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Novel Versatile Synthesis of Substituted Tetrabenzoporphyrins

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A novel general synthetic route to tetraaryltetrabenzoporphyrins (Ar_4TBP) with various peripheral functional groups is developed. The procedure includes (i) Barton−Zard condensation of 1-nitro- or 1-phenylsulfonylcyclohexenes with isocyanoacetic acid esters, (ii) condensation of the resulting 4,5,6,7-tetrahydroisoindoles with aromatic aldehydes to give fused tetraaryltetracylohexenoporphyrins (Ar_4TCHP), and (iii) aromatization of the metal complexes of Ar_4TCHP's into the corresponding Ar_4TBP's. Cu and Zn complexes of Ar_4TBP's are further demetalated to give the corresponding Ar_4TBP free bases. The overall yields for the sequence range from 15% to 40%, making the method suitable for the preparation of gram quantities of Ar_4TBP's in a single run. The scope of the method, the selection of the peripheral substituents, the choice of the metal ions, and their influence on the yields of aromatization are discussed. The basic spectroscopic properties of newly synthesized Ar_4TBP's and Ar_4TCHP's are reported together with the first X-ray crystallographic structure of the $NiAr_4TBP$ complex.

Introduction

Over the past decade interest in porphyrins fused with external aromatic rings has been on the rise.[1] Commonly referred to as *extended porphyrins*,[2] these macrocycles possess interesting properties, inviting applications in various branches of optical technology and biomedicine. Tetraannulated porphyrins (tetrabenzoporphyrins, tetranaphthaloporphyrins, etc.) and their metal complexes form an especially intriguing class of extended porphyrins. Due to the higher order of their molecular symmetry, the spectral features of these compounds are much sharper and better defined, and their absorption bands are shifted considerably farther to the infrared.[1d] From the structural point of view, the simplest representative of this class, tetrabenzoporphyrin (TBP), is an intermediate between "regular" nonextended porphyrins and phthalocyanines, partially retaining properties of both and providing a useful point in structure/property comparative studies.

Tetrabenzoporphyrins have been studied substantially more than other extended porphyrins. Their unique photophysical,[3] optoelectrochemical,[4] and other physicochemical properties[5] have attracted interest in different

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(2) Term *extended* refers to lateral π-conjugation, external to the core porphyrin macrocycle. Extension of the macrocycle itself by adding extra pyrrole moieties leads to *expanded* porphyrins (for review see: Sessler, J. L.; Gebauer, A.; Vogel, E. Heteroporphyrins, expanded porphyrins and related macrocycles. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Chapter 9).

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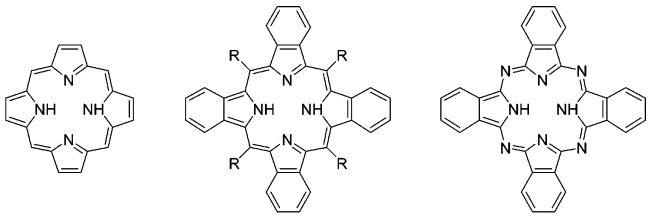
areas. For example, tetrabenzoporphyrins have been considered as agents for PDT,[6] optical limiters[7] and other types of nonlinear optical materials,[8] luminescent markers for oxygen[9] and pH[10] in biomedical imaging, etc. Nevertheless, compared to regular porphyrins and phthalocyanines, the chemistry of tetrabenzoporphyrins has been little investigated. The main reason for this has been the lack of robust and general synthetic methods leading to the tetrabenzoporphyrin system.



The first synthesis of tetrabenzoporphyrin, described by Helberger[11] and further developed in the works of Linstead et al.,[12] was inspired by the structural relation of the tetrabenzoporphyrin macrocycle to both porphine and phthalocyanine. Later data indeed revealed that the plain unsubstituted TBP resembles its structural homologues in a variety of ways, including extremely low solubility. The latter obviously presented a serious obstacle for the practical handling of TBP's and hampered the progress of their physicochemical studies. *meso*-Tetraaryl-substituted tetrabenzoporphyrins (Ar_4TBP), on the other hand, turned out to be much more soluble and better suited for practical work. The increased solubility of Ar_4TBP's is probably at least in part caused by their considerably nonplanar structures,[5e,i] which are due to the steric crowding induced by four *meso*-aryl substituents.

Early approaches to the TBP system (for reviews, see refs 1a,c) can be divided into two major groups. The first group consists of the most straightforward attempts to mimic the standard porphyrin synthesis, i.e., condensation of pyrroles with *meso*-carbon donors. To obtain TBP's, however, pyrroles have to be replaced by isoindole or its derivatives,[13] which in most cases are unstable and not easily available.[14]

The second group of methods, which subsequently led to a much wider array of TBP's, stemmed from basic phthalocyanine synthesis.[3d,e,4c,12b] In these methods the *meso*-carbons in the porphyrin skeleton come not from electrophilic carbonyls, as in traditional porphyrin condensations (Rothmund/Adler-Longo/Lindsey), but from nucleophilic CH acids. As a result, unstable isoindoles can be replaced by readily available phthalimides or their derivatives. One version of this approach, developed by Lukyanets and co-workers,[15] appeared useful for the synthesis of Ar_4TBP's. According to their method, phthalimide is condensed with CH acids (e.g. arylacetic acids) in the presence of metal salts, which are assumed to serve as templates. Using 3-arylidenphthalimidines instead of phthalimides was reported to give better yields of Ar_4TBP's.[15c] However, the conditions required for the condensation were so harsh (fusion at 350−400 °C) that only inert substituents in the starting materials, such as alkyl or halogen,[9d,15,16] could sustain the procedure. In addition, several studies[3j,17a] have demonstrated that the high-temperature syntheses of Ar_4TBP's, via both the isoindole[13f] and the phthalocylanie-type[15b] pathways, led to the complex mixtures of porphyrins with one to four *meso*-aryl substituents. Some minor improvements of the method have been proposed,[17b,18] but still low yields and extremely laborious purifications made it quite impractical.

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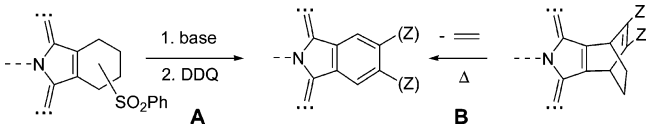
SCHEME 1



The recent search for better synthetic routes to the TBP system centered around "masked" isoindoles, i.e., *c*-annealated pyrroles. Such pyrroles, fused with nonaromatic rings, are readily available via Barton−Zard isocyanoacetate chemistry[19] and appeared to be useful synthones for other extended porphyrins.[20] Two methods based on this strategy were developed specifically for the TBP system (Scheme 1).

In the method of Cavaleiro et al. (Scheme 1, step A),[21] a sequence of reactions, including the modified Barton−Zard synthesis, leads at first to an intermediate tetracyclohexenoporphyrin, substituted with phenylsulfonyl groups. This precursor porphyrin is then aromatized into the TBP through base-catalyzed elimination of sulfinate, succeeded by the oxidation of octahydrotetrabenzoporphyrin with DDQ (Scheme 1, step A). Another approach, developed by Ono and co-workers,[22] is based on the retro-Diels−Alder extrusion of ethylene from porphyrins fused with bicyclo[2.2.2]octadiene fragments (Scheme 1, step B). The precursor pyrroles in this case are also synthesized by using the Barton−Zard route. Although it relies on a multistep reaction sequence and involves quite complex intermediates, Ono's method makes it possible to obtain TBP's in high purity and in virtually quantitative yields at the last stage.

A feature shared by both of these methods is that the aromatization requires the presence of a special "helper" functionality, which is removed at the last stages of the syntheses. An obvious drawback of this approach is that the introduction of an additional group leads to an extra synthetic effort. Moreover, it limits the choice of other substituents, which are to be retained in the target macrocycle. Avoiding the helper group by directly aromatizing fused cyclohexene rings would seem like a more atom-economical and cost-effective method, especially if the aromatization can be accomplished by using commonly available reagents, such as chloranil or DDQ.

There are a number of reports in the literature in which aromatization by DDQ has been employed to synthesize various asymmetrical extended porphyrins.[20c,23] For example, both monobenzoporphyrin[23a] and dibenzoporphyrin[24] have been prepared by oxidative aromatization with DDQ. Surprisingly, despite high interest in fully symmetrical extended porphyrins, the idea of direct oxidation of fused cyclohexene rings has never, to our knowledge, been contemplated as a pathway to TBP's.

Recently we began developing a synthetic scheme leading to the TBP system, which relies on oxidative aromatization of nonaromatized porphyrin precursors. In an earlier communication we reported on the synthesis of polysubstituted Ar_4TBP's by the oxidation of tetracyclohexeno-fused porphyrins,[25a] and in a more recent work a similar methodology was applied to the construction of further extended tetraaryltetra[2,3]naphthaloporphyrins (Ar_4TNP).[25b] Herein we present a more detailed account of this methodology, describing syntheses of Ar_4TBP's with both substituted and unsubstituted benzo rings. In addition, we present basic photophysical properties of a few new tetrabenzoporphyrins and report the first X-ray crystallographic structure of the NiAr_4-TBP complex.

Results and Discussion

Assuming that direct aromatization of the fused cyclohexene rings in tetracyclohexenoporphyrins (TCHP) is possible, the retrosynthetic analysis of the TBP system shown in Scheme 2 can be devised.

The scheme consists of two parallel routes (1 and 2), which are coupled via a set of similar Diels−Alder reactions. These can be performed, in principle, at any of the four stages, providing at least two pathways to each of the key compounds. The most important advantage of this scheme is very simple starting materials, i.e., Diels−Alder adducts of butadiene with alkenes bearing groups X. A large selection of such dienophiles is available, allowing for a variety of substituents in the resulting cyclohexene rings. Choosing symmetrically substituted alkenes helps to avoid multiple randomers at the stage of the macrocycle formation, although generally groups X are not required to be the same.

The key intermediate of the entire sequence is 4,5,6,7-tetrahydroisoindole ester (Route 2) and/or its Diels−Alder-coupled analogue in Route 1. Both pyrroles can be obtained via the modified Barton−Zard reaction, in which arylsulfinate plays the role of the leaving group.[26] The arylsulfonyl variant of the Barton−Zard condensation seems to be far more flexible than the original nitroolefin

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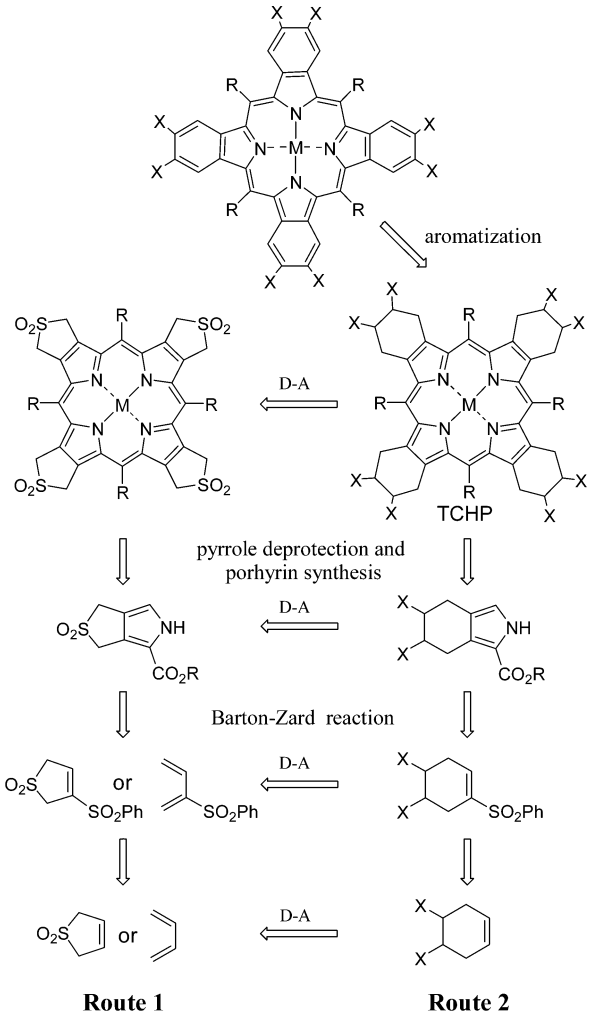
SCHEME 2. Retrosynthetic Analysis of the TBP System[a]



[a] D-A denotes Diels−Alder reactions.

version. While synthesis of 1-nitrocyclohexenes is rather inconvenient, the arylsulfonyl group can be easily placed near almost any carbon−carbon double bond (Route 2), using a reliable chlorosulfenylation−oxidation−elimination protocol,[27] or addition−elimination reactions.[28] In addition, 1-arylsulfonylcyclohexenes can be prepared through the Diels−Alder condensation from 2-arylsulfonylbutadiene (Route 1).[29]

The remaining elements of Scheme 2 are the deprotection of the pyrrole esters, the porphyrin synthesis itself, and the aromatization. The first two processes are very well documented and will be discussed below as they apply to our particular case. The aromatization, on the other hand, is a specific feature of the proposed scheme and will be discussed separately (also see below). Finally, it should be mentioned that some parts of the scheme have been implemented previously,[28b,30] but the target TBP structure has never been obtained in this way.

A specific pathway, derived from the retrosynthetic analysis outlined above (Route 2) and implemented in this work is shown in Scheme 3.

The starting materials for the Barton−Zard condensation (step a), i.e., isocyanoacetic acid esters and cyclic vinylsulfones (**4**), can be easily prepared from inexpensive precursors or, in some cases, are available commercially. In special cases, when no substituents X are needed in the target macrocycles, the simplest choice of the starting compound would be 1-nitrocyclohexene, available from a number of commercial sources. Tetrahydroisoindole esters **5**, obtained from the Barton−Zard reaction, are deesterified and decarboxylated (step b) into unsubstituted 4,5,6,7-tetrahydroisoindoles **6**. These are further reacted with aromatic aldehydes under Adler−Longo or Lidsey conditions (step c) giving *meso*-tetraaryl tetracyclohexenoporphyrins (Ar_4TCHP, **7**). The next step, which is the key to the whole sequence, is the oxidative aromatization (step d) of Ar_4TCHP's **7** into Ar_4TBP's **8**. As shown below, aromatization requires the presence of metals in Ar_4TCHP's, and later the metal ions must be removed to generate free base Ar_4TBP's. Thus, the choice of metals is critical for the success of the synthesis.

A detailed discussion of the procedures involved in the syntheses of two classes of Ar_4TBP's, i.e., with and without substituents X, is presented below.

***meso*-Tetraaryltetra(4,5-dimethoxycarbonyl)benzoporphyrins $Ar_4TBP(CO_2Me)_8$ (8a−e).** Octamethoxycarbonyltetrabenzoporphyrins ($Ar_4TBP(CO_2Me)_8$) and octacarboxytetrabenzoporphyrins ($Ar_4TBP(CO_2H)_8$) were our initial synthetic targets. The latter porphyrins can be easily modified by either esterification or coupling with amines, allowing for control over their solubility in media of different polarities. For example, $Ar_4TBP(CO_2H)_8$ and their PEG-ester derivatives are well soluble in water, making it possible to study their basicity[5i] and evaluate their efficacy in various biomedical applications,[9,10,25] where high aqueous solubility is a necessary requirement. A route to $Ar_4TBP(CO_2Me)_8$, developed in this work, is depicted in Scheme 4.

The starting material for the Barton−Zard reaction is cyclic vinylsulfone **4a**. **4a** was obtained from dimethyl tetrahydrophthalate **2**, whose cis isomer was prepared from the commercially available adduct of butadiene and maleic anhydride **1** (Scheme 4, a). The trans isomer of **2** was synthesized by the Diels−Alder reaction of dimethyl maleate (DMM) with 1,3-butadiene (Scheme 4, c), produced by the thermal extrusion of SO_2 from butadiene sulfone **1** (sulfolene).[31] Although from the standpoint of the target materials both *cis*-**2** and *trans*-**2** are equally well suited for the transformations to follow, in practice using each isomer revealed certain advantages and drawbacks (see below).

Compound **2** was further reacted with PhSCl (Scheme 4, b), succeeded by oxidation and elimination of HCl to give vinyl sulfone **4a** in a high yield (85%).[27] As shown in the scheme, **4a** also could be synthesized by first

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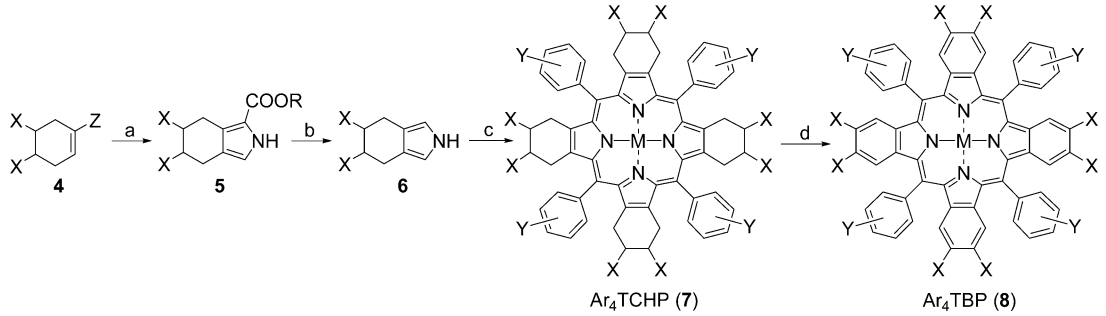
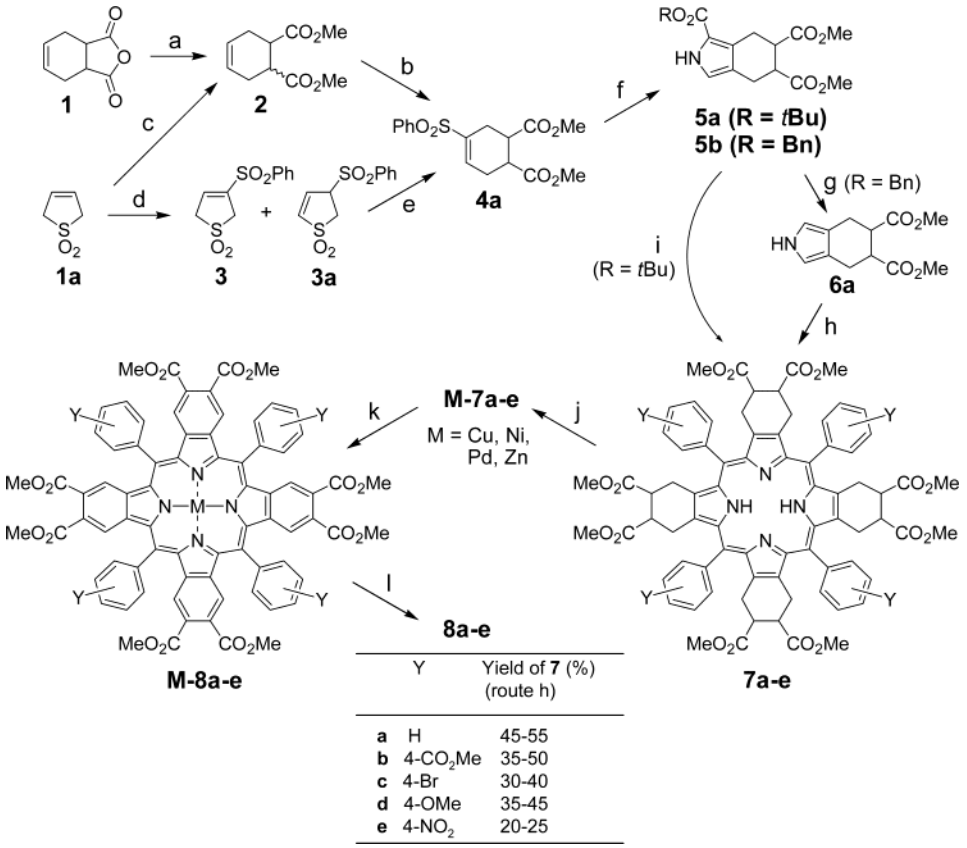
SCHEME 3[a]



[a] Reaction steps: (a) Barton−Zard condensation; (b) pyrrole−ester cleavage; (c) macrocycle assembly; (d) aromatization.

SCHEME 4[a]



	Y	Yield of **7** (%) (route h)
a	H	45-55
b	4-CO_2Me	35-50
c	4-Br	30-40
d	4-OMe	35-45
e	4-NO_2	20-25

[a] Reagents and conditions: (a) MeOH, TosOH cat., reflux (95%); (b) (i) PhSCl, CH_2Cl_2, rt; (ii) MCPBA, CH_2Cl_2, rt; (iii)DBU (85% for 3 steps); (c) DMM, py, toluene, 180 °C, pressure tube (85%); (d) (i) PhSCl, CH_2Cl_2, rt; (ii) MCPBA, CH_2Cl_2, rt, or oxone, MeOH−water; (iii) Et_3N (86% for 3 steps); (e) DMM, py, toluene, 180 °C, pressure tube (54%); (f) $CNCH_2CO_2R$, *t*BuOK, THF, 0 °C (75−95%); (g) for R = Bn: (i) H_2, Pearlman catalyst, THF−MeOH−Et_3N, rt; (ii) $(CH_2OH)_2$, reflux, 30 min (85−90% for 2 steps); for R = *t*Bu: TFA−CH_2Cl_2, rt (30%); (h) ArCHO, BF_3·Et_2O, CH_2Cl_2, rt, 1.5−2 h, then DDQ, overnight (20−55%); (i) ArCHO, AcOH, TsOH, air, reflux, 8 h (11% for Y = H); (j) metal salt (90−98%; see text for conditions); (k) DDQ, THF or MeCN, reflux, 0.5−3 h (90−95%); (l) M = Cu: (i) H_2SO_4 concentrated; (ii) MeOH (95% for **8a**−**c**, 5% for **8d**,**e**; yields are given for two steps).

transforming sulfolene **1a** into its phenylsulfonyl derivative (Scheme 4, d), obtained usually as a mixture of isomers **3** and **3a**, and then condensing it with DMM (Scheme 4, e). The yields of **4a** recovered in this route were, however, relatively low due to the dimerization of 2-phenylsulfonylbutadiene (30−40%).

Barton−Zard condensation of **4a** with *tert*-butyl and benzyl isocyanoacetates (Scheme 4, f) afforded the corresponding 4,5,6,7-tetrahydroisoindoles **5a**,**b** in 75−95% yield. Using the cis isomer of **4a** appeared advantageous, since purification of the *trans*-pyrrole ester **5b** was complicated by the presence of two regioisomers. Originally, we focused on using *tert*-butyl derivative **5a**, since it seemed more convenient to transform the ester into tetrahydroisoindole **6a** by using a simple one-pot deprotection−decarboxylation procedure and treatment with TFA (Scheme 4, g). The yields of **6a** obtained in this way, however, were quite low, 30−40%. On the other hand, a two-stage procedure, beginning with benzyl ester **5b**, was found to be much more efficient, and *cis*-**5b** could be obtained in a pure crystalline form. *cis*-**5b** was subjected to hydrogenolysis, followed by decarboxylation of the

resulting pyrrole carboxylic acid in refluxing ethylene glycol, giving *cis*-**6a** in 85−90% overall yield. The commercial Pd/C catalyst appeared ineffective in the ester cleavage, while Pearlman's catalyst,[32] i.e., $Pd(OH)_2/C$, afforded quantitative conversion of **5b** into the acid. The Pearlman catalyst is known for its ability to perform well in the cases where regular Pd/C catalysts fail.

Octamethoxycarbonyltetracyclohexenoporphyrins $Ar_4TCHP(CO_2Me)_8$ (**7a**−**e**) were synthesized in moderate to high yields (25−55%) by condensation of tetrahydroisoindole **6a** with aromatic aldehydes (Scheme 4, h) following the standard Lindsey method.[33] It is interesting that in some cases an alternative "one-pot" Adler−Longo type procedure (Scheme 4, i) could be implemented, in which *tert*-butyl ester **5a** reacted directly with aromatic aldehydes in the presence of TsOH. In these cases, pyrrole **6a** was generated in situ. Although lower yields were usually afforded (5−15%), this approach is still worth consideration, since it essentially removes two stages from the overall reaction sequence.

The resulting $Ar_4TCHP(CO_2Me)_8$'s (**7a**−**e**) were isolated as bright green porphyrin dications (acetates of chlorides). These dications formed instantly upon addition of DDQ (Lindsey method) causing a color change of the solution to deep green. An important property of porphyrins **7a**−**e** is that their dications could be fully deprotonated only in the presence of quite strong bases, such as triethylamine or DBU. For example, a solution of **7a** in CH_2Cl_2/pyridine (3:1) still contained about 50% of the dication, and even in pure pyridine about 10% of the porphyrin remained protonated. Such behavior of $Ar_4TCHP(CO_2Me)_8$'s is a result of their extremely high basicity, which, as shown below, appeared to be an important issue in the context of their conversion into the corresponding TBP's by oxidative aromatization.

The enhanced basicity of dodecasubstituted porphyrins has been well documented in the literature.[34] It is typically associated with their severe nonplanarity, although other factors affect it as well. In this respect, $Ar_4TCHP(CO_2H)_8$'s present a unique model for systematic studies of the factors influencing the basicity of the porphyrin macrocycle. The presence of eight carboxylic groups in these porphyrins ensures their excellent water solubility and allows for accurate measurements of their thermodynamic p*K* values.[5i] The latter are usually quite hard to assess due to the intrinsic hydrophobicity of porphyrins.

Subsequent aromatization of $Ar_4TCHP(CO_2Me)_8$'s required their conversion into metal complexes (see below). $MAr_4TCHP(CO_2Me)_8$'s (M = Zn, Ni, Cu, Pd) could be easily prepared by reacting the free base porphyrins with metal salts in appropriately chosen solvents (Scheme 4, j). Zn, Cu, and Ni were inserted in CH_2Cl_2/MeOH (9:1) under mild conditions, using the corresponding acetates, while insertion of Pd required prolonged heating of porphyrins with $PdCl_2$ in MeCN/THF (1:1) and could be driven to completion only in the presence of a base, e.g. Et_3N or K_2CO_3. Alternatively, Pd could be inserted by refluxing a porphyrin with $PdCl_2$ in benzonitrile, in which case the base was not required and insertion occurred much faster. Expectedly, Zn complexes of $Ar_4TCHP(CO_2Me)_8$'s were found to be much more acid sensitive than Cu, Ni, and Pd derivatives.

The next step of the sequence is the oxidative aromatization of tetracyclohexenoporphyrins into tetrabenzoporphyrins. Our initial discovery, however, was that under no conditions could $Ar_4TCHP(CO_2Me)_8$'s free bases be aromatized into $Ar_4TBP(CO_2Me)_8$'s by either *p*-chloranil or DDQ or any other oxidants available to us. Apparently, $Ar_4TCHP(CO_2Me)_8$'s taken as free bases immediately formed the corresponding dications upon addition of aromatizing agents. Consequently, no progress in aromatization could be observed even after several hours of refluxing $Ar_4TCHP(CO_2Me)_8$'s with DDQ, making it clear that porphyrin dications are totally inert in oxidation.

Metallo-$Ar_4TCHP(CO_2Me)_8$'s (**M-7a**−**e**), on the other hand, behaved completely differently. Porphyrinates of metals with easily accessible high oxidation states, such as Fe, Co, and Mn, refused aromatization, whereas complexes of bivalent metals, such as Zn, Cu, Ni, and Pd, could be readily oxidized into the corresponding metallo-$Ar_4TBP(CO_2Me)_8$'s (**M-8a**−**e**) upon refluxing in acetonitrile with DDQ (Scheme 4, k). However, large variations in stability made porphyrinates of the latter metals quite different in terms of practical handling. It appeared that more labile Zn complexes rapidly lost metal under aromatization conditions, thus yielding dications and causing incomplete conversions and low yields. Although the target $ZnAr_4TBP(CO_2Me)_8$'s and the remaining starting $Ar_4TCHP(CO_2Me)_8$'s always could be recovered by column chromatography, the whole procedure, involving intermediate separations, remetalations, and repetitive oxidations, was laborious and cumbersome. In contrast, aromatization of metalloporphyrins **M-7a**−**e** (M = Ni, Cu, Pd) resulted in nearly quantitative yields and no metal loss could be detected. In the latter cases, the aromatization usually took place in just a few minutes, causing drastic color changes of the reaction mixtures from characteristic red-brown ($MAr_4TCHP(CO_2Me)_8$'s) to deep green ($MAr_4TBP(CO_2Me)_8$'s). The presence of electron-withdrawing groups in *meso*-aryl rings markedly decreased the reaction rate. For example, aromatization of **Cu-7e** (Y = 4-NO_2) required a prolonged refluxing (2−3 h) in CH_3CN, while oxidation of **Cu-7a** (Y = H) was complete after 15−20 min. Nevertheless, in all the cases involving Ni, Cu, and Pd porphyrins, oxidation could be driven to completion and gave excellent yields of the target tetrabenzoporphyrins.

Since the oxidative aromatization of tetracyclohexenoporphyrins[35] into tetrabenzoporphyrins is central to the described synthetic scheme, it is interesting to consider possible mechanistic pathways for this transformation. In our opinion, the most feasible mechanism

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(35) In the following paragraphs, which deal with mechanistic aspects of the oxidative aromatization, the term "tetracyclohexenoporphyrins" refers to both octamethoxycarbonyl tetracyclohexenoporphyrins ($Ar_4TCHP(COMe)_8$) and benzo-unsubstituted tetracyclohexenoporphyrins (Ar_4TCHP), introduced later in the text. The term "tetrabenzoporphyrins" is used similarly.

involves the single-electron transfer (SET) from the metallo-Ar_4TCHP to DDQ with the formation of an ion-radical pair [$MAr_4TCHP^{+\bullet}/DDQ^{-\bullet}$] at the first stage. The semiquinone anion-radical $DDQ^{-\bullet}$ further induces the stepwise abstraction of a hydrogen atom and a proton, with the net result of dehydrogenation. Alternatively, this sequence can be presented as an abstraction of a hydride from MAr_4TCHP followed by the proton transfer, which might be, in fact, indistinguishable from the stepwise "fast" abstraction of the electron, "fast" transfer of the hydrogen atom, and "slow" transfer of the proton. Oxidations by DDQ are usually regarded within the framework of the SET/hydride abstraction mechanistic dualism.[36]

Generally, SET from a metalloporphyrin either leaves the unpaired spin to reside on the porphyrin macrocycle, yielding a metalloporphyrin cation radical, or changes the formal oxidation state of the metal, causing relatively little perturbation of the porphyrin electronic system.[37] Porphyrinates of electroactive metals, such as Fe, Co, and Mn, react with oxidants primarily in this latter way, which explains why we could not observe aromatization of the corresponding metallo-tetracyclohexenoporphyrins.

Complexes of metals with stable oxidation states (Ni, Pd, Cu) on the contrary give metalloporphyrin cation radicals with spin density delocalized over the porphyrin macrocycle. Similar to cation radicals of other aromatic molecules containing "benzylic"-type α-hydrogen atoms, these metalloporphyrin cation radicals are likely to lose protons to a concomitant base,[36] resulting in metalloporphyrin radicals. The abstraction of hydrogen atoms from the latter seems like a quite probable scenario. Given that the semiquinone anion radical can act as both the base and the scavenger of hydrogens, the overall dehydrogenation should be fast and effective.

Unlike metal complexes, tetracyclohexenoporphyrin free bases do not aromatize, but upon mixing with DDQ quickly form dications. Several scenarios of this transformation are plausible. On one hand, nonplanar tetracyclohexenoporphyrins possess such high proton affinities that even the smallest increase in the medium acidity would cause their immediate protonation. On the other hand, unlike cation radicals of metalloporphyrins, cation radicals of the free bases ($H_2P^{+\bullet}$) are highly transient species and can convert into the corresponding cations by abstracting hydrogen atoms from the solvent.[38] A support of this latter pathway comes from the quantum chemistry calculations. Apparently, the spin density in the porphyrin cation radical $H_2Ph_4TCHP^{+\bullet}$ resides primarily on the *meso*-carbon and imine nitrogen atoms, approximately matching the geometry of the $a_{2u}(\pi)$ HOMO in the free base H_2Ph_4TCHP (see the Supporting Information for the distribution of the spin density). Since the *meso*-positions are hindered by the phenyl substituents, hydrogen atoms from the solvent most certainly would become attached to the imine nitrogens, resulting in the cations.

It is interesting that the molecular complex between tetraphenylporphyrin (H_2TPP) and DDQ has been reported once in the literature,[39] although no structural evidence has been presented. At the same time, all the measured spectral properties of the described adduct were identical with those of the respective porphyrin dication. In view of the present discussion, it seems probable that the reported H_2TPP/DDQ complex was in fact the salt of the porphyrin dication with the conjugate base of hydroquinone.

The last step of the sequence is the demetalation of metallotetrabenzoporphyrins (Scheme 4, *l*), which is essential to gaining access to $Ar_4TBP(CO_2Me)_8$ free bases and subsequently to the other metal derivatives. The necessity of demetalation imposed quite strict constraints on the choice of the metal required for oxidation. On one hand, this metal had to give stable complexes with $Ar_4TCHP(CO_2Me)_8$'s, capable of sustaining the aromatization; on the other, the resulting $MAr_4TBP(CO_2Me)_8$'s had to be labile enough to permit effective demetalation. Choosing the metal was especially difficult because the basicity of $Ar_4TCHP(CO_2Me)_8$'s is generally a few orders of magnitude higher than that of the corresponding $Ar_4TBP(CO_2Me)_8$'s,[5i] making the metal complexes of the latter much more robust. In general, metal affinity of porphyrins decreases as their basicity increases. Basicity is affected by porphyrin nonplanarity[34] and extended π-conjugation.[5i] Tetrabenzoporphyrins are weaker bases than nonextended porphyrins[10] owing to the influence of the extended π-system, which acts as an absorber of electron density, pulling it away from the core nitrogens and making them more electron defficient.[5h] As a result, tetrabenzoporphyrins form much more stable metal derivatives, resembling in this respect phthalocyanines. For example, complexes of planar TBP's even with Zn require treatment with sulfuric[12] or hot phosphoric[9a] acid to complete removal of the metal, while Pd and Ni, whose complexes even with nonextended porphyrins are among the most stable ones known,[40] cannot be removed from TBP's without destroying the macrocycle.

Due to the effect of nonplanarity, Ar_4TBP's exhibit higher basicities than planar TBP's, and, consequently, their metal complexes are more labile. For example, unlike ZnTBP, $ZnPh_4TBP$ can be effectively demetalated by TFA in chloroform,[3j,15b] which, in principle, makes Zn a suitable candidate for the insertion/oxidation/demetalation sequence. Unfortunately, Zn complexes with $Ar_4TCHP(CO_2Me)_8$'s are so unstable that their aromatization is extremely ineffective (see above). In contrast, Ni and Pd complexes were excellent in aromatization, but removal of metals from either Ni or Pd $Ar_4TBP(CO_2Me)_8$'s is still impossible without destroying the macrocycles. In our experiments we went through a number of metals, looking for the one that would permit the aromatization, but at the same time would allow regeneration of $Ar_4TBP(CO_2Me)_8$ free bases. The best metal found so far is Cu.

Cu complexes of $Ar_4TCHP(CO_2Me)_8$'s are very effective in aromatization and indeed Cu can be removed from the

(36) See, for example: Utley, J. H. P.; Rozenberg, G. G. *Tetrahedron* **2002**, *58*, 5251 and references therein.

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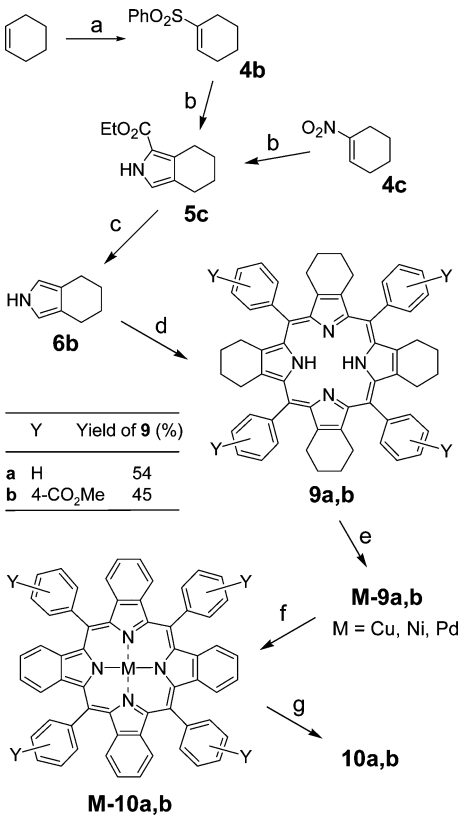
resulting tetrabenzoporphyrins; however, demetalation of $CuAr_4TBP(CO_2Me)_8$'s still required strong acidic conditions, e.g. prolonged treatment with concentrated H_2SO_4 (Scheme 4, *l*). Notably, $CuAr_4TCHP(CO_2Me)_8$'s could be fully demetalated upon treatment with glacial AcOH. According to the scale of Falk, Phillips, and Buchler, such reactivity places $CuAr_4TCHP(CO_2Me)_8$'s into one of the low-stability classes (Class IV), while $CuAr_4TBP(CO_2Me)_8$'s belong to the much more stable Class II (see ref 40 for details). Despite the harsh conditions required for demetalation, the yields of the free base tetrabenzoporphyrins **8a**−**c** were close to quantitative. Obviously, hydrolysis of the side methyl ester groups accompanied the removal of metal, but re-esterification could be easily achieved by simply pouring the reaction mixtures into MeOH and stirring the solutions overnight. Demetalation of metalloporphyrins **Cu-8d** and **Cu-8e**, however, was more problematic. In **Cu-8d** (Y = 4-MeO), the presence of electron-rich *meso*-aryl rings evidently facilitated undesired side reactions, e.g. sulfonation, and the target free base could be isolated in a quite poor yield (<5%). In contrast, electron-withdrawing nitro groups in **Cu-8e** (Y = NO_2) made this complex extremely robust. Even after keeping **Cu-8e** in warm H_2SO_4 for several days Cu was still partially retained in the porphyrin. Nevertheless, up until now we were unable to find a metal better suited for the aromatization/demetalation sequence than Cu.

$Ar_4TBP(CO_2Me)_8$ free bases **8a**−**e** as well as the metal complexes were isolated as dark blue-green crystalline solids, soluble in THF, CH_2Cl_2, and $CHCl_3$ and virtually insoluble in alcohols and ether. The overall yields of tetrabenzoporphyrins **8a**−**e** for the five-step sequence, beginning with tetrahydroisoindole ester **5a**, vary in the range 20−55%. The yields depend on the nature of the Y group, reaching their maximum at 45−55% for the *meso*-tetraphenyl derivative (**8a**, Y = H).

Benzo-Unsubstituted *meso*-Tetraaryltetrabenzoporphyrins (Ar_4TBP). Although benzo-unsubstituted tetraaryltetracyclohexenoporphyrins (Ar_4TCHP) have been known for more than a decade, no attempts to aromatize these porphyrins into the corresponding Ar_4TBP's by oxidation have been reported. This fact from the beginning kept us doubtful if such a conversion was at all possible. Nevertheless, synthesis of benzo-unsubstituted Ar_4TBP's via aromatization of Ar_4TCHP's appeared to be quite convenient and versatile. The route to Ar_4TBP's is shown in Scheme 5.

In the beginning, cyclohexene was transformed into 1-phenylsulfonylcyclohexene **4b** in 80% overall yield by using a reliable procedure, suitable for bulk preparations (Scheme 5, a).[27] As mentioned above, commercially available 1-nitrocyclohexene **4c** could be used instead of **4b** in the following Barton−Zard reaction with ethyl isocyanoacetate (Scheme 5, b). However, **4c** is a costly reagent, and the condensation involving sulfone **4b** proceeded, in our hands, much more smoothly, giving the desired tetrahydroisoindole ester **5c** in higher purity and almost quantitative yield. Tetrahydroisoindole **6b** was obtained from **5c** by refluxing the latter with an excess of KOH in ethylene glycol (Scheme 5, c). In a routine procedure, compound **6b** was introduced directly into the subsequent Lindsey synthesis (Scheme 5, d) without intermediate isolation and purification. The yields of the

SCHEME 5[a]



[a] Reagents and conditions: (a) (i) PhSCl, CH_2Cl_2, rt; (ii) MCPBA, CH_2Cl_2, rt, or oxone, MeOH−water; (iii) Et_3N (80% for three steps); (b) $CNCH_2CO_2Et$, *t*BuOK, THF, 0 °C (90%, starting with **4b**); (c) KOH, ethylene glycol, reflux, 1 h (pyrrole introduced directly to the next reaction); (d) ArCHO, $BF_3{\cdot}Et_2O$, CH_2Cl_2, rt, 2 h, then DDQ, overnight (yields for steps c + d are shown in the table); (e) metal salt, solvent (85−98%, see text for details); (f) DDQ, THF, reflux, 15−20 min (25−95%); (g) polyphosphoric acid, 85−90 °C, 4−5 h (70−80%).

resulting Ar_4TCHP's **9a**,**b** were quite high, i.e., up to 50%. These porphyrins were crystallized from CH_2Cl_2−ether mixtures and isolated as salts of the corresponding dications (usually chlorides). The dark-green crystalline dications are poorly soluble in THF and CH_3CN, but their solubility increases in the presence of acids, such as AcOH or TFA.

Metal complexes of porphyrins **9a**,**b** were prepared (Scheme 5, e) under the same conditions as were the $Ar_4TCHP(CO_2Me)_8$'s. The insertion of Pd in CH_3CN was hampered by very low solubilities of both the parent porphyrins and the metalated products, resulting in incomplete conversions. Nevertheless, large differences between the affinities of $PdAr_4TCHP$'s and the corresponding porphyrin dications to silica made it easy to separate the metal-free porphyrins and recycle them. Insertion of Pd in PhCN, on the other hand, was smooth and occurred quantitatively after 2−3 min of refluxing the mixtures.

Metalloporphyrins **M-9a**,**b** (M = Ni, Cu, Pd) were readily aromatized by DDQ into MAr_4TBP's (**M-10a**,**b**). The yields of Ni and Cu complexes, however, were somewhat lower compared to the analogous $MAr_4TBP(CO_2Me)_8$'s, since the aromatization, especially in the case of Ni complexes, was complicated by the formation of

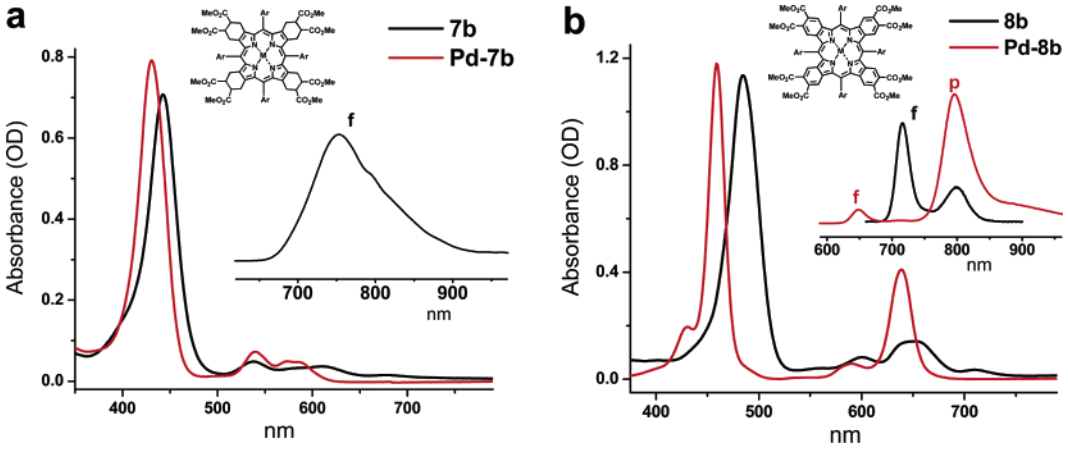


FIGURE 1. Absorption and corrected emission spectra (insets) of $Ar_4TCHP(CO_2Me)_8$'s (a) and $Ar_4TBP(CO_2Me)_8$'s (b): black lines, free bases; red lines, Pd complexes. The letters "f" and "p" indicate fluorescence and phosphorescence, respectively. Ar = 4-MeO_2C-C_6H_4.

undefined poorly soluble bright-green byproducts. These impurities, however, could be easily removed owing to their very high affinity to silica. The preferred solvent for aromatizations is THF, in which the yields of MAr_4TBP's varied from 25−30% for **Ni-10a** to 55% for **Ni-10b** to 60−80% for **Cu-10a**,**b**. The aromatization of **Pd-9a**,**b** was nearly quantitative (95%). It should be mentioned that a similar trend has been recently observed in aromatizations leading to tetraaryltetra[2,3]naphthaloporphyrins,[25b] where Pd complexes clearly showed an improved performance over some other metal complexes. The reasons why Pd derivatives behave better in aromatizations are currently not understood and require further studies.

Sulfuric acid could not be used for demetalation of Cu complexes of benzo-unsubstituted Ar_4TBP's, since these porphyrins are susceptible to electrophilic substitution.[9a,41] However, quantitative removal of Cu could be achieved after treating $CuAr_4TBP$'s with hot (80−90 °C) polyphosphoric acid for 4−5 h. It was crucial, however, to completely dissolve the Cu complexes, which required taking them as fine powders and rigorously stirring the reaction mixtures.

Spectroscopic Properties of Porphyrins and X-ray Structure of $NiPh_4TBP(CO_2Me)_8$ (Ni-8a). In the past, Ar_4TBP's have not been easily accessible, and therefore only very few studies of their spectroscopic properties have been accomplished. No doubt these molecules present an interesting class of chromophores, and their comprehensive photophysical assessment is yet to be done. Here, we would like to briefly illustrate the key spectroscopic features of the new Ar_4TBP's, emphasizing the difference between them and the Ar_4TCHP's, which bear exactly the same peripheral substituents but lack the extended π-system. A table containing the relative oscillator strengths for all the porphyrins synthesized in this work and their metal complexes is given in the Supporting Information. Here we discuss only the free base Ar_4TCHP's and Ar_4TBP's and the corresponding Pd complexes. Usually, free base porphyrins exhibit relatively strong $S_1 \rightarrow S_0$ fluorescence, while in Pd-porphyrins, Pd significantly raises the probability of the intersystem crossing into the triplet state T_1, making $T_1 \rightarrow S_0$ phosphorescence their predominant emission.[42]

TABLE 1. Photophysical Data for Ar_4TCHP's (9), $Ar_4TCHP(CO_2Me)_8$'s (7), Ar_4TBP's (10), and $Ar_4TBP(CO_2Me)_8$'s (9) and Their Pd Complexes in DMF (Ar = 4-C_6H_4-CO_2Me)

	absorption, λ_{max} (nm)		emission[a]	
porph	Soret	Q	λ_{max} (nm)	ϕ^b
9b	443	538, 610, 677	760 (f)	0.015
7b	442	537, 607, 676	752 (f)	0.014
Pd-9b	428	539, 574		
Pd-7b	431	540, 575		
10b	469	593, 642, 706	727, 811 (f)	0.027
8b	485	600, 652, 712	737, 826 (f)	0.022
Pd-10b	444	588, 633	645, 705 (f)	0.0006
			815 (p)	0.106[c]
Pd-8b	459	589, 639	648, 709 (f)	0.0005
			796 (p)	0.026[d]

[a] f = fluorescence, including delayed fluorescence; p = phosphorescence. [b] Quantum yields were measured with ZnTPP as a standard (ϕ = 0.033 in deoxygenated benzene).[46] Solutions were deoxygenated by prolonged bubbling of Ar. [c] τ = 105 μs. [d] τ = 32 μs.

The absorption and emission spectra of the free base octamethoxycarbonylporphyrins and their Pd complexes are shown in Figure 1 as examples, and their basic photophysical data are compiled in Table 1.

Similar to other nonplanar porphyrins, the absorption bands of Ar_4TCHP's (**9**) and $Ar_4TCHP(CO_2Me)_8$'s (**7**) are broadened and red-shifted compared to those of tetraphenylporphyrin (TPP). The effect of the macrocycle distortion on the spectra of porphyrins has been much discussed in the literature.[43] Compared to the free bases, $PdAr_4TCHP$ and $PdAr_4TCHP(CO_2Me)_8$ exhibit blue-shifted Soret bands, and have two peaks of almost equal intensity in the Q-band region. Free bases **9b** and **7b** fluoresce weakly ($\phi \approx 0.015$), compared to H_2TPP (ϕ = 0.11),[44] and reveal extremely large Stokes shifts (1613

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cm^{-1} for **9b**). Interestingly, Pd complexes of both Ar_4-TCHP and $Ar_4TCHP(CO_2Me)_8$ are practically not at all emissive, which is likely the result of strong internal conversions from the T_1 states. Large Stokes shifts, low emission quantum yields, and short lifetimes are well-known photophysical attributes of nonplanar porphyrins.[45]

The absorption bands of Ar_4TBP's are shifted to the red compared to those of Ar_4TCHP's. Since all the substituents are identical and the degrees of nonplanarity in Ar_4TBP's and Ar_4TCHP's are nearly the same,[5i] the extra red shifts in Ar_4TBP's are caused solely by the extra π-extension. Noteworthy is a much larger influence of the methoxycarbonyl groups in the case of Ar_4TBP's (**8b** vs **10b**), compared to the analogous Ar_4TCHP's (**7b** vs **9b**). Obviously, electronic coupling of substituents to the cores is mediated by extended π-conjugation.

The extended π-conjugation has significant effect on the emission properties of Ar_4TBP's. The Stokes shifts of the Ar_4TBP fluorescence fall down to 400−500 cm^{-1}, while the fluorescence quantum yields of the free bases **8b** and **10b** increase about 2-fold compared to the analogous Ar_4TCHP's. A much stronger increase is seen for the phosphorescence of the Pd complexes **Pd-8b** and especially **Pd-10b**, whose emission quantum yield is in the same order magnitude as that of Pd tetraarylporphyrins.[9a,42] It is likely that extra π-extension decreases the probability of nonemissive energy loss by making the Ar_4TBP macrocycles more rigid. Notably, the addition of methoxycarbonyl groups in **Pd-10b** slightly raises the energy of the triplet state but also decreases the emission lifetime almost 3-fold.

It is well-known that nonplanarity plays a major role in optical and other physical properties of porphyrins.[1b] For extended porphyrins, however, the influence of nonplanarity is not yet well documented, as all the available structural information is limited to only two structures, i.e., $ZnPh_4TBP$[5e] and the free base $Ph_4TBP(CO_2Me)_8$.[5i] Here we present a new X-ray structure of a metallotetrabenzoporphyrin, i.e., $NiPh_4TBP(CO_2Me)_8$ **(Ni-8a)** (shown in Figure 2)

In brief, the complex shown above exhibits the largest degree of distortion so far reported for extended porphyrins (D_{oop} = 3.43 Å). This distortion is heavily dominated by saddling (B2u, 3.30 Å), but also includes considerable ruffling (B1u, 0.93 Å) and in-plane distortions, A2g and A1g. For comparison, total out-of-plane distortion (D_{oop}) in the free base porphyrin **8a** is 2.97 Å[5i] and in $ZnPh_4TBP$[5e] it is 2.35 Å. The D_{oop} of the earlier reported $NiPh_4TCHP$,[48] on the other hand, is quite close to the one in

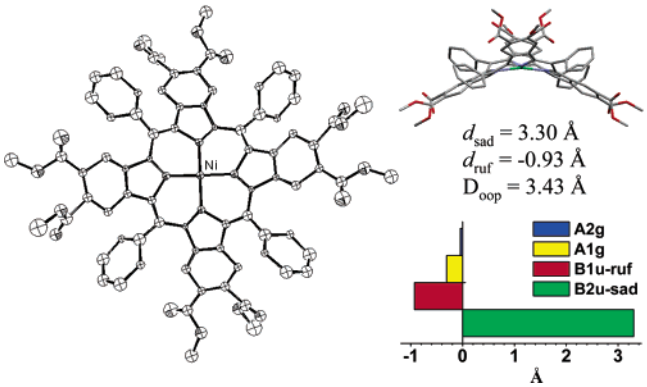

FIGURE 2. X-ray crystallographic structure of $NiPh_4TBP(CO_2Me)_8$ **(Ni-8a)**, shown together with its distortion modes, as deconvoluted by NSD.[47]

Ni-8a, i.e., 3.32 Å, suggesting that coordination to the Ni(II) ion affects Ar_4TCHP's and Ar_4TBP's in a similar manner.

Finally, we would like to mention that the NMR spectra of complex **Ni-8a** in DMSO-d_6 exhibit severe line broadening, typical for paramagnetic species. The spectra of Ni complexes of Ar_4TCHP's and benzo-unsubstituted Ar_4TBP's, on the other hand, are normally resolved. A possible interpretation of the unusual behavior of **8a** would be the formation of a high-spin complex upon binding of the DMSO molecule to $NiAr_4TBP(CO_2Me)_8$. Several examples of high-spin Ni-porphyrin complexes with oxygen-containing donors have been reported in the literature.[49] Usually, the trend to bind extra ligands by Ni-porphyrins is attributed to the decreased basicities of the corresponding porphyrin free bases. The basicities of $Ar_4TBP(CO_2R)_8$'s have been shown to be very low.[5i]

Conclusions

A general synthesis of polysubstituted tetraaryltetrabenzoporphyrins (Ar_4TBP) with and without functional groups in the fused benzo rings has been developed. The method relies on the oxidative aromatization of metal derivatives of nonaromatized porphyrin precursors and affords metallo-Ar_4TBP's in good yields. Subsequent demetalation of $CuAr_4TBP$'s by sulfuric or hot polyphosphoric acid opens a way to Ar_4TBP free bases and to other metal derivatives. The synthesis relies on inexpensive, readily available starting materials and includes 6−7 stages, depending on the method used in the preparation of the precursor porphyrins. A possible mechanism of the oxidative aromatization of cyclohexenoporphyrins is discussed. Basic photophysical properties of a few newly synthesized Ar_4TCHP's and Ar_4TBP's are reported along with the first X-ray crystallographic structure of $NiAr_4TBP(CO_2Me)_8$.

Experimental Section

tert-Butyl isocyanoacetate, ethyl isocyanoacetate, and benzyl isocyanoacetate were prepared according to the published procedures.[50] Compounds **3** and **3a** were synthesized from

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sulfolene **1a** in 86% yield, and compound **4b** was synthesized from cyclohexene in 80% yield according to the published method.[27] The cis isomer of **4a** (*cis*-**4a**) was synthesized in 85% yield from *cis*-**2**,[27] which was obtained from commercially available *cis*-1,2,3,6-tetrahydrophthalic anhydride in 95% yield. Compound *trans*-**4a** was synthesized from *trans*-**2** in 88% yield following the same method.[27] *trans*-**2** was obtained in 85% yield from sulfolene **1a** and dimethyl maleate.[31] Alternatively, *trans*-**4a** was synthesized by the Diels−Alder reaction from the mixture of sulfones **3** and **3a** and DMM in 54% yield.[31] The reported melting points are uncorrected.

2-Alkoxycarbonyl-4,5,6,7-tetrahydroisoindoles (5a−c). The pyrrole esters **5a**−**c** were synthesized by using a method similar to that published previously.[26b] THF was distilled over $LiAlH_4$ immediately prior to the synthesis. A solution of isocyanoacetate (7 mmol) in 20 mL of THF was added to a stirred suspension of ^{t}BuOK (0.9 g, 7 mmol) in 20 mL of THF and kept on an ice bath under Ar. A solution of sulfone (6 mmol) in 10−20 mL of THF was added dropwise to the mixture, after which the ice bath was removed, and the mixture was left to react at rt under continuous stirring. After 4 h the volume of the mixture was reduced by rotary evaporation and CH_2Cl_2 was added. The resulting solution was washed with water and brine and dried over Na_2SO_4. The solvents were removed in a vacuum, and the product was purified on a short (2 × 10 cm^2) silica gel column (CH_2Cl_2−THF, 20:1). The products were recrystallized from ether−hexane (**5a**,**b**) or hexane (**5c**). *cis*-**5a**: yield 1.62 g, 80%, white crystals, mp 126−127 °C; ^{1}H NMR ($CDCl_3$) δ 9.0 (br s, 1H), 6.61 (d, 1H), 3.66 (s, 3H), 3.68 (s, 3H), 2.6−3.5 (m, 6H), 1.50 (s, 9H); ES HRMS calcd for $C_{17}H_{23}NO_6$ + Na 360.3574, found 360.3577. *trans*-**5a**: 1.92 g, 95%, white crystals, mp 173−175 °C; ^{1}H NMR ($CDCl_3$) δ 8.95 (br s, 1H), 6.65 (d, 1H), 3.69 (s, 3H), 3.70 (s, 3H), 2.8−3.4 (m, 6H), 1.55 (s, 9H); ES HRMS calcd for $C_{17}H_{23}NO_6$ + Na 360.3574, found 360.3571. *cis*-**5b**: yield 1.67 g, 75%, white powder, mp 142−143 °C; ^{1}H NMR ($CDCl_3$) δ 8.95 (br s, 1H), 7.25−7.45 (m, 5H), 6.65 (d, 1H), 5.29 (q, 2H), 3.66 (s, 3H), 3.67 (s, 3H), 2.8−3.5 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 161.3, 161.2, 161.1, 124.0, 116.1, 115.6, 115.6, 113.1, 107.0, 106.8, 105.1, 53.3, 39.5, 28.5, 28.4, 11.4, 9.9; ES HRMS calcd for $C_{20}H_{21}NO_6$ + Na 394.3736, found 394.3740. **5c**: yield 1.04 g, 90%, pale yellow crystals, mp 82−83 °C; ^{1}H NMR ($CDCl_3$) δ 8.76 (br s, 1H), 6.64 (s, 1H), 4.29 (q, 2H), 2.81 (t, 2H), 2.54 (t, 2H), 1.74 (m, 4H), 1.34 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 149.6, 115.7, 109.4, 106.8, 105.2, 47.3, 11.0, 10.8, 9.5, 2.1; ES HRMS calcd for $C_{11}H_{15}NO_2$ + Na 216.2321, found 216.2318.

4,5,6,7-Tetrahydroisoindole 6a, Method A. *tert*-Butyl ester **5a** (0.5 g, 1.48 mmol) was dissolved in TFA (5 mL), and the solution was left for 30 min under Ar in the dark at rt. CH_2Cl_2 (20 mL) was added, and the mixture was poured into cold water. The organic layer was collected, washed with water, then with 10% solution of Na_2CO_3, and with water again, and dried over Na_2SO_4. The solvent was removed in a vacuum, and the residue was purified on a silica gel column (eluent CH_2Cl_2−THF , 20:1). The solvents were evaporated to give **6a** as a white crystalline solid (105 mg, 30%). Pyrrole **6a** gradually decomposes upon storing at rt. Therefore, it is desirable to use it up quickly following the preparation.

4,5,6,7-Tetrahydroisoindole 6a, Method B. Benzyl ester **5b** (1.0 g, 2.70 mmol) was dissolved in THF (30 mL), Et_3N (0.35 mL) was added, and the vial was flushed with hydrogen. Pearlman's catalyst[32] $Pd(OH)_2$/C (0.1 g) was cautiously added, and the reaction mixture was thoroughly stirred under hydrogen until the uptake of the gas stopped, and the TLC (CH_2Cl_2−THF, 20:1) showed that no **5b** was present in the mixture. The catalyst was filtered off, the solvent was removed under reduced pressure, and the residue was refluxed in ethylene glycol for 40 min. The mixture was cooled to 0 °C and CH_2Cl_2 was added. The organic phase was washed with water and brine and dried over Na_2SO_4 and the solvent was evaporated in a vacuum. The residue was purified on a short silica gel column (eluent CH_2Cl_2−THF, 20:1) to give **6a** (0.54−0.58 g) as a colorless crystalline residue. Pyrrole **6a** prepared by this method could be stored at 4 °C without noticeable decomposition for at least 10 days. ^{1}H NMR ($CDCl_3$) δ 8.05 (br s, 1H), 6.5 (d, 2H), 3.65 (s, 6H), 2.88−3.27 (m, 6H); ES HRMS calcd for $C_{12}H_{15}NO_4$ + Na 260.2416, found 260.2411.

Porphyrins 7a−e via the Lindsey Method. Pyrrole **6a** (2.5 mmol, 0.59 g) was dissolved in 250 mL of CH_2Cl_2, and an aromatic aldehyde (2.7 mmol) was added. The mixture was stirred under Ar for 10 min in the dark at rt. BF_3·Et_2O (0.5 mmol, 0.071 g) was added in one portion, and the mixture was stirred at rt for an additional 2 h. DDQ (2.8 mmol, 0.63 g) was added, and the mixture was left overnight under continuous stirring. The resulting solution was washed with 10% aq Na_2SO_3 and with 5% aq HCl and dried over Na_2SO_4. The solvent was evaporated in a vacuum and the residue was purified on a silica gel column (eluent CH_2Cl_2−THF, then CH_2Cl_2−THF−AcOH, green band collected), and then by repetitive precipitation from CH_2Cl_2−AcOH (10:1) with hexane. For further purification, porphyrins were converted into Cu complexes, chromatographed on silica gel (eluent CH_2Cl_2−THF), and demetalated by TFA. The free bases were obtained by washing the solutions of the porphyrin dications in CH_2Cl_2 with 10% aq Na_2CO_3, followed by reducing the solvent volumes to a few milliliters and precipitating the red-brown solids with hexane.[51] **7a**: yield 365−445 mg, 45−55%; mp >300 °C; UV−vis (CH_2Cl_2−Et_3N, 9:1) λ_{max} (log ϵ) 437 (5.24), 537 (4.08), 611 (3.54), 677 nm (3.24); ^{1}H NMR ($CDCl_3$−TFA) δ 8.41−7.92 (m, 20 H), 2.2−3.6 (m, 48H); MALDI, *m*/*z* for $C_{76}H_{70}N_4O_{16}$ + H calcd 1296.39, found 1295.44. **7b**: yield 335−430 mg, 35−50%; mp >300 °C; UV−vis (CH_2Cl_2−Et_3N, 9:1) λ_{max} (log ϵ) 445 (5.15), 539 (4.10), 611 (3.75), 675 nm (3.57); ^{1}H NMR ($CDCl_3$) δ 8.52−8.19 (m, 16H), 4.1 (s, 12H), 2.4−4.0 (m, 48H), −2.4 (br s, 2H); MALDI, *m*/*z* for $C_{84}H_{78}N_4O_{24}$ + H calcd 1528.53, found 1528.43. **7c**: yield 300−400 mg, 30−40%; mp >300 °C; UV−vis (CH_2Cl_2−Et_3N, 9:1) λ_{max} (log ϵ) 442 (5.22), 538 (4.17), 613 (3.69), 681 nm (3.22); ^{1}H NMR ($CDCl_3$−TFA) δ 8.1−8.3 (m, 16H), 2.25−4.0 (m, 48H), −0.5 (br s, 4H); MALDI, *m*/*z* for $C_{76}H_{66}Br_4N_4O_{16}$ + H, calcd 1611.97, found 1612.10. **7d**: yield 310−400 mg, 35−45%; mp >300 °C; UV−vis (CH_2Cl_2−Et_3N, 9:1) λ_{max} (log ϵ) 441 (5.25), 538 (4.08), 582 (3.79), 611 (3.69), 683 nm (3.45); ^{1}H NMR ($CDCl_3$) δ 8.15−7.95 (m, 8H), 7.35−7.20 (m, 8H, overlapped w/solv), 4.1 (s, 12H), 2.5−3.7 (m, 48H), −2.44 (br s, 4H); MALDI, *m*/*z* for $C_{80}H_{78}N_4O_{20}$ + H, calcd 1416.49, found 1416.07. **7e**: yield 185−230 mg, 20−25%; mp >300 °C; UV−vis (CH_2Cl_2−Et_3N, 9:1) λ_{max} (log ϵ) 456 (4.99), 544 (4.07), 615 (3.78), 689 nm (3.28); ^{1}H NMR ($CDCl_3$) δ 8.67 (m, 8H), 8.33−8.45 (m, 8H), 2.5−3.6 (m, 48H), −2.3 (br, 2H); MALDI, *m*/*z* for $C_{76}H_{66}N_8O_{24}$ + H, calcd 1476.38, found 1475.78.

Porphyrin 7a via the Adler−Longo Method. *tert*-Butyl ester **5a** (200 mg, 0.59 mmol), PhCHO (63 mg, 0.59 mmol), and TosOH (0.015 mg, 0.06 mmol) were dissolved in 12 mL of AcOH, and the mixture was refluxed in the dark under Ar. After 30 min the air was let into the flask, and the mixture was refluxed for 8 h. During this time the color gradually changed from dark-purple to dull green. The mixture was allowed to cool, stirred overnight, diluted with CH_2Cl_2, washed with water, with 10% aq Na_2CO_3, and with 5% aq HCl, and dried over Na_2SO_4. The solvent was evaporated to dryness, and the resulting dark material was purified on a silica gel column (eluent CH_2Cl_2−THF, then CH_2Cl_2−THF−AcOH). The bright green fraction was collected. The chromatography was repeated twice and followed by multiple precipitations of the

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(51) ^{13}C NMR spectra of porphyrins **7a**−**e** are not given. These compounds were isolated as mixtures of multiple stereoisomers and, therefore, their ^{13}C NMR spectra are not informative for identification purposes.

product from CH_2Cl_2−THF−AcOH by hexane. **7a** was isolated as the dication (28 mg, 11%).

Porphyrins 9a,b. A mixture of pyrrole ester **5c** (2.1 g, 10.9 mmol) and potassium hydroxide (~85%, 19.7 mmol, 1.3 g) in ethylene glycol (30 mL) was refluxed under Ar for 60 min. The mixture was cooled to 0 °C and CH_2Cl_2 (100 mL) was added. The organic phase was washed with water and with brine. The product (pyrrole **6b**) was extracted with CH_2Cl_2. The solution was washed with water and brine and dried over Na_2SO_4, and the solvent was evaporated in a vacuum. The residue was purified on a short silica gel column (eluent CH_2Cl_2), and the resulting solution was diluted with CH_2Cl_2 to about 1000 mL. The vial was protected from light and flushed with Ar, and the aromatic aldehyde (10 mmol) was added in one portion. The solution was stirred for 10 min, after which $BF_3{\cdot}Et_2O$ (2 mmol, 0.28 g) was added, and the mixture was stirred at rt for 2 h. DDQ (11 mmol, 2.5 g) was added, and the mixture was left overnight under continuous stirring. The resulting green solution was washed with 10% aq Na_2SO_3, with 10% aq Na_2CO_3, with 5% aq HCl, and finally with brine. The organic layer was dried over Na_2SO_4 and reduced in volume to about 100 mL. Methyl *tert*-butyl ether or diethyl ether was carefully laid over the surface of the CH_2Cl_2 solution to prevent rapid mixing of the solvents, and the resulting mixture was left overnight. Blue-green crystals formed, which were filtered off and washed with methyl *tert*-butyl ether or ethanol. The mother liqueur was evaporated to dryness and dissolved in the minimally necessary volume of CH_2Cl_2, and the crystallization procedure was repeated. The residue was filtered off and washed with methyl *tert*-butyl ether or ethanol to give the second crop as a fine green powder. **9a**: yield 1.37 g, 54%; mp >300 °C; UV−vis (CH_2Cl_2−TFA, 9:1) λ_{max} (log ϵ) 464 (5.37), 614 (4.07), 670 nm (4.32); ^{1}H NMR ($CDCl_3$) δ 8.36 (m, 8H), 7.8 (m, 12H), 2.46−2.50 (m, 8H), 1.98−2.01 (m, 8H), 1.62−1.64 (m, 8H), 1.1−1.20 (m, 8H), 0.23 (br s, 4H); ^{13}C NMR ($CDCl_3$) δ 144.2, 139.1, 136.9, 135.3, 129.8, 128.9, 118.0, 24.8, 22.8; MALDI, *m*/*z* for $C_{60}H_{54}N_4$ + H calcd 832.10, found 831.45. **9b**: yield 1.4 g, 45%; mp >300 °C; UV−vis (CH_2Cl_2−TFA, 9:1) λ_{max} (log ϵ) 473 (5.40), 618 (4.18), 676 nm (4.40); ^{1}H NMR ($CDCl_3$) δ 8.50−8.56 (m, 16H), 4.14 (s, 12H), 2.45−2.55 (m, 8H), 2.0−2.1 (m, 8H), 1.6−1.7 (m, 8H), 1.15−1.25 (m, 8H), 0.69 (br s, 4H); ^{13}C NMR ($CDCl_3$) δ 167.5, 143.9, 142.5, 136.9, 135.8, 131.4, 103.2, 117.6, 53.1, 25.2, 22.8; MALDI, *m*/*z* for $C_{68}H_{62}N_4O_8$ + H calcd 1064.24, found 1064.35.

Zn-7a−e. An excess of $Zn(OAc)_2{\cdot}2H_2O$ was added to a solution of a porphyrin (about 50 mg) in 50 mL of $CHCl_3$/MeOH (9:1). The mixture was stirred until the metal insertion was complete (after about 15 min), as evidenced by UV−vis spectroscopy. The mixture was washed with water and dried over Na_2SO_4 and the solvent was evaporated in a vacuum. The remaining solid was purified on a silica gel column with use of a CH_2Cl_2−THF (20:1) mixture as an eluent. CH_2Cl_2 in this procedure must be free from acid, as Zn complexes easily undergo demetalation. Zn porphyrins were recovered in 95−98% yields as dark red solids. As intermediate compounds, **Zn-7a−e** were identified by their UV−vis spectra only. See Supporting Information for details.

M-7a−e and M-9a,b (M = Cu, Ni). An excess of $Ni(OAc)_2{\cdot}4H_2O$ or $Cu(OAc)_2{\cdot}H_2O$ was added to a solution of a porphyrin (about 50 mg) in 50 mL of $CHCl_3$/MeOH (9:1), and the mixture was stirred at rt (Cu complexes) or refluxed for 10−15 min in the presence of an excess of Et_3N (Ni complexes). The conversion was monitored by UV−vis spectroscopy (solvent $CHCl_3$/AcOH) and considered complete when the Soret band of the dication at 468−472 nm disappeared. The mixture was washed with 10% aq AcOH, with 10% aq $NaHCO_3$, and with water and dried over Na_2SO_4. The solvent was evaporated in a vacuum, and the remaining material was purified on a silica gel column. Metalloporphyrins were recovered as red solids in 95−98% yields. Ni and Cu complexes of porphyrins **9a**,**b** were additionally recrystallized from CH_2Cl_2−ether mixtures. As intermediate compounds **M-7a−e** (**M** = **Cu**, **Ni**) were identified by their UV−vis spectra only. See Supporting Information for details. **Ni-9a**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 424 (5.32), 544 (4.27), 5.81 (4.27); ^{1}H NMR ($CDCl_3$) δ 7.80 (m, 12H), 7.5 (m, 8H), 2.15 (s, 16H), 1.35 (s, 16H); ^{13}C NMR ($CDCl_3$) δ 144.3, 142.4, 141.2, 134.4, 128.7, 128.2, 117.2, 26.6, 24.2; MALDI, *m*/*z* for $C_{60}H_{52}N_4Ni$, calcd 888.78, found 887.32. **Cu-9a**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 424 (5.30), 557 (4.30), 592 nm (4.08); MALDI, *m*/*z* for $C_{60}H_{52}N_4Cu$ + H calcd 893.63, found 892.91. **Ni-9b**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 428 (5.35), 547 (4.35), 584 nm (4.35); ^{1}H NMR ($CDCl_3$) δ 7.97−8.25 (m, 16H), 4.00 (s, 12H), 2.12 (s, 16H), 1.35 (s, 16H); ^{13}C NMR ($CDCl_3$) δ 167.4, 145.2, 144.0, 141.9, 133.8, 129.9, 128.9, 115.9, 52.5, 26.3, 23.4; MALDI, *m*/*z* for $C_{68}H_{60}N_4NiO_8$ + H calcd 1120.92, found 1119.36. **Cu-9b**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 429 (5.25), 562 (4.25), 597 nm (4.10); MALDI, *m*/*z* for $C_{68}H_{60}N_4CuO_8$, calcd 1125.77, found 1123.91.

Pd-7a,b and Pd-9b. $PdCl_2$ (88.7 mg, 0.5 mmol) was added to a solution of a free base porphyrin (0.5 mmol) in CH_3CN−THF (1:1, 50−100 mL), and the mixture was refluxed for 30 min. An additional portion of $PdCl_2$ (17.7 mg, 0.1 mmol) and Et_3N (1.01 g, 10 mmol) were added and the mixture was refluxed for an additional 30 min. Alternatively, an excess of $PdCl_2$ (17 mg, 0.1 mmol) and a free base porphyrin (0.06 mmol) were refluxed in PhCN (5−10 mL) for 3−5 min. The conversion was monitored by UV−vis spectroscopy (solvent $CHCl_3$−AcOH) and considered complete after the Soret band of the dication at 468−472 nm disappeared. The mixture was allowed to cool, diluted with CH_2Cl_2, and filtered through a thin layer of Celite to remove Pd black, and the solvent was evaporated. The product was purified by chromatography on silica gel with CH_2Cl_2 for **Pd-9b**, CH_2Cl_2−THF (20:1) for **Pd-7a**, and CH_2Cl_2−THF (12:1) for **Pd-7b** as eluents. Pd-porphyrins appeared as dark red bands. The solvent was evaporated and the residue was either recrystallized from CH_2Cl_2−ether (**Pd-9b**) or precipitated from CH_2Cl_2 with hexane (**Pd-7a,b**). **Pd-7a**: yield 620−670 mg, 88−95%; mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 425 (5.22), 536 (4.22), 570 nm (4.04); ^{1}H NMR ($CDCl_3$) δ 8.0−8.15 (m, 8H), 7.7−7.8 (m, 12H), 2.45−3.65 (m, 48H); MALDI, *m*/*z* for $C_{76}H_{68}N_4O_{16}Pd$ + H calcd 1400.79, found 1400.58. **Pd-7b**: yield 630 mg, 90%; mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 431 (4.91), 540 (3.92), 580 nm (3.76); ^{1}H NMR ($CDCl_3$) δ 8.0−8.15 (m, 8H), 7.7−7.8 (m, 12H), 2.45−3.65 (m, 48H); MALDI, *m*/*z* for $C_{84}H_{76}N_4O_{24}Pd$ + H calcd 1631.93, found 1631.52. **Pd-9b**: yield 500−515 mg, 85−88%; mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 429 (5.30), 540 (4.29), 575 nm (4.18); ^{1}H NMR ($CDCl_3$) δ 8.15−8.4 (m, 8H), 4.1 (s, 12H), 2.3 (s, 16H), 1.4 (s, 16H); ^{13}C NMR ($CDCl_3$) δ 167.4, 145.9, 142.0, 140.5, 134.2, 129.8, 128.8, 118.5, 52.4, 26.4, 23.4; MALDI, *m*/*z* for $C_{68}H_{60}N_4O_8Pd$ + H, calcd 1168.65, found 1167.12.

M-8a−e and M-10a,b (M = Ni, Cu, Pd). Metalloporphyrin (**M-7a−e** or **M-9a**,**b**) (1 equiv) was dissolved in 100−150 mL of a dry solvent (THF for **M-9a**,**b**, CH_3CN for **M-7a−e**). A 2-fold excess of DDQ (16 equiv) was added, and the mixture was refluxed for 20−40 min. In the case of **Cu-7e** a longer refluxing period (1−2 h) was required. During refluxing the color changed from red-brown to deep green. The mixture was allowed to cool, diluted with CH_2Cl_2, washed with a 10% aq solution of Na_2SO_3, with water, and with brine, and dried over Na_2SO_4. The solvent was removed in a vacuum, and the remaining solid was purified on a silica gel column with CH_2Cl_2 for **M-10a**,**b** and CH_2Cl_2/THF (20:1) for **M-8a−e** as eluents. The first dark-green fraction was collected. The solvents were evaporated and the residues were recrystallized from CH_2Cl_2−ether to give the products in the form of blue-green crystals (**M-8a−e**) or dark-green powders (**M-10a**,**b**). Yields: **M-8a−e** 90−95%; **Ni-10a** 25−30%; **Cu-10a** 60−65%; **Ni-10b** 50−55%; **Cu-10b** 75−80%; **Pd-10b** 90−95%.

Ni-8a: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 465 (5.34), 603 (4.34), 655 nm (4.92); ^{1}H NMR ($CDCl_3$) δ 7.8−8.1 (m, 20H), 7.42 (s, 8H), 3.85 (s, 24H); ^{13}C NMR ($CDCl_3$) δ 167.9, 139.4,

139.0, 138.4, 132.8, 129.6, 129.5, 128.2, 125.1, 117.0, 52.5; MALDI, *m/z* for $C_{76}H_{52}N_4NiO_{16}$ + H, calcd 1336.94, found 1335.04. **Cu-8a**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 474 (5.51), 608 (4.38), 658 nm (5.02); MALDI, *m/z* for $C_{76}H_{52}CuN_4O_{16}$, calcd 1341.79, found 1339.99. **Pd-8a**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 458 (5.39), 585 (4.12), 637 nm (4.89); ^{1}H NMR ($CDCl_3$) δ 8.20 (d, 8H), 8.03 (t, 4H), 7.94 (t, 8H), 7.49 (s, 8H), 3.87 (s, 24H); ^{13}C NMR ($CDCl_3$) δ 167.9, 140.3, 138.7, 138.2, 133.4, 129.7, 128.8, 125.7, 119.7, 52.5; MALDI, *m/z* for $C_{76}H_{52}PdN_4O_{16}$ + H, calcd 1384.66, found 1383.39. **Ni-8b**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 464 (5.38), 603 (5.18), 656 nm (4.96); ^{1}H NMR ($CDCl_3$) δ 8.06−8.55 (m, 16H), 7.37 (s, 8H), 4.13 (s, 12H), 3.82 (s, 24H); ^{13}C NMR ($CDCl_3$) δ 167.5, 166.6, 143.3, 139.2, 137.8, 133.1, 131.5, 130.7, 128.7, 124.9, 116.1, 52.6; MALDI, *m/z* for $C_{84}H_{60}N_4NiO_{24}$ + H, calcd 1569.08, found 1568.97. **Cu-8b**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 471 (5.60), 613 (4.64), 662 nm (5.14); MALDI, *m/z* for $C_{84}H_{60}CuN_4O_{24}$ + H, calcd 1573.93, found 1572.76. **Pd-8b** (this compound was synthesized in 92% yield by insertion of Pd into **8b** free base in refluxing benzonitrile); mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 458 (5.33), 589 (4.04), 640 nm (4.89); ^{1}H NMR ($CDCl_3$) δ 8.62−8.29 (m, 16H), 7.76 (s, 8H), 4.16 (s, 12H), 3.82 (s, 24H); MALDI, *m/z* for $C_{84}H_{60}N_4O_{24}Pd$ + H, calcd 1615.81, found 1615.53. **Ni-8c**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 464 (5.38), 605 (4.28), 657 nm (4.95); ^{1}H NMR ($CDCl_3$) δ 7.81−8.03(m, 16H), 7.46 (s, 8H), 3.95 (s, 24H); ^{13}C NMR ($CDCl_3$) δ 168.0, 139.7, 138.2, 136.9, 134.8, 133.3, 129.1, 125.4, 124.7, 116.1, 53.4; MALDI, *m/z* for $C_{76}H_{48}Br_4N_4NiO_{16}$ + H, calcd 1652.52, found 1649.66. **Cu-8c**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 472 (5.25), 613 (4.16), 659 nm (4.82); MALDI, *m/z* for $C_{76}H_{48}Br_4CuN_4O_{16}$ + H, calcd 1657.37, found 1656.88. **Ni-8d**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 470 (5.42), 603 (4.21), 654 nm (4.97); ^{1}H NMR ($CDCl_3$) δ 7.84 (d, 8H), 7.52 (s, 8H), 7.38 (d, 8H), 4.12 (s, 12H), 3.88 (s, 24H); ^{13}C NMR ($CDCl_3$) δ 167.6, 160.9, 139.1, 138.6, 133.7, 131.0, 127.8, 124.8, 116.3, 114.7, 55.5, 52.2; MALDI, *m/z* for $C_{80}H_{60}N_4NiO_{20}$ + H, calcd 1457.04, found 1455.01. **Cu-8d**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 479 (5.40), 610 (4.27), 658 nm (4.87); MALDI, *m/z* for $C_{80}H_{60}N_4CuO_{20}$ + H, calcd 1461.89, found 1459.30. **Cu-8e**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 469 (5.27), 612 (4.31), 664 nm (4.84); MALDI, *m/z* for $C_{76}H_{48}CuN_8O_{24}$ + H, calcd 1521.78, found 1519.04. **Ni-10a**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 446 (5.11), 591 (4.01), 643 nm (4.73); ^{1}H NMR ($CDCl_3$) δ 8.47 (d, 8H), 7.74−7.84 (m, 12H), 7.02−7.13 (m, 16H); ^{13}C NMR data are not available due to very low solubility of this compound; MALDI, *m/z* for $C_{60}H_{36}N_4Ni$ + H, calcd 872.65, found 871.21. **Cu-10a**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 446/458 (5.16), 599 (4.11), 647 nm (4.78); MALDI, *m/z* for $C_{60}H_{36}N_4Cu$ + H, calcd 877.50, found 875.26. **Ni-10b**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 448 (5.04), 596 (3.99), 649 nm (4.66); ^{1}H NMR ($CDCl_3$) δ 8.08−8.40 (m, 16H), 6.91−7.07 (m, 16H), 4.05 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 167.6, 145.7, 138.5, 137.0, 134.2, 131.1, 130.8, 125.7, 123.7, 115.3, 52.9; MALDI, *m/z* for $C_{68}H_{44}N_4NiO_8$ + H, calcd 1104.79, found 1103.92. **Cu-10b**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 445 (5.23), 602 (4.19), 650 nm (4.86); MALDI, *m/z* for $C_{68}H_{44}CuN_4O_8$ + H, calcd 1109.65, found 1107.32. **Pd-10b**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 433 (5.44), 584 (4.28), 633 nm (5.00); ^{1}H NMR ($CDCl_3$) δ 8.37−8.56 (m, 16H), 7.08−7.21 (m, 16H), 4.16 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 167.2, 146.1, 138.1, 137.6, 134.1, 130.8, 130.4, 125.7, 123.8, 117.3, 53.6; MALDI, *m/z* for $C_{68}H_{44}N_4O_8Pd$ + H, calcd 1152.52, found 1152.87.

Zn-8a. Zn-7a (30 mg, 0.022 mmol) was dissolved in 20 mL of dry CH_3CN. A 2-fold excess of DDQ (80 mg, 0.35 mmol) was added, and the mixture was refluxed for approximately 1 h. The UV−vis spectrum of the mixture revealed the presence of the Soret bands of both the product **Zn-8a** and the dication **7a**. The solvent was removed in a vacuum and the residue was dissolved in CH_2Cl_2. The solution was washed with 10% aq Na_2SO_3, with 5% HCl, and with brine and dried over Na_2SO_4. MeOH (10 vol %) and an excess of Zn acetate dihydrate (50 mg, 0.23 mmol) were added to the solution, and the mixture was stirred for 15 min at rt. The conversion of **7a** dication into the Zn complex was monitored by using UV−vis spectroscopy. The resulting mixture was washed with water, dried over Na_2SO_4, and filtered through a thin (about 1 cm) layer of silica gel. The solvent was removed in a vacuum, and the remaining solid was oxidized with DDQ (50 mg, 0.22 mmol). The following workup was carried out as described above. The product **Zn-8a** was separated from the remaining **7a** dication by chromatography on silica gel, using CH_2Cl_2−THF (20:1) and then CH_2Cl_2−THF−AcOH to recover **7a**. **Zn-8a** was recrystallized from CH_2Cl_2−ether. Yield: 13−18 mg, 45−60%; mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 483 (5.55), 620 (4.37), 666 nm (4.74); ^{1}H NMR (DMSO-d_6) δ 8.28−7.94 (m, 20 H), 7.45 (s, 8H), 3.81 (s, 24H); ^{13}C NMR (DMSO-d_6) δ 52.1, 118.2, 125.3, 127.8, 129.0, 129.2, 133.3, 139.3, 141.6, 142.8, 167.2; MALDI, *m/z* for $C_{76}H_{52}N_4O_{16}Zn$ + H, calcd 1343.63, found 1344.31.

Tetrabenzoporphyrins 8a−c. Cu complex of a tetrabenzoporphyrin (50−100 mg) was dissolved in 15−30 mL of concentrated H_2SO_4 and left under stirring at rt for 24h. The conversion was monitored by UV−vis spectroscopy, using HCl concentrated as a solvent, and was considered complete when the Soret band of the Cu complex completely disappeared. The Soret band of the dication TBP appeared at 510−520 nm. The solution was poured into 100 mL of MeOH (ice bath) and left overnight under stirring in a closed vial. CH_2Cl_2 and then water were added to the mixture. The organic layer was separated and washed with 10% aq Na_2CO_3. If re-esterification was complete, the aqueous layer remained colorless. The organic solution was further washed with water and dried over Na_2SO_4. The solvent was removed in a vacuum, and the remaining solid was purified on a short silica gel column (2 × 10 cm^2), using a $CHCl_3$/THF mixture (20:1) as an eluent. The main bright-green fraction was collected and evaporated to dryness, and the residue was recrystallized from CH_2Cl_2−ether. Porphyrins **8a−c** were isolated as blue-green crystals in 90−95%. **8a**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 479 (5.26), 598 (3.97), 653 (4.36), 709 nm (3.72); ^{1}H NMR ($CDCl_3$−TFA) δ 11.00 (TFA + NH), 8.50−8.02 (m, 20H), 7.79 (s, 8H), 3.87 (s, 24H); ^{13}C NMR ($CDCl_3$−TFA) δ 167.8, 141.3, 137.9, 135.7, 132.4, 131.8, 131.7, 130.3, 125.9, 117.0, 53.5; MALDI, *m/z* for $C_{76}H_{54}N_4O_{16}$ + H, calcd 1280.26, found 1279.32. **8b**: mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 480 (5.54), 598 (4.39), 647 (4.66), 708 nm (4.24); ^{1}H NMR ($CDCl_3$−TFA) δ 11.06 (TFA + NH), 8.68 (s, 16H), 7.77 (s, 8H), 4.24 (s, 12H), 3.83 (s, 24H); ^{13}C NMR ($CDCl_3$−TFA) δ 166.8, 166.7, 141.3, 136.0, 141.3, 132.9, 132.8, 131.5, 131.2, 125.7, 116.1, 53.2, 53.1; MALDI, *m/z* for $C_{84}H_{62}N_4O_{24}$ + H, calcd 1512.40, found 1511.87. **8c**: mp >300 °C; UV−vis (CH_2Cl_2−TFA, 9:1) λ_{max} (log ϵ) 509 (5.67), 653 (4.72), 701 nm (4.45); ^{1}H NMR ($CDCl_3$−TFA) δ 8.2−8.4 (m, 16H), 7.86 (s, 8H), 3.97 (s, 24H); ^{13}C NMR ($CDCl_3$−TFA) δ 168.0, 141.3, 136.9, 136.5, 133.7, 132.6, 132.5, 131.6, 127.6, 125.9, 116.2, 54.0; MALDI, *m/z* for $C_{76}H_{50}Br_4N_4O_{16}$ + H calcd 1595.84, found 1596.98.

Tetrabenzoporphyrin 8a from Zn-8a. TFA (1 mL) was added to a stirred solution of **Zn-8a** (~20 mg, 0.015 mmol) in 15 mL of CH_2Cl_2, which resulted in an immediate change of color from green to red-brown. The mixture was allowed to react for 15 min, after which 50 mL of CH_2Cl_2 was added. The solution was transferred into a separatory funnel and washed with water, with NaOH (10% solution), and with water again and dried over Na_2SO_4. The chromatographic purification of the resulting solution on silica gel (CH_2Cl_2/THF (12:1)) afforded **8a** in 95−97% yield.

Tetrabenzoporphyrin 10b. A solution of **Cu-10b** (50 mg, 0.045 mmol) in a small volume of CH_2Cl_2 (~5 mL) was poured into ~30 mL of hexane and the solvents were evaporated in a vacuum. Warm polyphosphoric acid (5 mL) was added to the resulting fine powder, and the mixture was kept under stirring at 85−90 °C in a sealed vial for 4−5 h. The UV−vis spectrum of the mixture (CH_2Cl_2−THF−TFA) revealed the Soret band of the dication of **10b** at 502 nm. The demetalation was

considered complete after the Soret band of the Cu complex disappeared. The mixture was poured into warm water, and the product was extracted with CH_2Cl_2. The organic layer was washed with 10% aq Na_2CO_3 and with water, dried over Na_2SO_4, and evaporated to dryness. The resulting solid was purified on a silica gel column with a CH_2Cl_2/THF (20:1) mixture as an eluent. The dark-green band was collected, the solvent was evaporated, and the residue was recrystallized from CH_2Cl_2−ether to give **10b** as a dark-green powder. Yield: 33−38 mg, 70−80%; mp >300 °C; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 467 (5.48), 595 (4.32), 644 (4.65), 701 nm (4.26); ^{1}H NMR ($CDCl_3$) δ 8.63 (m, 16H), 7.2 (br, 8H), 4.17 (s, 12H), −1.05(br, 2H); ^{13}C NMR ($CDCl_3$) δ 167.8, 146.6, 135.3, 131.2, 130.7, 126.8, 124.7, 115.5, 53.1; MALDI, *m*/*z* for $C_{68}H_{46}N_4O_8$ + H, calcd 1048.12, found 1047.56.

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Supporting Information Available: Details of X-ray structure determination, quantum chemistry calculations, and NSD (Normal-Coordinate Structural Decomposition), as well as a table with UV−vis spectroscopic data for all newly synthesized porphyrins and metalloporphyrins and copies of their NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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