

The case of TAPP (the -NH2 data in Table 1) illustrates that even neutral H2[TAPP] may be viewed as an incipient hyperporphyrin, with significant shifts of its Q band and oxidation potential (which serves as an indicator of the relative energy position of the HOMO). Yet, the magnitude of the hyperporphyrin effect induced by protonation is dramatically larger (Figure 9). Diprotonation of the porphyrin ring induces strong nonplanarity (saddling) of the porphyrin ring, primarily as a result of steric repulsion among the four internal pyrrole hydrogens.33,44 Characteristic hyperporphyrin effects have been observed for a wide range of porphyrin diacids, including those derived from octaethylporphyrin and \( \beta \)-octahalogeno-meso-tetraarylporphyrins.45 The most distinctive cases of free-base hyperporphyrin spectra occur with TPP diacids with strongly electron-donating para-substituents, exemplified by the aforementioned \( \text{H}_2\text{[TAPP]} \) dication or its dimethylamino analogue. In these cases, protonation occurs preferentially on the central nitrogens even though the peripheral amino substituents are also basic.

3.1. Charge Transfer from Multiple Strong Electron Donors to Protonated Porphyrins (Aminophenylporphyrins)

Protonation of various \( p \)-aminophenylporphyrins has been the most thoroughly studied, with either amino or dimethylamino,35,36 as para substituents. Resonance forms for the doubly protonated porphyrin underscore transfer of electronic charge from the amino groups to the porphyrin ring; Chart 2 illustrates representative resonance forms of the three distinct types. We use the categorization proposed by Gouterman and co-workers when they first documented this type of hyperporphyrin.34 Type A depicts positive charges localized on the porphyrin pyrrole nitrogens; Type B shows one charge delocalized to one of the para-amino groups; and Type C shows both charges delocalized to two para-amino groups,
which are necessarily cis. Types B and C have multiple different forms depending on which combinations of substituents are utilized.

Examination of the resonance forms offers a number of insights that correlate well with experimental observations.

(i) The aryl-porphyrin interactions can sustain up to two charge-transfer interactions of the type described, and cis rather than trans is required to delocalize the two charges. The magnitude of the hyperporphyrin effect can be most readily tracked by the position and extinction coefficient of the far-red Q band. With just two para-amino groups (the others being para-carbomethoxy), the cis regioisomer exhibits a hyperporphyrin band with $\lambda_{\text{max}}$ at 763 nm ($\varepsilon = 60 \text{ mM}^{-1} \text{ cm}^{-1}$), while for the trans regioisomer it is at 756 nm ($\varepsilon = 41 \text{ mM}^{-1} \text{ cm}^{-1}$).

(ii) The hyperporphyrin effect increases with additional donor substituents, where the tri- and tetrasubstituted cases offer multiple modes for the resonance delocalizations of both Type B and Type C. In the limit of four para-amino groups, the hyperporphyrin Q band appears at 813 nm ($\varepsilon = 89 \text{ mM}^{-1} \text{ cm}^{-1}$) (Figure 9).

(iii) Although monoprotonated porphyrins are rarely observed, they have been proposed for monoamino TPPs where the other three substituents are electron-withdrawing carbomethoxy or sulfonato groups. In these cases, Type B resonance forms are stabilized, but Type C are not, so the second protonation is retarded.

Table 1. Lowest-Energy Q Band Maxima (and Substituent-Induced Shifts) for Tetra(p-X-phenyl)porphyrins and Their Diprotonated Forms Compared with Redox Potentials (and Substituent-Induced Shifts) for the Tetra(p-X-phenyl)porphyrins, All in DMSO Solvent

| para substituent X | Hammett $\sigma_p$ | $\lambda_{\text{max}}$ (nm) | $\Delta \lambda_{\text{max}}$ (nm) | Redox Potentials (V vs SCE) |
|--------------------|-------------------|-----------------|-----------------|--------------------------|
| −COOCH$_3$         | 0.47              | 644 (−2)        | 656 (−3)        | $+1.14 (+0.10)$          |
| −H                 | 0.00              | 646 (0)         | 659 (0)         | $+1.04 (0)$              |
| −OCH$_3$           | −0.28             | 651 (+5)        | 696 (+37)       | $+0.94 (−0.10)$          |
| −NH$_2$            | −0.57             | 669 (+23)       | 811 (+152)      | $+0.48 (−0.56)$          |

Figure 10. CAMY-B3LYP/STO-TZ2P Kohn−Sham MO energy (eV) level diagram for the four species studied, with the solvent (dichloromethane) modeled with COSMO. The irreps refer to the point groups indicated in Chart 3. Briefly, the $D_{4h}$ irreps $a_2u$ and $a_1u$ transform as $a_1$ and $a_2$, respectively, for the $C_{2v}$ point group used for the free-base porphyrins, and as $b_2$ and $b_1$, respectively, for the $D_{2d}$ point group of the diacids. Reproduced from ref 52. Copyright 2021 American Chemical Society.
(iv) Excess acid ultimately protonates all the peripheral amino substituents and destroys the hyperporphyrin effect.\textsuperscript{34,41}

Although the resonance forms are suggestive, the shapes and relative energies of the frontier MOs afford more detailed insight into the origin of the hyperporphyrin effect. The effect has been thought to arise for a single \textit{para}-aminophenyl group via
elevation of an aminophenyl-based MO to the level of molecular HOMO; in the tetrasubstituted case, both the HOMO and HOMO−1 have been thought to be aminophenyl-based. Thus, the hyperporphyrin transition is described as an aminophenyl-to-porphyrin charge transfer, as suggested by the resonance forms. This picture holds up moderately well, but far from perfectly, in light of modern DFT calculations. NMR, FTIR, and resonance Raman studies of hyperporphyrin
systems support the key structural features implied by the resonance forms, i.e., notably enhanced bonding between the porphyrin meso carbon and the aryl ipso carbon.

3.2. Origins of the Hyperporphyrin Effect: Recent TDDFT Results

We have recently reported a TDDFT study aimed at a better understanding of the dramatic hyperporphyrin spectrum of TAPP diacid. Toward this end, we studied both TPP and TAPP (both symmetrized to $C_{2v}$) and their diacids, the latter as their highly symmetric ($D_{2d}$) bisformate complexes (Chart 3). We found it essential to employ both a hybrid functional (such as B3LYP or CAM-B3LYP) and a solvation scheme (in this case COSMO with CH$_3$Cl$_2$) to obtain good simulations of experimental spectra. The results, highlighted here by relevant MO energy level diagrams (Figure 10) and plots of the relevant MOs (Figure 11), led to several concrete insights, including multiple factors manifesting themselves as hyperporphyrin spectra.

For all four species studied, both free bases and diacids, the Q band consists primarily of HOMO($a_{1u}$)-to-LUMO/LUMO+1 transitions. Two different effects appear to account for the Q band redshifts. For diprotonation of the free-base forms, the major factor underlying Q band redshifts is a lowering of the LUMOs as a result of infusion of meso-aryl character. Elevation of the “$a_{1u}$” HOMO plays a smaller role. In contrast, the redshifted Q band of free-base H$_2$[TAPP] relative to H$_2$[TPP] reflects destabilization of the “$a_{1u}$” HOMO because of antibonding “filled—filled” interactions with aminophenyl-based occupied MOs, while the LUMOs are less affected energetically.

Beyond the Q bands (i.e., for the Soret bands as well as certain pre-Soret and post-Soret bands), the transitions of the diacid forms are more complex, with meso-aryl → LUMO character mixing in with classic Gouterman “a” → LUMO transitions. Indeed, some of these transitions may be described as primarily meso-aryl or aminophenyl-based.

3.3. Charge Transfer from Deprotonated Electron Donors to Neutral Porphyrins (Hydroxyphenylporphyrins)

5,10,15,20-Tetakis(p-hydroxyphenyl)porphyrin (THPP) and related derivatives have been studied extensively by Milgrom and others for many years because of their unusual property of being very easily oxidized to phenoxy radicals, even in air for some derivatives. This observation already suggests that the HOMO is localized on the hydroxyphenyl group and that spectrophotometric titrations of H$_2$[THPP] and analogues must be carried out with the careful exclusion of oxygen. Base titrations of TPPs with one to four para-hydroxy groups show clear hyperporphyrin spectra, assigning the dianionic forms to hyperporphyrins via the resonance structures shown in Chart 4. Resonance forms of Type B are not shown but are also possible. In this case, an anionic, strongly electron-donating group is generated via the deprotonation of the phenol substituents while the porphyrin remains uncharged. Similar hyperporphyrin effects have also been demonstrated with Ni[THPP] in a strong base.

In the case of monosubstituted p-hydroxyphenylporphyrin, the choice of solvent can affect whether a hyperporphyrin spectrum is observed. In DMF, deprotonation leads to the
expected hyperporphyrin spectrum, but in 50% aqueous DMF, there is no hyperporphyrin effect, presumably as a result of strong hydrogen bonding that lowers the orbitals of the phenoxide group so they are no longer the HOMO. Analogous to the case of excess acid with protonated hyperporphyrins, excess base can deprotonate the porphyrin core of H₂[Tripp] and thereby destroy the hyperporphyrin effect.

3.4. Push—Pull Charge Transfer through Protonated Porphyrins (Aminophenyl/Pyridylporphyrins)

Type C resonance forms (Charts 3 and 4) feature two double bonds that are exocyclic to the porphyrin ring. In the limit of four such exocyclic double bonds, the derivatives are called oxoporphyrinogens, which are generally formed via the oxidation of porphyrins. The most common example of an oxoporphyrinogen is that formed by oxidation of 5,10,15,20-tetrakis(3,5-t-butyl-4-hydroxyphenyl)porphyrin, a THPP analogue that incorporates the steric hindrance of t-butyl groups to stabilize the oxidized form. Because the pyrrole nitrogens in these cases are readily derivatized, these oxoporphyrinogens have been studied as catalysts and sensors, as well as in other applications.

One case of a hyperporphyrin with a proposed oxoporphyrinogen resonance form has been reported, in which the additional exocyclic double bonds are formed by charge transfer through the porphyrin core between an electron-rich aryl group and an electron-deficient aryl group. Thus, acid titration of 5,10,15-tris(4-aminophenyl)-20-pyridylporphyrin (H₂[TAPyP]) shows a hyperporphyrin spectrum at the triprotonated state (Figure 12). At the triprotonated stage, two aminophenyl groups delocalize the positive charge from the two interior protonations, while the third protonation forms a pyridinium group that can interact with the third aminophenyl group in a push—pull charge transfer across the porphyrin ring (Chart 5). This resonance form with four exocyclic double bonds represents a new type for hyperporphyrins (Type D).

This novel type of hyperporphyrin effect is quite strong; the Q band appears at 781 nm (ε = 84 mM⁻¹ cm⁻¹), but a λmax comparable to that of a triamino-TPP at 784 nm (ε = 53 mM⁻¹ cm⁻¹), but an intensity comparable to that of TAPP at 813 nm (ε = 89 mM⁻¹ cm⁻¹).

3.5. Enhanced Charge Transfer via Ethynyl Linkers (Arylethynylporphyrins)

Aryl-to-porphyrin charge transfer interactions are enhanced when ethynyl linkers are inserted between the porphyrin meso positions and phenyl substituents, allowing for greater coplanarity of the two rings. The cases studied included para-dimethylamino and para-hydroxy substituents, but were limited by the synthetic method to two ethynyl-linked aryl groups located trans to one another. For protonation of the porphyrin with trans dimethylaminophenyls and ethynyl linkers, the Q band at 802 nm (ε = 49 mM⁻¹ cm⁻¹) was found to be considerably more redshifted (but less intense) than that in the analogue without the ethynyl linkers (723 nm, ε = 60 mM⁻¹ cm⁻¹). The corresponding porphyrins with para-hydroxyphenoxy groups were studied in both acidic and basic media. In acidic medium, the hyperporphyrin effect of hydroxy groups was found to be smaller but nonetheless enhanced with the ethynyl linkers (736 nm with ethynyl linkers and 671 nm without). In basic medium, the λmax values are 752 nm with ethynyl linkers and 671 nm without.
3.6. Hyperporphyrins Based on Charge Transfer from Porphyrin to Aryl Have Not Been Observed

In theory, one can imagine a variety of different circumstances in which charge transfer can be induced between a porphyrin and an attached aryl group, as illustrated in Chart 6.

In this paper, we have cited both types of aryl-to-porphyrin LLCT, specifically protonated TAPP as emblematic of Type I and deprotonated THPP of Type II. To our knowledge, hyperporphyrins in which charge transfer goes from porphyrin to aryl substituents have not yet been reported in the literature. Protonation of pyridylporphyrins (and N-methylpyridiniumyl) do not show hyperporphyrin effects as suggested in Type I’. Deprotonation should make the porphyrin ring a much stronger electron donor as suggested in Type II’. However, deprotonation of tetrakis(4-nitrophenyl)porphyrin (TNPP) was reportedly unsuccessful using TBAOH in various solvents.50 Tetrakis-(N-methyl-4-pyridiniumyl)porphyrin (TMPyP) has been reported to be deprotonated in aqueous solution with an apparent pK of 12.6; however, the proposed result was a single deprotonation and an unremarkable spectrum.61–63 The interior pyrrolic hydrogens of porphyrins are weakly acidic, even with strong electron-withdrawing substituents, and it may be that stronger base systems will be required to observe a hyperporphyrin with a porphyrin-to-aryl charge-transfer.

Beyond the four types of LLCT interactions described in Chart 6, one could imagine a push−pull hyperporphyrin that did not rely upon either protonation or deprotonation. In such a case, the presence of both strong electron donation and electron withdrawal at different sites on a porphyrin ring could lead to a push−pull resonance form analogous to that shown as Type D in Chart 5. A large number of porphyrins, including some with appropriate push−pull substituents, have been prepared for different applications, for example, as anticancer agents, but none showed hyperporphyrin behavior in aqueous solution.64 A copper porphyrin with trans meso substituents of dimethylaminophenylethenyl and nitropheneylethenyl also showed no hyperporphyrin effects.65 We are not aware of any free-base porphyrins that show hyperporphyrin effects without the assistance of an acid or base.

3.7. Hyperporphyrins in Redox and Photoredox Reactions

Aside from protonation reactions, porphyrins can also acquire positive charges via oxidation. Here, again, strongly electron-donating groups engender hyperporphyrin effects. Hyperporphyrin effects in the oxidation of H donors engender hyperporphyrin effects. Here, again, strongly electron-withdrawing substituents, and it may be that stronger base systems will be required to observe a hyperporphyrin with a porphyrin-to-aryl charge-transfer.

In acidic media, protonated amino substituents would ordinarily fail to yield hyperporphyrin effects. In this case, however, oxidation followed by the loss of two protons generates a +6 form that can still sustain hyperporphyrin resonance, i.e., Type C’ forms in which additionally both pyrroles and both anilino groups are protonated.

3.8. Free-Base Hypercorroles

The Gouterman four-orbital model has been successfully applied to corroles; the four frontier orbitals of unsubstituted gold corrole, Au[Cor], are depicted in Figure 13.10,68 The spectra of free-base corroles present a number of interpretational challenges. The molecules are not only strongly nonplanar as a result of steric repulsion among the three central hydrogens, but they also exist as a mixture of two tautomers. Furthermore, free-base corroles are partially to fully ionized in many common solvents (such as DMF and DMSO), even in the absence of an added base.69−72 Free-base corroles, however, can only undergo a single protonation at their cores, and the protonated site can only interact with three meso substituents. While these features distinguish free-base corroles from porphyrins, many of the same principles of hyperporphyrin spectra apply.

Acid titrations of all the isomers (o,m,p) of meso-tris(aminophenyl)corrole, H3[TAPC], have been studied.73 Comparison of the para TAPC isomer with the corresponding porphyrin (TAPP) is particularly instructive. Successive protonations (Figure 14) lead first to neutralization of the anion to form the neutral corrole and subsequently to the monoprotonated form {H+TAPC}+ with clear hyperporphyrin...
in (hypercorrole) characteristics. Upon treatment with excess acid, the spectrum returns to normal.

Chart 8 depicts the resonance forms of the para isomer of $H_4[TAPC]^+$; one localizes the positive charge on a pyrrole nitrogen (Type A), and there are three options for delocalizing the charge to aminophenyl groups (Type B). Unlike for TAPP diacid (see Chart 2), a Type C resonance form is not possible. The resonance forms suggest that $H_4[TAPC]^+$ has fewer pathways for charge delocalization interactions (as well as fewer aminophenyl substituents) relative to TAPP diacid. The net result is that the hyperporphyrin effect in TAPP diacid (see Figure 9) is distinctly stronger than what is observed for $H_4[TAPC]^+$. Thus, the Q band positions and extinction coefficients are 813 nm (89 mM$^{-1}$ cm$^{-1}$) for TAPP diacid and 764 nm (20 mM$^{-1}$ cm$^{-1}$) for $H_4[TAPC]^+$. As the peripheral amino groups become successively protonated (Figure 14c), the effects gradually diminish, without clear isosbestic points since multiple species are present, and the spectrum ultimately returns to a normal Q band at 687 nm.

4. METALLOTRIARYLCORROLES

While many 4d and 5d corroles presumably exhibit hypso spectra (a point that still needs verification), many first-row transition metal corroles clearly exhibit d-type hyper spectra. Among the latter, many (but not all) meso-triarylcorrole derivatives exhibit a remarkable substituent effect, which is not observed for meso-tetraarylporphyrins. The Soret maximum in these systems redshifts systematically with increasing electron-donating character of the para substituent on the meso-phenyl groups. Such substituent effects are particularly well-established for Mn, Fe, Co, and Cu corroles (Table 2). A variety of probes have established that the effect is specific to noninnocent metalcorroles, i.e., those having partial corrole$^{2−}$ radical character, which typically arises via one of two orbital interactions depicted in Figure 15. Although few of these spectra have been theoretically analyzed, a TDDFT study of copper triarylcorroles suggests that the substituent-sensitive components of the Soret manifolds are aryl-to-corrole$^{2−}$ charge transfer transitions, not unlike a number of LLCT transitions mentioned above. Some of the main classes of noninnocent metalcorroles are described below.

4.1. The Manganese Case

While all Mn corroles exhibit complex d-type hyper spectra relative to “normal” Al and Ga corroles, the Mn[TpXPC]Cl series exhibits substituent-sensitive Soret bands, implicating a noninnocent Mn$^{III}$-corrole$^{2−}$ description. In contrast, the Mn(III) and Mn[TpXPC]Ph series (Figure 16) are thought to involve an innocent corrole.

4.2. The Iron Case

In an exact parallel to Mn triarylcorroles, FeCl$^{77−79}$ triarylcorroles exhibit substituent-sensitive Soret maxima clearly indicative of aryl-to-corrole LLCT transitions and hyperporphyrin character, but FePh triarylcorroles do not (Figure 17). In an unexpected development, FeNO$^{80}$ triarylcorroles were found to exhibit substituent-sensitive Soret maxima, suggesting a novel {FeNO}$_7$-corrole$^{2−}$ description, which was later supported by several other lines of evidence. Similarly, μ-oxo diiron triarylcorroles also exhibit mildly substituent-sensitive Soret maxima, suggesting the following intramolecularly spin-coupled description

$$\text{corrole}^{2−} (\downarrow) \rightarrow \text{Fe}^{III}(\uparrow\uparrow) \rightarrow \text{Fe}^{III}(\downarrow\downarrow) \rightarrow \text{corrole}^{2−} (\uparrow)$$
which was also supported by broken-symmetry DFT calculations.

4.3. Cobalt Corroles

One of our more surprising findings in recent years is that the five-coordinate Co[TpXPC](py)₂ series in CH₂Cl₂, however, one of the pyridine ligands falls off and the resulting solutions, in which the main species is Co[TpXPC](py), exhibit substituent-sensitive Soret maxima (Figure 19). Worth noting in this connection is that the Rh[TpXPC](PPh₃)₈³ series involves innocent corrole macrocycles.

4.4. The Coinage Metals

Among copper corroles,⁸⁴–⁸⁶ both the simple triarylcorrole series Cu[TpXPC] and the β-substituted series Cu[Br₅TpXPC] and Cu[[CF₃]₄TpXPC] exhibit substituent sensitive Soret maxima (Figure 20), indicative of a Cuᴵ⁻corrole⁸²− description. Gold triarylcorroles, in sharp contrast, do not exhibit such substituent sensitivity, which indicates (on the basis of other additional lines of evidence) an innocent Auᴵᴵ⁻corrole³⁻ electronic description.⁸⁷–⁸⁹ This difference manifests itself most dramatically in the structures of isoelectronic coinage metal corroles: while Au corroles are planar, Cu corroles, uniquely among metallocorroles, are inherently saddled. The saddled conformation is associated with a Cu(dₓ²−y²)⁻corrole(π) orbital interaction (depicted in Figure 15), which allows part of the corrole(π) electron density to flow into the formally empty Cu(dₓ²−y²) orbital, resulting in an overall Cuᴵ⁻corrole⁸²− description. In the Au case, the relativistically destabilized 5dₓ²−y² orbital is too high in energy to engage in a similar interaction, explaining both the substituent-insensitive Soret bands in the Au[TpXPC] series and the planar macrocycle geometries.⁸⁸,⁸⁹

Silver corroles are special in this regard. While the Ag[TpXPC] series exhibits essentially planar macrocycles and substituent-insensitive Soret maxima (like Au[TpXPC], see Figure 20), the more sterically hindered Ag[Br₅TpXPC] series exhibits strongly saddled macrocycles and substituent-sensitive Soret maxima (like their Cu counterparts). The observations suggest that while the Ag[TpXPC] series is essentially innocent, the Ag[Br₅TpXPC] series is noninnocent.⁹⁰

4.5. Platinum Corroles

A series of neutral, paramagnetic complexes Pt[TpXPC](Ar)⁻(Ar)⁺ exemplify some of the best examples of uncoupled corrole radicals.⁹⁰ The complexes, which may be described as Pt[V(TpXPC)](Ar)(Ar)⁺, exhibit hypercorrole spectra with prominent split Soret bands in which the main visible peak is strongly substituent-dependent (Figure 21). In contrast, the true Pt(IV) series Pt[TpXPC](Ar)(py) exhibits much sharper, slightly split Soret bands, whose positions are essentially substituent-independent.⁹¹ These probably also have some hyper character, but theoretical assignments are still lacking.

5. CONCLUSIONS AND PROSPECTS

We have presented a contemporary and somewhat personal perspective of hyperporphyrin spectra by focusing on two major classes of compounds: centrally protonated meso-tetraarylporphyrins and noninnocent metallocorrole macrocycles. Classic p-type and d-type hyperporphyrins have also been briefly covered, while a discussion of spectral redshifts due to conjugating β-substituents (such as halogen, alkoxy, alkylthio, amino, etc.) has been deferred for a different occasion.

Hyperporphyrin spectra can reflect various types of charge transfer transitions—MLCT, LMCT, LLCT, and combinations thereof. The term thus appears to unite a class of related electronic phenomena and a rather diverse menagerie of molecules that exhibit them. Because of the importance of porphyrins as optoelectronic materials, the ability to create hyperporphyrin effects by simple structural perturbations such
as the complexation of certain elements, certain types of peripheral substituents, and acid–base reactions may be a particularly useful paradigm. Compared with Gouterman’s days, there are many new approaches to the design of NIR-absorbing and emitting dyes, such as porphyrin ring reduction, 92,93 loss of aromaticity, 94,95 and especially porphyrinoids with extended conjugations (e.g., nanographenes). 96 In spite of the plethora of options, the hyperporphyrin paradigm remains attractive on account of its practical simplicity. Below are some musings on how the concept can serve as a creative force in both fundamental and application-oriented areas.

Let us consider hemes and their model compounds, including metallocorroles, that exhibit hyperporphyrin spectra. A deeper understanding of the spectra may improve our understanding of their reactivity and potentially facilitate their deployment as catalysts and therapeutics (e.g., as antioxidants for disorders mediated by oxidative stress). Such an understanding may be further enhanced by MCD 97 and XAS spectroscopy. 78 Many such studies of “electronic structure contributions to reactivity” have been reported by Solomon et al., but only rarely for heme and metalloporphyrin systems. 98,99 Such studies would be a welcome addition to the heme and metalloporphyrin literature.

A significant amount of interest in porphyrins centers around their potential application to solar energy conversion, analogous to the role of chlorophyll in photosynthesis. A push–pull charge transfer motif has been at the heart of many synthetic porphyrins designed for this purpose. 100–102 Thus, some of the most efficient photosensitizers employed in dye-sensitized solar cells are porphyrins with an N,N-diarylamino meso substituent and a carboxyphenyl anchoring group. 103,104 The unique Type D resonance form illustrated earlier has been suggested as a potential two-electron hydride donor by analogy to the NADH/
NAD⁺ couple (Figure 22). In this case, the N–H bond of a protonated pyridine is suggested as a hydride donor, leaving behind an oxidized porphyrin. Such a process might be photochemically induced.

In spite of their attractive spectra for solar absorption, typically extending into the far red, hyperporphyrin systems based on protonated tetraphenylporphyrins have not been directly examined as photosensitizers. Presumably, because it is necessary to generate such systems under strongly acidic conditions, they have been little used for solar sensitization, as well as biomedical applications such as in photodynamic therapy. That said, protonated tetraphenylporphyrins have been used as sensors for gases such as ammonia, hydrogen sulfide, and sulfur dioxide.105,106

As a final example, 5d metalloporphyrins and metallocorroles, which are of great interest as triplet photosensitizers, might be considered.25,107–109 Gouterman himself devoted the latter part of his career to developing phosphorescent Pt porphyrins as pressure-sensitive paints for airplane wings.110,111 In one of our own laboratories, we are developing 5d metalcorroles as dyes for oxygen sensing, photodynamic therapy, and triplet–triplet annihilation upconversion.25 Although several of these complexes are actually of the hypso type, the use of suitable substituents might significantly redshift key absorption and emission features.11 In such a case, the hypso/hyper distinction might become moot. We hope to illustrate such applications of the hyperporphyrin concept by synthesizing new classes of 5d metalcorrole-based photosensitizers.

ACKNOWLEDGMENTS

C.C.W. acknowledges support from the National Science Foundation, Grant CHE-0911186. A.G. acknowledges the Research Council of Norway for long-term support, most recently via grant no. 324139. We are deeply grateful to our many collaborators who contributed to this work over the years.

REFERENCES

(1) Handbook of Porphyrin Science, Vol. I–IV; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; World Scientific, 2010.
(2) Sessler, J. L.; Gross, Z.; Furuta, H. Introduction: Expanded, Contracted, and Isomeric Porphyrins. Chem. Rev. 2017, 117, 2201–2202.
(3) Ghosh, A. An Exemplary Gay Scientist and Mentor: Martin Gouterman (1931–2020). Angew. Chem. Int. Ed. 2021, 60, 9760–9770.
(4) Gouterman, M. Spectra of porphyrins. J. Mol. Spectrosc. 1961, 6, 138–163.
(5) Gouterman, M.; Wagniére, G. H.; Snyder, L. C. Spectra of Porphyrins. Part II. Four-Orbital Model. J. Mol. Spectrosc. 1963, 11, 108–115.
(6) Gouterman, M. Optical Spectra and Electronic Structure of Porphyrins and Related Rings. In The Porphyrins, Vol. III, Part A; Dolphin, D., Ed.; Academic Press: New York, 1978; pp 1–165.
(7) The calculated data on Al[11]TPC(NH₃)₂ have been compared to experimental data on Al[11]TPP(C)py; Mahammed, A.; Gross, Z. Aluminum Corrolin, A Novel Chlorophyll Analogue. J. Inorg. Biochem. 2002, 88, 305–309.
(8) Bendis, J.; Dmochowski, I. J.; Gray, H. B.; Mahammed, A.; Simkhovich, L.; Gross, Z. Structural, Electrochemical, and Photo-physical Properties of Gallium(III) 5,10,15-Tris(pentafluorophenyl)-corrole. Angew. Chem. Int. Ed 2000, 39, 4048–4051.
(9) Kowalska, D.; Liu, X.; Tripathy, U.; Mahammed, A.; Gross, Z.; Hirayama, S.; Steer, R. P. Ground- and Excited-State Dynamics of Aluminum and Gallium Corroles. Inorg. Chem. 2009, 48, 2670–2676.
(10) Ghosh, A.; Wondimagegn, T.; Parusel, A. B. J. Electronic Structure of Gallium, Copper, and Nickel Complexes of Corrole. High-Valent Transition Metal Centers Versus Noninnocent Ligands. J. Am. Chem. Soc. 2000, 122, 5100–5104.
(11) Ghosh, A.; Conradie, J. The Dog That Didn’t Bark: A New Interpretation of Hypsoporphpyrin Spectra and the Question of Hypsocorroles. J. Phys. Chem. A 2021, 125, 9962–9968.
(12) Hanson, L. K.; Eaton, W. A.; Slatger, S. G.; Gunsalus, I. C.; Gouterman, M.; Connell, C. C. Origin of the anomalous Soret spectra of carboxyctochrome P-450. J. Am. Chem. Soc. 1976, 98, 2672–2674.
(13) Sayer, P.; Gouterman, M.; Connell, C. R. Metalloid Porphyrins and Phthalocyanines. Acc. Chem. Res. 1982, 15, 73–79.

Figure 22. Speculative use of a Type D hyperporphyrin as a hydride donor. Reproduced from ref 36. Copyright 2014 American Chemical Society.
(14) Buchler, J. W. Synthesis and Properties of Metalloporphyrins. In The Porphyrins, Vol. I, Part A; Dolphin, D., Ed.; Academic Press: New York, 1978; pp 389–483.

(15) Cissell, J. A.; Vaid, T. P.; Yap, G. P. A. Reversible Oxidation State Change in Germanium(tert-terephthalamorphyrin) Induced by a Dative Ligand: Aromatic GeIV(TPP) and Antiaromatic GeIV(TPP)(pyridine)2, J. Am. Chem. Soc. 2007, 129, 7841–7847.

(16) Barbe, J. M.; Ratti, C.; Richard, P.; Lecomte, C.; Gerardin, R.; Guillard, R. Tin(II) porphyrins: synthesis and spectroscopic properties of a series of divalent tin porphyrins. X-ray crystal structure of (2,3,7,8,12,13,17,18-octaethylporphinato)tin(II). Inorg. Chem. 1990, 29, 4126–4130.

(17) Arnold, D. P.; Blok, J. The coordination chemistry of tin porphyrin complexes. Coord. Chem. Rev. 2004, 248, 299–319.

(18) Luobeznova, I.; Raizman, M.; Goldberg, I.; Gross, Z. Synthesis and Full Characterization of Molybdenum and Antimony Corroles and Utilization of the Latter Complexes as Very Efficient Catalysts for Highly Selective Aerobic Oxidation Reactions. Inorg. Chem. 2006, 45, 386–394.

(19) Lemon, C. M.; Maher, A. G.; Mazzotti, A. R.; Powers, D. C.; Gonzalez, M. I.; Nocera, D. G. Multielectron C–H photoactivation with an Sb(V) oxo corrole. Chem. Commun. 2020, 56, 5247–5250.

(20) Mondal, S.; Garai, A.; Naik, P. K.; Adha, J. K.; Kar, S. Synthesis and characterization of antimony(V)-oxo corrole complexes. Inorg. Chim. Acta 2020, 501, 119300.

(21) Cissell, J. A.; Vaid, T. P.; Rheingold, A. L. An Antiaromatic Porphyrin Complex: Tetraphenylporphyrinato(silicon)(Li)(L = THF or Pyridine). J. Am. Chem. Soc. 2005, 127, 12212–12213.

(22) Weiss, A.; Hodgson, M. C.; Boyd, P. D. W.; Siebert, W.; Brothers, P. J. Diboryl and Diboranyl Porphyrin Complexes: Synthesis, Structural Motifs, and Redox Chemistry: Diboronyl Porphyrin or Diboranyl Isolophin? Chem. Eur. J. 2007, 13, 5982–5993.

(23) Conradie, J.; Brothers, P. J.; Ghosh, A. Main-Group-Element Isolophin Complexes Revisited: The Question of a Subvalent Central Atom. Inorg. Chem. 2019, 58, 4634–4640.

(24) Parkin, G. Valence, Oxidation Number, and Formal Charge: Three Related but Fundamentally Different Concepts. J. Chem. Educ. 2006, 83, 791–799.

(25) Alemayehu, A. B.; Thomas, K. E.; Einrem, R. F.; Ghosh, A. Hyperporphyrin Spectra: TDDFT Calculations on Diprotonated Tetraphenylporphyrins. J. Phys. Chem. B 2003, 107, 3486–3496.

(26) Meot-Ner, M.; Adler, A. D. Substituent effects in noncoplanar π systems. ms-Porphins. J. Am. Chem. Soc. 1975, 97, 5107–5111.

(27) Stone, A.; Fleischer, E. B. The Molecular and Crystal Structure of Porphyrin Dications. J. Am. Chem. Soc. 1966, 80, 2735–2748.

(28) Cheng, B.; Munoz, O. Q.; Marques, H. M.; Scheidt, W. R. Analysis of Porphyrin Molecular Flexibility: Use of Porphyrin Dications. J. Am. Chem. Soc. 1997, 119, 10732–10742.

(29) Washbotten, I. H.; Conradie, J.; Ghosh, A. Electronic Absorption and Resonance Raman Signatures of Hyperporphyrins and Nonplanar Porphyrins. J. Phys. Chem. B 2003, 107, 3613–3623.

(30) Hibblet, F.; Hunte, K. P. P. Kinetic and equilibrium studies of the protonation of meso-tetraphenylporphyrin in dimethyl sulfoxide–water. J. Chem. Soc., Perkin Trans. 1977, 2, 1624–1628.

(31) Zurita, A.; Duran, A.; Ribó, J. M.; El-Hachemi, Z.; Crusats, J. Hyperporphyrin effects extended into a J-aggregate supramolecular structure in water. RSC Adv. 2017, 7, 3353–3357.

(32) Vitasovic, M.; Gouterman, M.; Linschitz, H. Calculations on the origin of hyperporphyrin spectra in meso-(dimethylaminophenyl)porphyrins. J. Porphyrins Phthalocyanines 2001, 5, 191–197.

(33) Wang, C.; Wamsers, C. C. NMR Study of Hyperporphyrin Effects in the Protonations of Porphyrins with 4-Aminophenyl and 4-Pyridyl Mesot Substituents. J. Phys. Chem. A 2014, 118, 3605–3615.

(34) Ojadi, E. C. A.; Linschitz, H.; Gouterman, M.; Walter, R. I.; Lindsey, J. S.; Wagner, R. W.; Droupaudi, P. R.; Wang, W. Sequential Protonation of meso-<(p-Dimethylamino)<(phenyl)porphyrins: Charge-Transfer Excited States Producing Hyperporphyrins. J. Phys. Chem. 1993, 97, 13192–13197.

(35) Guo, H.; Jiang, J.; Shi, Y.; Wang, Y.; Dong, S. Solvent effects on spectrophotometric titrations and vibrational spectroscopy of 5,10,15-triphenyl-20-(4-hydroxyphenyl)porphyrin in aqueous DMF. Spectrochim. Acta, Part A 2007, 67, 166–171.

(36) Wang, C.; Wamsers, C. C. NMR Study of Hyperporphyrin Effects in the Protonations of Porphyrins with 4-Aminophenyl and 4-Pyridyl Mesot Substituents. J. Org. Chem. 2015, 80 (15), 7351–7359.
(54) Guo, H.; Jiang, J.; Shi, Y.; Wang, Y.; Liu, J.; Dong, S. UV-Vis Spectrophotometric Titrations and Vibrational Spectroscopic Characterization of meso-(p-Hydroxyphenyl)porphyrins. J. Phys. Chem. B 2004, 108, 10185–10191.

(55) Guo, H.; Jiang, J.; Shi, Y.; Wang, Y.; Wang, Y.; Dong, S. Sequential Deprotonation of meso-(p-Hydroxyphenyl)porphyrins in DMF: From Hyperporphyrins to Sodium Porphyrin Complexes. J. Phys. Chem. B 2006, 110, 587–594.

(56) Hill, J. P.; Hewitt, I. J.; Anson, C. E.; Powell, A. K.; McCarty, A. L.; Kari, P. A.; Zandler, M. E.; D’Souza, F. Highly Nonplanar, Non Deficient, N-Substituted tetra-Oxocyclohexadienylidene Porphyrinogens: Structural, Computational, and Electrochemical Investigations. J. Org. Chem. 2004, 69, 5861–5869.

(57) Chahal, M. K.; Payne, D. T.; Matsushita, Y.; Labuta, J.; Ariga, K.; Hill, J. P. Molecular Engineering of β-Substituted Oxo-porphyrinogens for Hydrogen-Bond Donor Catalysis. Eur. J. Org. Chem. 2020, 2020, 82–90.

(58) Goldberg, P. K.; Pundsack, T. J.; Splan, K. E. Photophysical Investigation of Neutral and Diprotonated Free-Base Bis(Arylethynyl)-porphyrins. J. Phys. Chem. A 2011, 115, 10452–10460.

(59) Evens, K. K.; Kaplan, K. E. Spectroscopic characterization of free-base hydroxy(arylethynyl)porphyrins in acidic and basic media. J. Porphyrins Phthalocyanines 2017, 21, 680–691.

(60) Gündüz, N.; Gündüz, T.; Hayvali, M. Titrations in non-aqueous media: potentiometric investigation of symmetrical and unsymmetrical tetra-aryl porphyrins with 4-nitrophenyl and 4-aminophenyl substituents in nitrobenzene sovent. Talanta 1999, 48, 71–79.

(61) Hambright, P.; Fleischer, E. B. The Acid-Base Equilibria, Kinetics of Copper Ion Incorporation, and Acid-Catalyzed Zinc Ion Displacement from the Water-Soluble Porphyrin αβγδ-Tetra(4-N-methylpyridyl)porphine. Inorg. Chim. Acta 1970, 9, 1757–1761.

(62) Pasternack, R. F.; Huber, P. R.; Boyd, P.; Engasser, G.; Francesconi, L.; Gibbs, E.; Fasella, P.; Venturo, G. C.; Hinds, L. deC. On the Aggregation of Meso-Substituted Water-Soluble Porphyrins. J. Am. Chem. Soc. 1972, 94, 4511–4517.

(63) Santiago, P. S.; Gandini, S. C. M.; Moreira, L. M.; Tabak, M. Interaction of cationic water-soluble meso-tetrakis(4-N-methylpyridinium)porphyrin (TMPyP) with ionic and nonionic micelles: aggregation and binding. J. Porphyrins Phthalocyanines 2008, 12, 942–952.

(64) Meng, G. G.; James, B. R.; Skov, K. A.; Korbelik, M. Porphyrin chemistry pertaining to the design of anti-cancer drugs; part 2, the sensitive Soret bands as a distinctive feature of high-valent \( \text{Fe}^{2+} \) complex. J. Am. Chem. Soc. 2003, 125, 17378–17380.

(65) LeCours, S. M.; Phillips, C. M.; De Paula, J. C.; Therien, M. J. Synthesis, Transient Absorption, and Transient Resonance Raman Spectroscopy of Novel Electron Donor-Acceptor Complexes: [5,15-Bis(4-nitrophenyl)ethyl] 10,20-diphenylporphinato]copper(II) and [5-([4-(Dimethylamino)phenyl]ethyl] 15-([4-nitrophenyl]-ethyl)-10,20-diphenylporphinato]copper(II). J. Am. Chem. Soc. 1997, 119, 12578–12589.

(66) Walter, M. G.; Wamser, C. C. Preparation of Electrolyzer-Nitrogen Complexes. J. Phys. Chem. C 2010, 114, 7563–7574.

(67) Day, N. U.; Walter, M. G.; Wamser, C. C. Preparations and Electrochemical Characterizations of Conductive Porphyrin Polymers. J. Phys. Chem. C 2015, 119, 17378–17388.

(68) Ghosh, A. Electronic Structure of Corrole Derivatives: Insights from Molecular Structures, Spectroscopy, Electrochemistry, and Quantum Chemical Calculations. Chem. Rev. 2017, 117, 3798–3881.

(69) Mahammed, A.; Weaver, J. J.; Gray, H. B.; Abdelas, M.; Gross, Z. How Acidic Are Corroles and Why? Tetrahedron Lett. 2003, 44, 2077–2079.

(70) Jimenez, H. R.; Julve, M.; Faus, J. A Solution Study of the Protonation and Deprotonation Equilibria of \( \text{S}_{10,15,20}-\text{Tetra(p-sulphonato)porphyrin}. \) Stability Constants of its Magnesium-

(II), Copper(II) and Zinc(II) Complexes. J. Chem. Soc., Dalton Trans. 1991, 1945–1949.

(71) Song, Y.; Fang, Y.; Ou, Z.; Capar, J.; Wang, C.; Conradie, J.; Thomas, K. E.; Wamser, C. C.; Ghosh, A.; Kadish, K. M. Influence of β-octakis(Trifluoromethyl)Corroles: New Paradigms for Ligand Substituent Effects in Transition Metal Complexes. Inorg. Chem. 2008, 47, 10469–10478.

(72) Alemayehu, A. B.; Ghosh, A. Gold Corroles Phthalocyanines 2011, 15, 106–110.

(73) Thomas, K. E.; Alemayehu, A. B.; Conradie, J.; Beavers, C.; Ghosh, A. Synthesis and Molecular Structure of Gold Triarylcorroles. Inorg. Chem. 2011, 50, 12844–12851.
(98) Hocking, R. K.; Wasinger, E. C.; Yan, Y.-L.; de Groot, F. M. F.; Walker, F. A.; Hodgson, K. O.; Hedman, B.; Solomon, E. I. Fe L-Edge X-ray Absorption Spectroscopy of Low-Spin Heme Relative to Nonheme Fe Complexes: Delocalization of Fe d-Electrons into the Porphyrin Ligand. J. Am. Chem. Soc. 2007, 129, 113–125.

(99) Wilson, S. A.; Kroll, T.; Decreau, R. A.; Hocking, R. K.; Lundberg, M.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. Iron L-Edge X-ray Absorption Spectroscopy of Oxy-Picket Fence Porphyrin: Experimental Insight into Fe−O2 Bonding. J. Am. Chem. Soc. 2013, 135, 1124–1136.

(100) Imahori, H.; Kurotobi, K.; Walter, M. G.; Rudine, A. B.; Wamsler, C. C. Porphyrin- and Porphycene-Based Solar Cells. In Handbook of Porphyrin Science, Vol. 18; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; World Scientific: Singapore, 2012; pp 57–121.

(101) Walter, M.; Rudine, A. B.; Wamsler, C. C. Porphyrins and phthalocyanines in solar photovoltaic cells. J. Porphyrins Phthalocyanines 2010, 14, 759–792.

(102) Milgrom, L. Synthesis of some New Tetra-aromatic porphyrins for Studies in Solar Energy Conversion. J. Chem. Soc. Perkin Trans. 1 1983, 2535–2539.

(103) Bessho, T.; Zakeeruddin, S. M.; Yeh, C.-Y.; Diao, E. W.-G.; Grätzel, M. Highly Efficient Mesoscopic Dye-Sensitized Solar Cells Based on Donor–Acceptor-Substituted Porphyrins. Angew. Chem. Int. Ed 2010, 49, 6646–6649.

(104) Lu, H.-P.; Tsai, C.-Y.; Yen, W.-N.; Hsieh, C.-P.; Lee, C.-W.; Yeh, C.-Y.; Diao, E. W.-G. Control of Dye Aggregation and Electron Injection for Highly Efficient Porphyrin Sensitizers Adsorbed on Semiconductor Films with Varying Ratios of Coadsorbate. J. Phys. Chem. C 2009, 113, 20990–20997.

(105) Tuerdi, G.; Nizamidin, P.; Kari, N.; Yimit, A.; Wang, F. Optochemical properties of gas-phase protonated tetraphenylporphyrin in investigated using an optical waveguide NH3 sensor. RSC Adv. 2018, 8, 5614–5621.

(106) Maimaiti, A.; Abdurahman, R.; Kari, N.; Ma, Q.-r.; Wumaier, K.; Nizamidin, P.; Abzik, S.; Yimit, A. Highly sensitive optical waveguide sensor for SO2 and H2S detection in the parts-per-trillion regime using tetraaminophenyl porphyrin. J. Mod. Opt. 2020, 67, 507–514.

(107) Naik, A.; Rubbiano, R.; Gasser, G.; Spangler, B. Visible-Light-Induced Annihilation of Tumor Cells with Platinum–Porphyrin Conjugates. Angew. Chem. Int. Ed 2014, 126, 7058–7061.

(108) Mahammed, A.; Gross, Z. Corroles as triplet photosensitizers. Coord. Chem. Rev. 2019, 379, 121–132.

(109) Natale, C. d.; Gros, C. P.; Paolesse, R. Corroles at work: a small macrocycle for great applications. Chem. Soc. Rev. 2022, 51, 1277–1335.

(110) Gallery, J.; Gouterman, M.; Callis, J.; Khalil, G.; McLachlan, B.; Bell, J. Luminescent thermometry for aerodynamic measurements. Rev. Sci. Instrum. 1994, 65, 712–720.

(111) Gouterman, M. Oxygen Quenching of Luminescence of Pressure Sensitive Paint for Wind Tunnel Research. J. Chem. Educ. 1997, 74, 697–702.